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CONCEPTS IN HETEROGENEOUS CATALYSIS

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This paper reviews some milestones in the development of theories on catalysis and discusses some of the more significant contemporary concepts. It also attempts to integrate the new field of electrocatalysis and particularly the field of electrocatalytic hydrocarbon oxidation with the general field of catalysis. Therefore, the chapter on heterogeneous catalytic oxidation is discussed in considerable detail while other areas of catalysis are discussed only briefly. Due to the interest in fuel cell research, considerable advances were made in electrocatalysis during the last dozen years, but
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few correlations were made by the electrochemists and the workers in catalysis. It is hoped that this review will help to close this gap.

Encouragement to write this review was given by Dr. J. R. Huff, Chief, Electrochemistry Division, USAMERDC, Fort Belvoir, VA.

CONTENTS

CONCEPTS IN HETEROGENEOUS CATALYSIS

I. INTRODUCTION

Catalytic phenomena have been known for a long time, but the term "catalysis" was not used until 1836 when Berzelius suggested that certain reactions take place on surfaces of solids as a result of a catalytic force. Although catalysis gained great importance in industry, no progress in understanding its mechanisms was made until the early 20th century. At that time, mainly as a result of the kinetic studies of Bodenstein and Ostwald and the principles of thermodynamics enunciated by Van't Hoff, it became apparent that catalysts can only affect the rates of reactions which are thermodynamically feasible. The first interpretation of the mechanism of catalysis was given by Sabathier[1] who suggested that chemical affinity between catalyst and reactants leads to the formation of intermediate compounds on the catalyst surface which then decompose to yield the reaction products whereupon the catalyst returns to its original state. This pioneering theory later lost some of its appeal when it was felt that much of catalysis could be interpreted in terms of the collective electronic properties of solids. Now, the theory is appreciated once again.

The understanding of catalysis was considerably furthered by Langmuir's studies on adsorption which showed that strong chemical forces were involved in adsorption and catalysis.[2] This was the beginning of the concept of chemisorption although the distinction between chemisorption and physical adsorption was not emphasized. This distinction became apparent during the 1920's and was clearly brought out in 1931 by the work of Benton and White,[3] Garner and Kingman,[4] and Taylor and Williamson.[5] Taylor suggested that an activation energy was necessary for the chemisorption process and introduced the term "activated adsorption."[6] In 1932, physical adsorption and chemisorption were formulated by Lennard-Jones in terms of potential energy diagrams.[7] For the interpretation of bimolecular catalytic reactions on surfaces of solids, two different mechanisms were proposed. In the Langmuir-Hinshelwood mechanism, it is postulated that both reacting molecules are chemisorbed on adjacent surface sites before

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[1] P. Sabathier, "La Catalyse en Chemie Organique," Librairie Polytechnique, Paris (1913).

[2] I. Langmuir, J. Am. Chem. Soc., 38, 2221 (1916); 40, 1361 (1918).

[3] A. F. Benton and T. A. White, J. Am. Chem. Soc., 52, 2325 (1930).

[4] W. E. Garner and M. Kingman, Trans. Faraday Soc., 27, 322 (1931).

[5] H. S. Taylor and A. T. Williamson, J. Am. Chem. Soc., 53, 2168 (1931).

[6] H. S. Taylor, J. Am. Chem. Soc., 53, 578 (1931).

[7] J. E. Lennard-Jones, Trans. Faraday Soc., 28, 333 (1932).

they react.[8] The Rideal-Eley mechanism envisages the reaction of one chemisorbed species with another species which is only physically adsorbed.[9] Examples for both of these mechanisms were found.

In the 1920-1930 decade, the concept of heterogeneity of the surfaces of solids emerged. Pease[10] observed that traces of certain gases can poison catalysts, and Garner[11] and Taylor[12] established that in many cases the heats of adsorption decreased appreciably with increasing coverage. On the basis of these reselts, Taylor proposed that catalytic reactions do not occur on the whole catalyst surface but on certain "active centers."[13] This concept has remained important ever since, and it is even more appreciated in recent years than in some of the decades which have passed in the meantime.

II. CONCEPTS EMPHASIZING GEOMETRIC CONSIDERATIONS (GEOMETRIC FACTOR IN CATALYSIS)

As x-ray methods led to more precise knowledge of crystal structures and bond lengths, relations between the geometry of the surfaces of solids and their adsorptive power and catalytic activity were sought. One of the first to consider surface geometry was Balandin[14] who proposed in his "Multiplet Theory" that the activity of a catalyst depends on the presence in the lattice of correctly spaced groups of atoms (called multiplets) to accommodate the particular reactant molecules. Because of the small effective radius of the chemical forces which determine covalent bonds, Balandin suggested that reactant molecules as a whole do not take part in catalytic reactions but only certain parts of the molecules (called index groups or atoms) which are in a geometrically favored position to interact with a multiplet on the catalyst surface. With this terminology, hydrogen-deuterium exchange reactions are classified as doublet reactions, benzene hydrogenation or dehydrogenation as sextet reactions. Sextet reactions on metals played a considerable role in the efforts to prove or disprove the multiplet theory. Balandin proposed that the benzene molecule adsorbs on metal surfaces by forming bonds from the six carbon atoms to six metal atoms, and he postulated that octahedral symmetry of the metal lattice as well as the proper values of the inter-atomic distances between the metal atoms were necessary preconditions for benzene adsorption. Only the (111)

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[8] I. Langmuir, Trans. Faraday Soc., 17, 621 (1921); C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford Univ. Press 145 (1926).

[9] E. K. Rideal, Proc. Cambridge Phil. Soc., 35, 130 (1939); Proc. Roy. Soc., A 178, 429 (1941).

[10] R. N. Pease, J. Am. Chem. Soc., 45, 2235 (1923)

[11] E. A. Blench and W. E. Garner, J. Chem. Soc., 1288 (1924); W. E. Garner and D. McKie, *ibid.*, 2451 (1927); H. I. Bull, W. E. Garner, and M. H. Hall, *ibid.*, 837 (1931).

[12] R. A. Beebe and H. S. Taylor, J. Am. Chem. Soc., 46, 43 (1924); G. B. Kistiakowsky, E. W. Flosdorf, and H. S. Taylor, J. Am. Chem. Soc., 49, 2200 (1927).

[13] H. S. Taylor, Proc. Roy. Soc., A, 108, 105 (1925).

[14] A. A. Balandin, Z. phys. Chem., 132, 289 (1929); Advances in Catalysis, 19, 1 (1969).

planes of face-centered cubic metals exhibit this symmetry. Experimental results appeared to support Balandin's hypothesis,[15] [16] but later work showed that cubic body-centered metals also can be active catalysts for benzene hydrogenation.[17] [18] In more recent times, it was pointed out that the observed activation energies were much too low for a mechanism in which six metal carbon bonds have to be broken.[19] In conclusion, it can be said that the Multiplet Theory is not so universally applicable as Balandin proposed, but it contained ideas which were very fruitful and which again appeared in other forms.

There is ample evidence that geometric factors in catalysis cannot be ignored. More than 30 years ago, Horiuti[20] calculated, following the lead of Eyring,[21] that the lattice spacing played an important role in determining the magnitude of the activation energy of, for instance, hydrogen adsorption on nickel. Beeck was able to prepare oriented metal films by vacuum deposition and found that the (110) face of nickel (the face with the least atomic density and highest surface energy) was five times more catalytically active than films with random orientation.[22] Sosnovsky[23] observed that the kinetic parameters of the formic acid decomposition differ significantly amongst the (100), (110), and (111) planes of silver crystals. LEED investigations showed that the (100) face of tungsten is active in ammonia chemisorption and decomposition while the (110) phase is passive.[24] [25] These examples illustrate the concept of geometric factor in catalysis. A deeper insight into this field was obtained through crystal field theory and molecular orbital theory which will be discussed later.

III. CONCEPTS EMPHASIZING THE ROLE OF THE COLLECTIVE ELECTRONIC PROPERTIES OF CATALYSTS (ELECTRONIC FACTOR IN CATALYSIS)

After it was realized that strong chemical forces are involved in chemisorption and catalysis, more and more attention was paid to electronic processes in catalysis. Initially,

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[15] J. H. Long, J. C. W. Frazer, and E. Ott, J. Am. Chem. Soc., 56, 1101 (1934).

[16] P. H. Emmett and N. Skau, J. Am. Chem. Soc., 65, 1029 (1943).

[17] O. Beeck and A. W. Ritchie, Disc. Faraday Soc., 8, 159 (1950).

[18] P. H. Emmett, "New Approaches to the Study of Catalysis," Ch. 3, Priestley Lecture, The Pennsylvania State University, University Park (1962).

[19] H. Noller and E. Hantke, Z. f. Elektrochemie, 63, 97 (1959).

[20] G. Okamoto, J. Horiuti, and K. Hirota, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 29, 233 (1936).

[21] A. Sherman and H. Eyring, J. Am. Chem. Soc., 54, 2661 (1932).

[22] O. Beeck, Rev. of Mod. Physics, 17, 61 (1945).

[23] H. M. C. Sosnovsky, J. Phys. Chem. Solids, 10, 304 (1959).

[24] P. J. Estrup and J. Andersen, J. Chem. Phys., 49, 523 (1968).

[25] J. W. May, R. J. Szostak, and L. H. Germer, Surface Science, 15, 37 (1969).

Roginsky,[26] Lennard-Jones,[26a] Schmidt,[27] and Nyrop[28] became aware that catalysts may function as electron sources or sinks. Seitz[29] showed experimentally that electron transfer and exchange phenomena between surfaces of solids and adsorbates do occur, whereby neutral molecules can yield ions or radicals depending on the electronegativities of the surface and the molecular fragments. DeBoer[30] observed ionization of adsorbed molecules and described the effect of adsorption layers on the work function of metals. These were the beginnings of a great research effort designed to relate the electronic structure of solids with their catalytic activities. In 1950, Dowden wrote a fundamental paper on "The Theoretical Basis of Heterogeneous Catalysis"[31] which considerably furthered the concepts underlying the electronic factor in catalysis. He used the band theory of solids to interpret catalytic reactions on surfaces of metals and semiconductors and related the rates of catalytic reactions to the ionization potential of the adsorbed species and the work function and Fermi level of the catalyst. Pauling's valence bond theory of metals (to be discussed later) as well as geometric aspects were included in Dowden's study.

1. **Electronic Factor in Catalysis on Metals.** Schwab[32] was one of the first to make systematic investigations designed to relate the collective electronic properties of metals and their catalytic activity. His work on the dehydrogenation of formic acid on surfaces of homogeneous Hume-Rothery alloys, such as silver containing some Cd, In, Sn, Sb, Hg, Tl, Pb, or Bi, showed that the increased electron concentration caused by the addition of multivalent metals results in increased activation energies. Parallel with this increase in the activation energy, the electrical resistivity and mechanical hardness increased when multivalent metals were alloyed to silver. It was concluded that electrons must pass from the formic acid into the metal in order to form an active transition state. This process needs more energy the more the metal is already saturated with electrons.

In 1949, Boudart[33] and subsequently Beeck[34] suggested that Beeck's results for ethylene hydrogenation on oriented metal films could perhaps be better interpreted

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[26] S. Z. Roginsky and Schultz, Z. phys. Chem., A 138, 21 (1928).

[26a] J. E. Lennard-Jones, Trans. Faraday Soc. 28, 333 (1932).

[27] Schmidt, Chem. Reviews, 12, 363 (1933).

[28] Nyrop, "The Catalytic Action of Solids," Williams and Norgate, 1937.

[29] F. Seitz, J. Appl. Physics, 8, 246 (1937).

[30] J. H. DeBoer, "Electron Emission and Adsorption Phenomena," Cambridge University Press (1935).

[31] D. A. Dowden, J. Chem. Soc., 242 (1950).

[32] G. M. Schwab, Trans. Faraday Soc., 42, 689 (1946); Disc. Faraday Soc., 8, 166 (1950).

[33] M. Boudart, J. Am. Chem., 72, 1040 (1949).

[34] O. Beeck, Disc. Faraday Soc., 8, 118 (1950).

using Pauling's valence bond theory[35] and relating the catalytic activities to the percentage *d*-character of the metallic bond rather than on the basis of proper lattice spacings as discussed under the heading "Geometric Factor in Catalysis."

Pauling's theory is often used in the interpretation of catalysis on metals and will be briefly outlined here. Prior to this theory, it was believed that *d*-electrons make no significant contribution to the cohesive forces in metals. Pauling, however, pointed out that the properties of transition metals can be adequately described in terms of dsp hybrid covalent bonds between metal atoms. His analysis indicated that there are two kinds of *d*-bands in transition metals. One is described by diffuse (bonding) wave-functions, the other by localized (antibonding) wave-functions. To account for the properties of transition metals, Pauling suggested that from the five *d*-orbitals, on the average, 2.56 *d*-orbitals are involved in bond formation (bond orbitals) through hybridization with the s and p orbitals and that the number of covalent bonds increases from one to six in the sequence of potassium, calcium, scandium, titanium, vanadium, chromium, remains nearly constant from chromium to nickel, and begins to decrease with copper. The remaining 2.44 *d*-orbitals (atomic orbitals) are occupied by antibonding electrons which are mainly responsible for the ferromagnetic and paramagnetic properties of metals. The extent to which *d*-electrons participated in dsp bonds was expressed as the percentage *d*-character of the metallic bond which represents a measure of the unavailability of electrons in atomic *d*-orbitals. This theory provided a qualitative interpretation of many properties of transition metals such as interatomic distance, characteristic temperature, hardness, and compressibility, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic metals.

The application of Pauling's valence bond theory of metals to problems in catalysis marks the beginning of the awareness of researchers in catalysis of the importance of vacant atomic *d*-orbitals (valence bond theory) or holes in the *d*-band (electron band theory).[36] [37] The remarkable difference in catalytic activity of group VIII and group IB metals, neighbors in the periodic table of elements, became understandable: The group VIII metals have vacant atomic *d*-orbitals (holes in the *d*-band) which were expected to promote chemisorption and catalysis by facilitating covalent bond formation between the metal surface and the adsorbate. In group IB metals, no vacant atomic *d*-orbitals (holes in the *d*-band) are present.

In the following years, the electron band theory was favored, and chemisorption and catalysis were more and more interpreted as an interaction of the adsorbed species

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[35] L. Pauling, Phys. Rev., 54, 899 (1938); Proc. Roy. Soc. (London), A 196, 343 (1949).

[36] F. Seitz, "Modern Theory of Solids," McGraw-Hill Co., New York (1940).

[37] N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys," Oxford University Press (1936).

with the electrons or holes which belong to the whole lattice. From magnetic measurements, it is known that, for instance, nickel has approximately 0.6 holes in the *d*-band. These holes can be filled by alloying nickel with a group 1B metal such as copper. All the holes in the *d*-band are filled when 60 atom percent of copper is alloyed with nickel. The alloys between group VIII and 1B metals received considerable attention. A change of the catalytic properties was expected at the alloy composition where the holes in the *d*-band are becoming filled. The first experimental studies along these lines were encouraging,[38-40] but a number of investigators did not find changes of catalytic activity as expected.[41-44] Work carried out in the 1960's (to be discussed later) showed that considering mainly the collective electronic properties of metals does not lead to a satisfactory interpretation of catalysis. Localized interactions have to be considered also.

2. Electronic Factor in Catalysis on Semiconductors. Beginning in the 1930's, measurements of electrical conductivity have established that chemisorption of gases on semiconductors is accompanied by electron transfer—either from the semiconductor to the chemisorbed gas or vice versa.[45-49] A decrease in the conductivity of n-type semiconductors as a result of chemisorption implies that electrons have been transferred from the conduction band of the semiconductor to the chemisorbed gas. A decrease in the conductivity of a p-type semiconductor indicates an electron transfer from the chemisorbed gas to the semiconductor. Although the electron transfer is in opposite direction in these two processes, both are accompanied by a depletion of carriers in the semiconductor and are classified as examples of depletive chemisorption. The reverse situation of an increase in conductivity upon chemisorption implies that carriers have been accumulated in the semiconductor surface and is referred to as cumulative chemisorption.

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[38] D. A. Dowden and P. W. Reynolds, Disc, Faraday Soc., 8, 184 (1950).

[39] A. Couper and D. D. Eley, Disc. Faraday Soc., 8, 172 (1950).

[40] P. W. Reynolds, J. Chem. Soc., 265 (1950).

[41] R. J. Best and W. W. Russel, J. Am. Chem. Soc., 76, 838 (1954).

[42] W. K. Hall and P. H. Emmett, J. Phys. Chem., 62, 816 (1958); J. Phys. Chem., 63, 1102 (1959).

[43] P. B. Shallcross and W. W. Russel, J. Am. Chem. Soc., 81, 4132 (1959).

[44] M. K. Gharpurey and P. H. Emmett, J. Phys. Chem., 65, 1182 (1961).

[45] C. Wagner and K. Hauffe, Z. f. Elektrochemie, 44, 172 (1938).

[46] W. E. Garner, T. J. Gray, and F. S. Stone, Proc. Roy. Soc. A, 197, 314 (1949); Disc. Faraday Soc., 8, 246 (1950).

[47] W. E. Garner, F. S. Stone, and P. F. Tiley, Proc. Roy. Soc., A 211, 472 (1952).

[48] R. M. Dell, F. S. Stone, and P. F. Tiley, Trans. Faraday Soc., 49, 201 (1953).

[49] M. Boudart, J. Am. Chem. Soc., 74, 1531 (1952).

a. **Boundary Layer Theory.** In 1952, Hauffe and Engell,[50] Aigrain and Dugas,[51] and Weisz[52] independently suggested that depletive chemisorption on semiconductor surfaces could be treated as an electronic boundary layer problem in analogy to the boundary layer problem encountered when a semiconductor and a metal are brought into contact. Metal semiconductor contacts have been studied in considerable detail in view of their importance in rectification.[53] [54] The ideas of Hauffe, Aigrain and Dugas, and Weisz are known as "Boundary Layer Theory," "Randschichttheorie," or "Charge Transfer Theory of Chemisorption and Catalysis." In this theory, it is proposed that adsorbed atoms give rise to localized levels for electrons at the surface. These levels can be filled by current carriers, which are thus immobilized, or they can be emptied and so provide extra carriers. The field of these adsorbed ions sets up a space-charge layer near the surface. The voltage drop across this space-charge region represents a change in work function of the surface and changes in turn the energy of the surface levels with respect to the Fermi level. Let us explore the concepts of this theory in more detail. For depletive chemisorption on an n-type semiconductor (anionic chemisorption), the energy of chemisorption will depend on the difference between the electron affinity of the adsorbed species and the work function of the semiconductor. As more atoms are adsorbed and more electrons are transferred, levels deeper in the solid are used to yield their electrons and a space charge builds up in the boundary layer. As a result, the potential energy of electrons in the boundary layer becomes modified and, in passing from the semiconductor to the chemisorbate, electrons have to surmount a potential barrier. Finally, equilibrium is established when the potential energy of electrons in the adsorbate equals the potential energy of electrons in the semiconductor (i.e. Fermi level). Beyond this point, chemisorption can no longer proceed with a decrease in free energy. For depletive chemisorption on a p-type semiconductor, the energy of chemisorption depends on the difference between work function and the ionization potential of the adsorbate. Equilibrium is established when the Fermi level reaches the height of the electronic level of the adsorbate. The boundary layer theory was emphasized again and discussed in more detail in Hauffe's later publications,[55] [56] and by Garret.[57] This theory was formulated to explain catalytic reactions which affect the concentration of current carriers and the work function of the catalysts. Therefore, the

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[50] K. Hauffe and H. J. Engell, Z. f. Elektrochemie, 56, 366 (1952); Z. f. Elektrochemie, 57, 762 (1953).

[51] P. Aigrain and C. Dugas, Z. f. Elektrochemie, 56, 363 (1952).

[52] P. B. Weisz, J. Chem. Phys., 20, 1483 (1952).

[53] W. Schottky, Z. Phys., 113, 367 (1939).

[54] N. F. Mott, Proc. Roy. Soc., A 171, 25, 281 (1939).

[55] K. Hauffe, "Reaktionen in und an Festen Stoffen," Springer Verlag, Berlin-Göttingen-Heidelberg (1955).

[56] K. Hauffe, "Semiconductor Surface Physics" R. H. Kingston, Ed., University of Pennsylvania Press, Philadelphia, Pennsylvania, 259 (1956).

[57] C. G. B. Garret, J. Chem. Phys., 33, 966 (1960).

boundary layer theory cannot be expected to be applicable to all catalytic reactions. Hauffe was aware that heterogeneous reactions may take place without intermediate electron exchange and may be catalyzed only by a lowering of the activation energy affected by the action of stray surface fields.[58] He called this kind of catalytic activation "heterogeneous polarization catalysis" but considered it to be comparatively less important.

The boundary layer theory stimulated a great deal of experimental work. This theory predicts that for depletive chemisorption the coverage at equilibrium should be small. There is considerable evidence that this pattern is followed.[59] Many investigations were carried out with semiconducting metal oxides whose carrier concentration had been modified by addition of altervalent ions. In a p-type semiconducting oxide, such as NiO, the addition of a monovalent cation like Li^+ increases the number of positive holes and, hence, the conductivity. The addition of trivalent ions such as Cr^{3+} decreases the number of positive holes and conductivity. Schwab and Block[60] found that addition of Li^+ not only increased the conductivity but also decreased the activation energy for oxidation of carbon monoxide on NiO surfaces. It was concluded that the formation of a positive ion on the p-type semiconductor surface is the rate-determining step. In an n-type semiconductor like ZnO, the addition of Li^+ results in a decrease in the number of free electrons and, consequently, a decrease of the conductivity. The addition of trivalent ions like Ga^{3+} increases the conductivity by increasing the supply of free electrons. Li^+ doping resulted in an increased activation energy, Ga^{3+} doping in a decreased activation energy for the carbon monoxide oxidation. These results are consistent with the idea that the catalytic oxidation of carbon monoxide on ZnO surfaces involves the chemisorption of oxygen as the slow step. Since oxygen is an electron acceptor, the greater the supply of electrons at the surface of the ZnO the easier will be the formation of the surface oxygen ions and, hence, the lower the activation energy for the catalytic process.

Other examples of a relationship between semiconductivity and catalytic activity are known. However, the relationship is not at all as clear and straightforward as the above examples might lead one to believe. For instance, when Parravano[61] studied the oxidation of CO over doped NiO, he found the opposite result to that of Schwab. The activation energy of carbon monoxide oxidation increased rather than decreased as the concentration of the Li^+ ions in the NiO was increased. Conversely, the addition of Cr^{3+}

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[58] K. Hauffe, "Semiconductor Surface Physics," R. H. Kingston, Ed., University of Pennsylvania Press, Philadelphia, Pennsylvania, 259 (1956).

[59] F. S. Stone, in "Chemisorption," Proc. Chem. Soc. Symposium (1956), W. E. Garner, Ed., page 181, Academic Press, New York (1957).

[60] G. M. Schwab, J. Block, Z. phys. Chem. N.F., 1, 42 (1954); Z. f. Elektrochemie, 58, 756 (1954); "Semiconductor Surface Physics," R. H. Kingston, Ed., University of Pennsylvania, 283 (1956).

[61] G. Parravano, J. Am. Chem. Soc., 75, 1352, 1448 (1953).

caused a lowering of the energy of activation rather than an increase. Schwab's work was later confirmed by Dry and Stone,[62] Paravano's by Roginsky.[63] There are some differences in how these experiments were conducted. The most important is that Schwab studied the carbon monoxide oxidation in the temperature range of 250-450°C and Parravano, in the range between 180 and 250°C. However, this reversal of the dopent effect with temperature cannot be interpreted on the basis of the boundary layer theory. Dell and Stone[64] investigated the chemisorption of oxygen, hydrogen, and carbon monoxide on nickel oxide and found already in 1954 that electrostatic effects alone do not provide a satisfactory interpretation of these processes. Since then, much information was obtained which shows that chemical effects such as bonding to surface sites of different nature and energies are often more important than current carrier concentration and position of the Fermi level. Much work along these lines was done by Teichner,[65] as well as Burwell[66] which will be discussed in a later section. Corroborating these views are the results of Gray[67] (presented later) which indicate that deep lying trapping levels (sites of different nature and energy) may be more important in catalysis than the principal donor or acceptor levels (free electrons or holes).

The boundary layer theory is based on the band model of the solid state. However, as pointed out by DeBoer and Verwey,[68] Mott,[69] and Morin,[70] the 3 *d*-oxides Cr_2O_3, Mn_2O_3, Fe_2O_3, CoO, NiO, and CuO, unlike ZnO, do not appear to form a 3 *d*-band but have 3 *d*-levels localized around the cations. Consequently, theory also indicates localized interaction in chemisorption on the oxides from Cr_2O_3 to CuO, rather than interaction with free electrons or holes.

b. Volkenstein Theory. The most comprehensive study of the electronic factor in catalysis was carried out by Volkenstein in his "Electronic Theory of Catalysis on Semiconductors."[71] Volkenstein terms it a quantum mechanical examination of the interaction of foreign molecules with crystal lattices. Contrary to the boundary layer theory, the Volkenstein theory includes chemisorption without electron transfer.

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[62] M. E. Dry and F. S. Stone, Disc. Faraday Soc., 28, 192 (1959).

[63] N. P. Keler, S. Z. Roginsky, and P. S. Sasonova, Dokl. Acad. Nauk. SSSR, 106, 859 (1956).

[64] R. M. Dell and F. S. Stone, Trans. Faraday Soc., 50, 501 (1954).

[65] P. C. Gravelle and S. J. Teichner, Advances in Catalysis, 20, 167 (1969), and references therein.

[66] R. L. Burwell, G. L. Haller, K. C. Taylor, and J. F. Read, Advances in Catalysis, 20, 1 (1969).

[67] T. J. Gray and P. Amignes, Surface Science, 13, 209 (1969).

[68] J. H. DeBoer and E. J. W. Verwey, Proc. Phys. Soc. (London), 49, 66 (1937).

[69] N. F. Mott, Proc. Phys. Soc. (London), 62A, 416 (1949).

[70] F. S. Morin, Bell System Tech. J., 37, 1047 (1958); "Semiconductors," N. B. Hannah, Ed., ACS Monograph 140, chapter 14, Reinhold, New York (1959).

[71] F. F. Volkenstein, "The Electronic Theory of Catalysis on Semiconductors," Pergamon Press Book (1963).

Volkenstein postulated that localization of a free electron or hole on or near an adsorbed particle produces a change in the nature of its bond with the surface, leading to strengthening of the bond. Therefore, two kinds of bonds in chemisorption are distinguished. One is "weak" chemisorption in which the chemisorbed particles remain electrically neutral and in which the bond between the particle and the lattice is brought about without the participation of a free electron or hole from the crystal lattice but by deformation of the electron cloud of the foreign molecule or the ion of the lattice which is the adsorption center. This bond is analogous to one-electron bonds in molecules. In the "strong" chemisorption, the chemisorbed particle retains in its neighborhood a free electron or hole which is involved in the chemisorptive bond. If an electron is captured, the strong bond formed is called an n-bond, or acceptor bond. If a free hole is captured, a strong p-bond, or donor bond, is formed. Acceptor and donor bonds can be ionic or homeopolar or of mixed type depending on how the electron or hole is captured and distributed. The electrons or holes may be taken from the lattice or they may be obtained from the atoms or ions of the lattice which act as adsorption centers.

Free electrons or free holes in a crystal perform the functions of free negative or positive valencies. Consequently, "strong" chemisorption indicates a free surface valency being involved in the bond. In other words, valency-saturated particles are being converted to radicals or ion radicals which leads to increased reactivity. It can be concluded that the different forms of chemisorption are distinguished not only by the character and strength of the bond but also by the reactivity of the chemisorbed particle.

The various forms of chemisorption may be converted into one another, i.e., in the course of its life in the adsorbed state, the adsorbed particle may change the character of its bond with the surface. This happens as a result of localization or delocalization of free electrons or holes. A particle held by a "weak" chemisorptive bond which has an affinity for a free electron is reflected in the energy band representation of solids by a local acceptor level; a particle having an affinity for a hole corresponds to a local donor level. The occurrence of an electron at the local acceptor level or the removal of an electron from a local donor level indicates the transition from "weak" to "strong" bonding. The removal of an electron from an acceptor level or a hole from a donor level indicates the transition from the "strong" to "weak" form of chemisorption. In the "Boundary Layer Theory," weak bonding is not considered, and the removal of an electron from an acceptor level or a hole from a donor level means desorption of the particle, signifying the disappearance of the local level itself. Volkenstein stresses that this notion of an acceptor level which exists only as long as it is occupied by an electron or a local donor level which is always deprived of its electron renders meaningless the very concept of a local level as a level capable of accepting or giving up an electron.

When electronic equilibrium has been established, the relative concentrations of different forms of chemisorption on the surface and thereby the reactivity of the chemisorbed particles as well are determined by the position of the Fermi level on the surface of the crystal. If the Fermi level is close to the conduction band, the relative number of strong acceptor bonds will be great. If the Fermi level is situated close to the valence band, the relative number of strong donor bonds will be great. The relative concentration of the "weak" form of chemisorption will be greatest when the Fermi level is equidistant from the conduction and valence bands. Different forms of chemisorption reflect different reactivities of the adsorbed particles. The reaction rate will be higher the higher the concentration of the active forms. Consequently, the rates of reactions will depend on the position of the Fermi level of the solid. In cases where different reactions can occur, such as for instance dehydration or dehydrogenation of alcohols, the relative activity of the catalyst for dehydration or dehydrogenation (the course of the reaction) will also depend on the position of the Fermi level.

According to the variation of reaction rates with the position of the Fermi level, Volkenstein divides all heterogeneous reactions into two classes. To one of these belong the reactions which proceed more rapidly the higher the Fermi level (all other conditions being equal). These are reactions accelerated by electrons and are called acceptor reactions, or n-class reactions. To the other class belong reactions whose rate is the greater the lower the Fermi level. They are called donor reactions, or p-class reactions. Not only different reactions but also the different reaction stages of a given reaction may belong to opposite classes. An acceptor stage may be followed by a donor stage and vice versa. Stages in which the rate of reaction does not depend on the position of the Fermi level are also possible. Volkenstein shows that the position of the Fermi level depends to some degree on the condition under which the reaction occurs, i.e., on the temperature and the partial pressures of the reactants. Since the Fermi level position is to a certain extent a function of the temperature, it enters the experimental activation energy as a component. This consideration may permit the interpretation of Schwab's[72] and Parravano's[73] divergent results on carbon monoxide oxidation which were obtained with identically doped NiO as catalyst but at different temperatures.

"Strong" chemisorption on semiconductors leads to charging of the surface and the appearance of a space charge. This produces bending of the energy bands near the surface, and the distance between the Fermi level and the energy bands will be different near the surface (E_s) as compared to this distance inside of the crystal (E_v). Using the condition of electrical neutrality of the crystal as a whole, Volkenstein showed that E_s depends on E_v. Since surface properties such as catalytic activity are determined by E_s and bulk properties such as electrical conductivity by E_v, a correlation between surface and bulk properties is established. However, the parallel change of electrical conductivity

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[72] G. M. Schwab, J. Block, Z. phys. Chem. N.F., 1, 42 (1954); Z. f. Elektrochemie, 58, 756 (1954); "Semiconductor Surface Physics," R. H. Kingston, Ed., University of Pennsylvania, 283 (1956).

[73] G. Parravano, J. Am. Chem. Soc., 75, 1352, 1448 (1953).

and activity can be direct or inverse. If an n-class reaction on an n-semiconductor or a p-class reaction on a p-semiconductor occurs, the relation between electrical conductivity and catalytic activity will be direct. In the case of an n-class reaction on a p-semiconductor or a p-class reaction on an n-semiconductor, the relationship will be inverse. It is also emphasized that a connection between electrical conductivity and catalytic activity may not exist in all cases, and parallel changes of these quantities cannot be expected when comparing semiconductors differing in their chemical nature.

The relationship between the surface and bulk properties breaks down in the case of a "quasi-isolated surface." This can happen when the surface concentration of electrons and holes localized in surface acceptor and donor levels are nearly the same. Under these conditions, a change in the distance of the Fermi level from the energy bands in the inside of the crystal is not accompanied by a change in this distance on the surface.

In the Volkenstein theory, poisoning and promoting effects of impurities are discussed. Under the term "impurity" not only foreign atoms are meant but also any local disturbance of the lattice. The role of an impurity is also fulfilled by chemisorbed particles participating in the reaction. Two types of impurities are distinguished—namely, acceptor and donor impurities—which play the role of localization centers for lattice free electrons and holes respectively. The same foreign particle dissolved in the lattice can assume the role of an acceptor or donor impurity depending on the manner of its inclusion in the lattice, i.e., whether it is in an interstitial position or substitutes for a regular lattice ion. Acceptor impurities always displace the Fermi level downward, donor impurities upward. By increasing the temperature or lowering the impurity content, the Fermi level is always drawn to the center of the forbidden region. Since the position of the Fermi level affects the activation energy, all of this results in promoting or poisoning effects. Acceptor reactions are accelerated by donor impurities and slowed by acceptor impurities. Donor reactions are accelerated by acceptor impurities and slowed by donor impurities. These considerations show that the same impurity in the same catalyst may act as a promotor in one reaction and as a poison in another. If a reaction consists of two or more consecutive stages belonging to donor and acceptor classes, an increase in impurity content (displacement of the Fermi level) may shift the rate-limiting step from one stage to the other. This shows that an impurity which acts for a particular reaction at one concentration as a promotor may be a poison at another concentration.

Another interesting aspect of Volkenstein's views is the influence of fine dispersion of catalysts on their catalytic properties. The space charge is uniformly spread over the whole volume of very small semiconductor particles if the ratio of volume to surface of the particle is equal or smaller than the diameter of the surface space in which the energy bands are bent (screening length). In other words, the Fermi level is the same on the surface and in the inside of the particle. This will affect the adsorption capacity and catalytic activity. This effect can be expected when the surface area reaches tens of square meters per gram. The screening length is usually 10^{-4}-10^{-5} cm.

In a more recent paper,[74] Volkenstein emphasized that in chemisorption the term "electron transfer" is not to be understood in a geometrical sense but in terms of energy as a transition of an electron from one energy level to another. The term "electron transfer" in its direct geometrical sense should be discarded in works on chemisorption and catalysis, just as at one time the concept of electron orbits was discarded in the theory of the atom. Volkenstein also stressed that the concept of local and cooperative interactions is fundamental to the electron theory. In the first case, we deal with the interaction of an adsorbed particle with an adsorption center. In the second case, the entire collective of free electrons and holes of the lattice comes into play. Problems of the first kind belong to quantum mechanics; those of the second kind to quantum statistics.

With his "Electronic Theory of Catalysis on Semiconductors," Volkenstein demonstrated the possibility of a formalized theory with consideration of weak and strong chemisorptive bonding, the variation between bulk and surface characteristics, and the structure sensitivity of these features. The Volkenstein Theory has many parameters which is not surprising in view of the complexity of catalysis. However, due to the large number of parameters, it is difficult to prove or disprove the theory or to use it as a guide for the discovery of new catalysts.

In this and the following paragraph, some experimental work with relevance to the Volkenstein theory will be discussed. In the Volkenstein theory, the formation of radicals and radical ions on surfaces is postulated. This matter was studied experimentally by Kasansky and Pariisky[75] who found in electron spin resonance investigations that free radicals forming a weak, one-electron bond with the catalyst can only be found on surfaces of insulators. These bonds were found to be so weak that these species are not expected to be important in catalysis. (They can be observed only at temperatures below -130°C.) On semiconductor surfaces, this form of radicals was not found probably because they trap free electrons and transform to strongly chemisorbed molecules. Radical ions formed by localization of free electrons on the adsorbed particles were found on semiconductor surfaces and are expected to be important in catalysis.

The many experimental studies aimed at correlating semiconductivity and catalytic activity carried out mainly in the 1950's did not yield conclusive results. In more recent

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[74] F. F. Volkenstein, 4th International Congress on Catalysis, Moscow, 1968, reprints of papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 5, p. 2092.

[75] V. B. Kasansky and G. B. Pariisky, Proc. 3rd International Congress on Catalysis, Vol. 1, page 367. North-Holland Publishing Co., Amsterdam (1965).

times, Vrieland and Selwood[76] dealt again with this problem. They recognized that the rare earth oxides Eu_2O_3 and Gd_2O_3 are about as nearly identical as two solids can be except for the difference in their semiconductivity. Eu_2O_3 has one less electron in the 4f-shell and offers the possibility of reduction to the 2+ oxidation state. Owing to the shielding of the outer electrons, exchange effects are minimal in both these oxides. Both are n-type oxides, but the semiconductivity of Eu_2O_3 is greater by a factor of 19 at 800°C than that of Gd_2O_3. Since the experiments showed that the rate for the decomposition of ammonia and the activation energy for this reaction are almost identical for each of the oxides, the conclusion was drawn that there is no relation between semiconductivity and catalytic activity in this case.

c. The Role of Electrons and Holes in Surface Reactions on Semiconductors as Discussed by H. Gerischer. Gerischer's discussion of electron transfer processes on semiconductor surfaces is interesting from the viewpoints of both electrochemistry and catalysis.[77] In these processes, he distinguishes the cases of weak and strong interaction between reactants and semiconductors. In weak interaction, the energy levels of the reactants and of the semiconductor remain unchanged. In strong interaction, new energy states are formed by combination of suitable states of the reactants and the semiconductor.

In the case of weak interaction, electron transfer is most likely if the energy levels of the reactants and the semiconductor surface are on the same height and will be limited to a range of energy levels differing by not more than kT. This principle excludes all energy levels of donors or acceptors within the band gap from electron transfer. If surface states are present with energy levels within the forbidden zone, they can contribute to the electron exchange to some extent. This may become important in cases where the direct exchange rate is small because the energy levels of the reactants are in the energy range of a wide band gap semiconductor. When the overlapping of the orbitals of surface atoms and reactants is large enough and the necessary symmetry conditions are fulfilled, new quantum states for electrons are generated in the surface (strong interaction). The favorable bonding states will be close to the valence band energy levels; the corresponding antibonding orbitals will have energies near the range of the conduction band. Bond breaking between surface atoms will occur if the energy levels of the new bonds are below the top of the valence band. The new bonds can be formed easily if unoccupied quantum states are available in the valence band and if the excess electrons can be transferred into bonding quantum states. Otherwise, electrons of the reactants would have to be excited to antibonding states which excludes bond formation.

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[76] E. G. Vrieland and P. W. Selwood, J. Catalysis, 3, 539 (1964).

[77] H. Gerischer, Surface Science, 13, 265 (1969).

Surface atoms in the radical intermediate state with one unpaired electron can interact much more readily. If a reactant approaches such a radical surface atom, a new chemical bond is formed by combination of the orbitals of the radical surface state and the highest occupied state of the reactant. Bonding occurs since two electrons are incorporated into the new bonding orbital while one must be promoted into an antibonding orbital. The strongly adsorbed reactant now has one unoccupied electronic state available which can pick up an electron from the conduction band. If this occurs, the bonding will be weakened so much that desorption can follow, particularly if the desorbing species is able to carry away the excess electron and to undergo an irreversible change in chemical structure.

An example of such behavior is the reduction of H_2O_2 which occurs on germanium only after interaction with a radical surface state. Electron transfer and decomposition into OH^- and $OH_{adsorbed}$ follow. The rate-determining step is the generation of radical surface states which is controlled by the concentration of electrons in the surface.

An analogous mechanism can be postulated for the oxidation of electron donors which cannot transfer electrons directly into the valence band of the semiconductor. The strong interaction between the electron states of the surface and the reactants brings the occupied energy levels of the adsorbed molecules into the energy range of the valence band and charge transfer becomes possible. If holes are present in the surface, they can be transferred to the adsorbed molecules. This leads to a weakening of the bond and an oxidized species can be desorbed.

Gerischer concludes that the efficiency of electrons and holes in redox processes is primarily controlled by the energy correlations between the quantum states in the energy bands of the semiconductor and the donor or acceptor levels in the potential reactants. Since the quantum states in the range of the energy bands do often little overlap with electronic systems outside the semiconductor, radical surface states will be most important for chemical interaction (chemisorption). The energy levels of these radical surface atoms will be located within the band gap.

An electroneutral catalytic reaction must include an oxidation and a reduction step in parallel. This becomes more unlikely the larger the band gap is. On the other hand, with increasing band gap, the importance of surface states within the gap will increase. These surface states are "active centres" for adsorption and can catalyze the electronic interaction between potential reactants and the electrons in the bands of the crystal if a charge transfer process is involved in the net reaction. It seems much more probable that catalytic reactions on semiconductor surfaces depend on the presence of surface states rather than on the electron distribution over the energy bands in the crystal interior. This is in contrast to electrochemical reactions where the electrons and holes have a decisive function in most cases.

Gerischer's theory appears to be more in line with current results and thinking in catalysis research as compared to Volkenstein's views. Volkenstein, for instance, considered strong adsorption to be mainly due to interaction of adsorbed particles with conduction electrons or holes. It is interesting to note the similarity between Gerischer's surface states and the deep-lying trapping levels observed by Gray.

d. The Role in Catalysis of Deep-Lying Levels as Compared to the Role of the Principal Donor or Acceptor Levels as Discussed by T. J. Gray. Adsorption and desorption phenomena on ZnO were widely investigated[78-83] and frequently interpreted in terms of the boundary layer theory and Volkenstein Theory, i.e., they were directly and exclusively related to the donor level of 0.12 to 0.15 eV. However, Gray had already pointed out in 1960 that deeper lying levels may play a significant role also. In a recent paper,[84] Gray and Amigues obtained more information on these levels and found indications that deep-lying levels may be more important for catalysis than the principal donor or acceptor levels which give rise to semiconductivity. These results were obtained with ZnO, an n-type semiconductor, which was extensively used in investigations aimed at correlating semiconductivity and catalytic activity. Gray and Amigues use [illegible] technique of thermally stimulated electron currents whereby extremely pure [illegible]O or TiO_2 was illuminated at -196°C (using UV light exceeding in energy the respective band gaps) and then slowly and uniformly warmed in the dark whereby temperature and current were continuously recorded. The exact location and occupancy of various trapping electron levels could be determined in this way. Even in extremely pure ZnO (99.999%), levels at 0.4-0.5 eV, 0.6 eV, 0.8 eV, 1.0 eV, and 1.1-1.2 eV were found as well as the well-known donor level at 0.12-0.15 eV. The level at 0.4-0.5 eV could be identified as being due to a residual copper impurity of about 0.3 ppm. The trapping level at 0.8 eV is associated with the adsorption of the O^- ion, and the level at 1.1 eV was attributed to an ionic conduction process with an activation energy of 1.1 eV. Experiments in different atmospheres revealed that adsorption or desorption of oxygen, hydrogen, water vapor, or hydrocarbons has a more profound effect on the trappings of deep-lying levels than on the donor level. Consequently, it appears that the deep-lying levels have greater significance in catalysis than the principal donor level. Gray points out that this should not surprise chemists since the energy of

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[78] T. J. Gray, Actes du Deuxieme Congress International de Catalyse, p. 1561, Editions Technip (1961).

[79] T. J. Gray and D. Carpenter, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 463, North-Holland Publishing Company, Amsterdam (1965).

[80] F. S. Stone and T. I. Barry, Proc. Roy. Soc. (London), A255, 124 (1960).

[81] I. A. Myasnikov, Dokl. Akad. Nauk SSSR, 99, 125 (1954).

[82] A. N. Terenin and Y. P. Solomitzin, Disc. Faraday Soc., 28, 28 (1959).

[83] F. F. Volkenstein and S. M. Noran, J. Chim. Phys. SSSR, 55, 483 (1958).

[84] T. J. Gray and P. Amigues, Surface Science, 13, 209 (1969).

the principal donor level corresponds to a heat of adsorption of only 2.7-3.5 Kcal/mole while a heat of adsorption of 8-18 Kcal/mole, corresponding to the energy of the deeper levels, is in a more reasonable range. Gray also stressed that his results which show the importance of deep-lying levels in chemisorption and catalysis may bring about a reconciliation of the views expressed in the electronic theory of catalysis with those which constitute the acid site concept.

IV. RECENT CHEMICAL CONCEPTS IN CATALYSIS

1. **Crystal Field Theory in Catalysis.** In 1951, crystal field theory was used the first time to interpret the spectra of transition metal complexes.[85] This approach was very successful and resulted during the following decade in an avalanche of research activity in inorganic chemistry. Some years later, crystal field theory also began to have some impact on research in catalysis. Therefore, it will be briefly discussed here: In a transition metal ion which is isolated from all other species, as for instance in vacuum, the five *d*-orbitals are degenerate which means they have identical energies. In solution and in the solid state, each transition metal ion is surrounded by negative ions or by dipoles; as a consequence, it is more difficult to place electrons in the *d*-orbitals of the transition metal ion. In other words, the energy of the *d*-orbitals increases as ligands approach the orbitals. In addition, the interaction of the *d*-orbitals of the transition metal ions with the ligands leads to a removal of the degeneracy, and the five *d*-orbitals of identical energy become split into sets of different energies. This is a consequence of the geometry of the *d*-orbitals, of which some can be approached closer by ligands than others. In the case of octahedral symmetry, two sets of energy levels are formed and the distance between these is designated 10 Dq or Δ. One of the new energy levels is of lower energy than the hypothetical non-split level. Therefore, placing of electrons into the lower energy level leads to an increase of the stability which is known under the term "crystal field stabilization energy." In going from left to right in the first long period of the periodic table of elements, one sees that the crystal field stabilization energy increases from zero at d^0 (Ti^{4+}) to a maximum at d^3 (Cr^{3+}) and falls to zero at d^5 (Mn^{2+} or Fe^{3+}). Then, the crystal field stabilization energy increases again and reaches another maximum at d^8 (Ni^{2+}) after which it falls again to reach zero at d^{10} (Zn^{2+}). The same twin peak was found when comparing properties of transition metal compounds such as lattice energies, heats of hydration, or stability constants. It turned out that these trends in transition metal compound properties could be interpreted by considering the crystal field stabilization energies.

Dowden and Wells[86] recognized that an analogous activity pattern (twin peak) existed for catalytic reactions on surfaces of transition metal compounds and suggested

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[85] F. Ilse and H. Hartmann, Z. phys. Chem., 197, 239 (1951).

[86] D. A. Dowden and D. Wells, Actes du Deuxieme Congres International de Catalyse, p. 1499, Edition Technip, Paris (1961).

that the crystal field stabilization energy may be a significant factor in chemisorption and catalysis. They pointed out that the transition metal ions which are at the surface of a solid do not have their energetically most favorable coordination. When chemisorption occurs, the coordination shell becomes completed. This leads to a gain in energy which will be greatest where the crystal field stabilization energy is greatest. Considering chemisorption as a form of coordination change, the energetics of chemisorption could be estimated using the known crystal field stabilization energies. For a (100) plane, chemisorption amounts to a coordination change from square pyramidal to octahedral; for a (110) plane, to a change from tetrahedral to octahedral; and for a (111) plane, to a change from trigonal to octahedral. Consequently, the gain in crystal field stabilization energy when oxygen is adsorbed on a d^8 system such as NiO is 2 Dq (4.6 Kcal mole^{-1}) on a (100) plane, 8.4 Dq (19 Kcal mole^{-1}) on a (110) plane, and 1.1 Dq (2.5 Kcal mole^{-1}) on a (111) plane.

The crystal field considerations provided a theoretical foundation for expecting different catalytic activity for different crystal faces (geometric factor in catalysis). It also became more understood that geometric and electronic factors can ultimately not be separated because crystal geometry depends on the arrangement of orbitals in the atoms. By applying the crystal field theory, attention was directed to individual surface atoms rather than to the collective electronic properties of solids. The efforts to interpret chemisorption and catalysis with the crystal field theory considerably stimulated research in catalysis. However, it was soon realized that the contribution of the crystal field stabilization energies to the overall energy changes is relatively small when changes in the valency state of catalyst cations are occurring during the catalytic process.[87]

2. Formation of Surface Compounds as Intermediates. In the 1950's, hopes were high that catalysis could be interpreted in terms of the electronic properties of solids. Much work was done within this framework, but it became increasingly apparent that more emphasis must be placed on the properties of individual atoms and complexes at the surface than on collective electronic properties of solids. As a consequence of this, a renaissance of interest in the purely chemical aspects of catalysis ensued. More advanced techniques and the deepened understanding of the problems provided a better basis for this approach than in earlier times. The application of crystal field theory to problems in catalysis was an important step in this direction. Strong impetus came from the Dutch school of catalysis which stressed that regularities in catalysis should be related to regularities in the general field of chemistry.

The work of Fahrenfort, Van Reijen, and Sachtler[88] on the decomposition of formic acid on metal surfaces received considerable attention. These authors found that

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[87] P. G. Dickens and M. B. Sutcliffe, Trans. Faraday Soc., 60, 1272 (1964).

[88] J. Fahrenfort, L. L. Van Reijen, and W. M. H. Sachtler, Z. f. Elektrochemie, 64, 216 (1960); "The Mechanism of Heterogeneous Catalysis," J. H. deBoer *et al.*, Ed, Elsevier Publ. Co., Amsterdam, p. 23.

the curve representing the catalytic activity of metals as a function of the heat of formation of the respective metal formates has a maximum for metals whose formates have intermediate values of the heat of formation (so-called volcano curve). It was concluded that metal formats are intermediates in the decomposition of formic acid on metal surfaces and that the metals which form moderately strong bonds with the formate group (intermediate heat of formation) are the best catalysts. These conclusions gained strong support from infrared investigations which indicated that formates were actually formed on the surface of metal catalysts. Kinetic work led to a better understanding of the facts which give rise to the volcano relationship in formic acid decomposition on metals. On non-noble metals such as iron, cobalt, or nickel, whose formates have relatively high heats of formation, zero-order kinetics and relatively high activation energies and frequency factors were found. This indicates that the surface is fully covered and that the relatively high strength of the metal-formate bonds limits the overall rate to the rate of the surface formate decomposition. On noble metals such as gold, where the heat of formation of formates is low, the rate is limited by the adsorption step in which the surface formate is formed—a reaction which has a very low frequency factor. The formates of the platinum metals have intermediate bond strengths and consequently these metals are the most active catalysts, i.e., these metals are on the top of the volcano-shaped curve. All these results show the wisdom in Sabathier's original suggestion that heterogeneous catalysis functions through intermediate compound formation.[89] However, the modern view of an adsorption surface complex is not exactly the same as Sabathier's.

It must be said here that the purely chemical approach to catalysis has been pursued throughout the years. A notable contributor to this field was Balandin[90] [91] who stressed the importance of bond length and bond strength (Balandin's principles of structure and energy correspondence) and generated the ideas which are known as volcano relationship or volcano curve This subject will be briefly discussed here: Balandin analyzed the relationship between the adsorption potential q (defined as the sum of the adsorption energies of all reactants) and the energy of formation E' and the energy of decomposition E'' of the intermediate surface complex. E' and E'' were expressed as the sum of the energies of all formed and broken bonds. The graphic representations of E' and E'' as a function of the adsorption potential are straight lines which intercept at a point where q is one half of the energies of the involved bonds, i.e., the average of the energies of the broken and newly formed bonds. (This constitutes Balandin's energy correspondence principle.) To the left of the resulting maximum, the rates are limited by the energies of formation of the intermediate complex, to the right of the maximum,

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[89] P. Sabathier, " La Catalyse en Chemie Organique," Librairie Polytechnique, Paris (1913).

[90] A. A. Balandin, Z. phys. Chem., 132, 289 (1929); Advances in Catalysis 19, 1 (1969).

[91] A. A. Balandin, Advances in Catalysis, 10, 96, (1958); "Catalysis and Chemical Kinetics," Acad. Press, Inc., New York (1964); Advances in Catalysis, 19, 1 (1969).

by the energies of decomposition of the intermediate complex. At the maximum, the energies of formation and decomposition are equal and optimum catalytic rates can be expected (volcano curve). For endothermic reactions, a sharp maximum is indicated by the theory. For exothermic reactions, the adsorption potential of the most active catalyst may differ from the adsorption potential at the point of intersection of the E′ and E″ lines but by not more than one half of the heat of reaction. Balandin's considerations are based also on a semiempirical linear relationship between the energies of formation and decomposition of the intermediate complex and the activation energy. This semiempirical relationship is the reason for some criticism of Balandin's work.

3. Concepts in Heterogeneous Catalytic Oxidation

a. Reduction-Oxidation Mechanism. As early as 1936, Schenck,[92] and later Rienäcker,[93] correlated the catalytic activity of oxides for oxidation reactions with ΔH_{M-O} , the energy necessary to remove one mole of oxygen from the oxide surface. In the 1960's, several groups of investigators devoted considerable effort to this subject which will be discussed in the following paragraphs.

Sachtler and DeBoer[94] investigated the oxidation of propylene to acrolein and found that the catalytic activity of eight different oxides could be correlated with their reducibilities by hydrogen. These results indicated that, in oxidation reactions on metal oxides, oxygen is removed from the oxide surface by the molecules which are oxidized and then resupplied from the gas phase. Using radioactive labeled propylene, Sachtler and DeBoer also showed that propylene is adsorbed dissociatively by splitting off one hydrogen atom from the methyl group and forming an adsorbed symmetric π-bonded allyl group. The formation of this intermediate surface complex was observed also by Adams.[95] [96] In a more recent work, Sachtler *et al.*[97] studied the oxidation of benzaldehyde to benzoic acid on MnO_2, V_2O_5, and V_2O_5-SnO_2 as catalysts. Oxygen tensions of these oxides as a function of temperature were determined, and the free energy, enthalpy, and entropy of the oxygen release were calculated. The results showed that the free energy of oxygen release and the catalytic activity are inversely

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[92] R. Schenck, Angew. Chem., 49, 649 (1936); Z. anorg. Chem., 260, 154 (1949).

[93] G. Rienäcker and R. Schneeberg, Z. anorg. allgem. Chem., 282, 222 (1955).

[94] W. M. H. Sachtler and N. H. DeBoer, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 252, North-Holland Publishing Company, Amsterdam 1965.

[95] C. R. Adams and T. J. Jennings, J. Catalysis, 2, 63 (1963).

[96] C. R. Adams, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 240, North-Holland Publishing Company, Amsterdam (1965).

[97] W. M. H. Sachtler, G. J. H. Dorgelo, J. Fahrenfort, R. J. H. Voorhoeve, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, p. 453.

related. The increased catalytic activity of V_2O_5-SnO_2 as compared to V_2O_5 (promotor action of SnO_2 which is very little active itself) could also be rationalized in these terms, since the free energy of oxygen release was found to be lower when SnO_2 was present. The increased catalytic activity of oxide mixtures had already been observed in 1852 by Wöhler[98] and correctly interpreted in the 1930's and 1940's by Schenck *et al.*,[99] and Hüttig *et al.*[100] Electron spin resonance work of Sachtler *et al.* indicated that the lower free energy for oxygen release of V_2O_5-SnO_2 as compared to V_2O_5 is probably due to the formation of V^{4+} ions which dissolve in the SnO_2 lattice, occupying tin sites. Sachtler's main conclusion, that oxygen is taken from the oxide and resupplied from the gas phase, was supported by infrared studies which showed that the benzaldehyde is adsorbed dissociatively on oxygen sites of the oxide surface whereby a benzoate-type surface complex is formed. Infrared work by Fahrenfort and Rol[101] provided information on the type of oxygen ions that are most likely of dominant importance in the benzaldehyde oxidation on V_2O_5. Before going further, the structure of V_2O_5 must be discussed. According to Bachmann *et al.*,[102] the lattice of V_2O_5 consists of warped layers consisting of the vanadium ions and four-fifths of the oxygen ions, while one-fifth of the oxygen ions are located between these layers. The latter oxygen ions have only one vanadium ion in each layer as near neighbors. On the surface, these oxygen ions can be considered to be coordinated to only one vanadium ion. Now, let us return to Fahrenfort's reflection infrared work. His spectra showed that the adsorption of benzaldehyde affects the height of the peak which is attributed to the V-O stretching vibration of the singly coordinated oxygen ions but not the height of the peak which is attributed to the stretching vibration of the V-O bonds in the layers. Consequently, it could be concluded that the singly coordinated oxygen ions are the catalytically active sites.

Investigations by Sachtler *et al.*[103] indicated that the selectivity of oxide catalysts for partial oxidation of hydrocarbons or total oxidation of hydrocarbons to carbon dioxide and water is influenced by the thermodynamics of the oxygen release from the oxides. They found that on oxides with a high gradient $\frac{\partial \Delta H}{\partial x}$ (ΔH = enthalpy of oxygen release; x = degree of reduction due to oxygen release), partial oxidation is favored, but on oxides with a low gradient $\frac{\partial \Delta H}{\partial x}$, total oxidation. A high gradient of $\frac{\partial \Delta H}{\partial x}$ implies that

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[98] F. Wöhler, Liebigs Ann. Chem., 81, 255 (1852).

[99] R. Schenck and F Kurzem, Z. anorg. allgem. Chem., 235, 97(1937).

[100] G. F. Hüttig, *Handbuch der Katalyse*, G. M. Schwab, Ed., Springer Verlag (1943).

[101] J. Fahrenfort and N. C. Rol, quoted by W. M. H. Sachtler, Catalysis Reviews, 4(1), 46 (1970).

[102] H. Bachmann, F. R. Ahmed, and W. H. Barnes, Z. Krist., 115, 110 (1961).

[103] W. M. H. Sachtler, G. J. H. Dorgelo, J. Fahrenfort, R. J. H. Voorhoeve, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, p. 453.

the successive removal of a second or third oxygen atom from the same site requires considerably more energy than the removal of the first oxygen atom. Consequently, partial oxidation is favored on catalysts with a high $\frac{\partial \Delta H}{\partial x}$ gradient. These considerations improved the understanding of selectivity. Prior to this, only the metal-oxygen bond strengths were considered to be important. It was suggested that catalysts having low oxygen-metal bond strengths facilitate total oxidation of hydrocarbons to CO_2 and H_2O while catalysts with higher oxygen-metal bond strength catalyze selective oxidation to partially oxidized products.[104, 105]

Boreskov and coworkers[106-108] conducted extensive investigations on oxygen isotope exchange reactions and catalytic oxidation reactions on metal oxide surfaces. They found that on oxides which had been heat treated in an oxygen atmosphere, i.e., on those containing the equilibrium amount of oxygen, very similar rates, activation energies, and reaction orders were always obtained for the homomolecular exchange ($O_2^{16} + O_2^{18} \rightarrow 2\,O^{16}O^{18}$) and the heteromolecular exchange ($O_2^{18} + O^{16}_{surface} \rightarrow O^{16}O^{18} + O^{18}_{surface}$). This result indicated that oxide oxygen participates in catalytic reactions. Consequently, breaking of the metal-oxygen bond must take place, and the strength of this bond will affect the catalytic reaction. In accordance with this, Boreskov[109] was able to correlate the heats of formation of oxides with their catalytic activity for oxidation. In a more recent paper, Boreskov[110] presented work in which a more direct measure of the metal-oxygen bond strength was obtained, namely the heats of oxygen desorption which were determined by measuring the oxygen pressure of the oxides at different temperatures. The results showed that the activation energies for the isotopic oxygen exchange reaction as well as for oxidation of hydrogen and methane increased with increasing oxygen desorption energies of the oxide catalysts, all of which indicates that the breaking of the metal-oxygen bond of the oxide catalyst is important in the rate-limiting step of the above reactions. The following sequence of increasing oxygen desorption energy and decreasing catalytic activity was found: $Co_3O_4 > CuO > NiO > MnO_2 > Cr_2O_3 > Fe_2O_3 > ZnO > V_2O_5 > TiO_2$. The catalytic activity of platinum, whose surface in oxidation reactions is covered with oxygen, was found near that of Co_3O_4.

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[104] W. M. H. Sachtler and N. H. DeBoer, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 252, North-Holland Publishing Company, Amsterdam 1965.

[105] A. A. Balandin, Advances in Catalysis, 10, 96 (1958); "Catalysis and Chemical Kinetics," Acad. Press, Inc., New York (1964); Advances in Catalysis, 19, 1 (1969).

[106] G. K. Boreskov, Advances in Catalysis, 15, 285 (1964), and references therein.

[107] G. K. Boreskov, Disc. Faraday Soc., 41, 263 (1966).

[108] G. K. Boreskov, V. V. Popovsky, V. A. Sazonov, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, p. 580.

[109] G. K. Boreskov, Advances in Catalysis, 15, 285 (1964), and references therein.

[110] G. K. Boreskov, V. V. Popovsky, V. A. Sazonov, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2 p. 580.

Boreskov[111] observed also that oxides which were not equilibrized by a heat treatment in an oxygen atmosphere but heated in vacuum behaved differently. They displayed high initial activities even at comparatively low temperatures, but this activity was unstable and was lost upon heating in oxygen. The catalytic activity of oxides which were heat treated in vacuum was studied in considerable detail by Teichner and coworkers[112] and others and will be discussed in a later section.

The role of the metal-oxygen bond strength of oxide catalysts was stressed also by Moro-oka *et al.*[113] [114] These investigators studied the catalytic oxidation of hydrocarbons on surfaces of metal oxides and some noble metals and related the observed rates and reaction orders to a quantity (ΔH_0) which is defined as the heat of formation of the catalyst metal oxide divided by the number of oxygen atoms in the oxide molecule. The larger the ΔH_0, which signifies the metal-oxygen bond strength, the smaller was the activity of the catalyst and the higher was the reaction order with regard to hydrocarbon. Catalysts with low ΔH_0 values such as platinum and palladium are characterized by negative orders in hydrocarbon and nearly first orders in oxygen. This was interpreted as an indication that the surface is fully covered with hydrocarbons, and the slow step of the oxidation reaction is the adsorption of oxygen. For catalysts with medium ΔH_0 values, such as Co_3O_4 or Fe_2O_3, nearly zero orders in hydrocarbon and nearly one-half orders in oxygen were found. It was concluded that both reactants occupy the surface and that the surface reaction is the slow step. Catalysts with high ΔH_0 values are characterized by first-order kinetics in hydrocarbon and zero-order kinetics in oxygen which indicates that the surface is fully covered by oxygen. The slow step on this type of catalyst would be either the hydrocarbon adsorption or the surface reaction. Consistent with these views is that in competitive reactions, where different hydrocarbons are present, some hydrocarbons inhibit the oxidation of other hydrocarbons on catalysts with low and medium ΔH_0 values. On catalysts with high ΔH_0 values, no inhibiting effects of hydrocarbons were found. The sequence of hydrocarbon adsorption strength was found to be iso-$C_4H_8 > C_2H_2 > C_3H_6 > C_2H_4 > C_3H_8$ which is the reverse of the reaction order and reactivity sequence.

It may be useful to discuss also the work of Roiter *et al.* and Golodetz *et al.*[115] [116]

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[111] G. K. Boreskov, V. V. Popovsky, V. A. Sasonov, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, p. 580.

[112] P. C. Gravelle and S. J. Teichner, Advances in Catalysis, **20**, 167 (1969), and references therein.

[113] Y. Moro-oka, Y. Morikawa, and A. Ozaki, J. Catalysis, **7**, 23 (1967).

[114] Y. Moro-oka and A. Ozaki, J. Catalysis, **5**, 116 (1966).

[115] V. A. Roiter, G. I. Golodetz, and Yu. Pyatnitsky, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, page 628.

[116] G. I. Golodetz and V. A. Roiter, Ukr. Khim. Zh., **29**, 667 (1963).

Like Balandin, Boreskov, and other Russian workers, Roiter *et al.* used the Brönsted equation ($k = gK^{\alpha}$) to relate thermodynamics and kinetics (k is the rate constant, K the equilibrium constant, and g and α are constants). Basically, the same is done in the linear free energy correlations which are widely used in organic chemistry and which were applied also in the field of heterogeneous catalysis.[117] Correlations of this kind are made to compare similar reactions of structurally closely related compounds in which case the constants g and α do not change appreciably, thus permitting comparisons. Using the Brönsted equation and the axiom that highest catalytic activity is to be expected where the rate constant k_1 of the catalyst binding process (formation of the intermediate) and the rate constant k_2 of the catalyst liberation process (decomposition of the intermediate) are equal, Roiter *et al.* deduced that for the optimum catalyst the free energy of the intermediate complex formation must be one-half of the overall free energy change ($(\Delta F_1)_{opt.} = \Delta F/2$). For many reactions, the entropy changes will be small. Consequently, for the optimum catalyst, the heat of formation of the intermediate complex will be one-half of the overall heat of reaction as well ($(q_1)_{opt.} \approx Q/2$). It is obvious that these considerations constitute a derivation of the volcano relationship. Roiter *et al.* made it very clear that thermodynamics can only be expected to predict the relative catalytic activities of groups of closely related catalysts. Predictions of absolute catalytic activities and of relative activities of different classes of catalyst are impossible. The plots of catalytic activities of metal oxides versus the $\frac{Q}{2}$ values show that for catalytic oxidation of hydrogen or propane, Co_3O_4 is near the top of the volcano curve, MnO_2 and NiO slightly left of it, and CuO slightly right of it. With further increasing $\frac{Q}{2}$ values, the catalytic activities fall in the sequence Fe_2O_3, ZnO, and TiO_2. The rates of the catalytic oxidation of hydrogen or hydrocarbons on metals such as Pt, Pd, and Rh are reported by Roiter *et al.* to be orders of magnitudes higher than the rates on oxides having the same $\frac{Q}{2}$ value. This exemplifies that activities of different groups of catalysts cannot be predicted. The higher rates with these metals as catalysts as compared to the oxides are attributed to another capacity for hydrogen activation.

Roiter *et al.* also analyzed the factors affecting the reactivities of different hydrocarbons in oxidation on one catalyst. For this case, they suggested that the nature of the molecule will influence only k_2, the rate of decomposition of the intermediate complex. If this step is rate determining for all reactions compared, the differences in oxidation rates for various hydrocarbons will be only due to differences in k_2 and the relative reactivities will be mainly determined by q_2, i.e., the heat of decomposition of the intermediate complex. Since reactions on one catalyst are considered here, the catalyst-oxygen bond energy is constant. The carbon-oxygen bond energies are

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[117] M. Kraus, Advances in Catalysis, 17, 75 (1967).

considered to be essentially constant and, consequently, it was proposed that the reactivities of different hydrocarbons will depend mainly on the strength of the weakest carbon-carbon bond, the attack of which by oxygen appears to be often the rate-determining step. Experimental data support the predicted relationship between the carbon-carbon bond strength and the reactivity for oxidation.[118] Also, the hydrocarbon reactivity sequence which was found by Moro-oka[119] appears to agree with the theoretical reactivity sequence of Roiter *et al.*

The widely discussed relationship between catalytic activity of oxides and the energy of the metal-oxygen bond prompted Klier[120] to attempt a theoretical calculation of these bond energies. He defined the standard enthalpy ΔH° of the reaction $\frac{1}{n}\ Me_xO_y + \frac{1}{2}\ O_2 \rightarrow \frac{1}{n}\ Me_xO_{y+n}$ as the metal-oxygen bond energy and showed that the periodic variation of ΔH° in 3*d* oxides depends mainly on the variation of the ionization potentials of the metal corrected by the smaller but not negligible contributions of the crystal field stabilization energies. This is also true for the variation in the enthalpies of oxygen chemisorption. For redox reactions such as $MeO \rightleftharpoons Me_2O_3$, the third ionization potential was considered.

Klier pointed out that the trends in ΔH° values parallel the trends in the standard free energy values ΔF°, i.e., the oxidation-reduction potentials of the redox couples Me_xO_y/Me_xO_{y+n}. Thus, the oxidation-reduction potentials of oxides are determined by the binding energy of oxygen, i.e., the M-O bond strength. The plot of ΔF° versus catalytic activity results in the often discussed volcano shaped curves with the couples Co_3O_4/CoO, Cu_2O/CuO, and MnO_2/Mn_2O_3 near the maximum. At high ΔF° values (Ti_2O_3/TiO_2, Zn/ZnO) energy effects dominate. The rates are small because the high metal-oxygen bond energies cause the activation energies to be high. At low ΔF° values, concentration effects dominate. In this case, the oxygen is weakly bound and reactive which will lead to a low concentration of oxidized sites, and the catalytic activity will be limited by depletion of oxidized sites. The data indicated that this is the case with Cr_2O_3.

The importance of the M-O bond strength in oxidation catalysis, i.e., the catalyst oxidation-reduction mechanism, was confirmed in a very instructive way by Keulks.[121] The oxidation of propene on bismuth molybdate was studied using isotopically labeled oxygen ($^{18}O_2$). Only 2.0 to 2.5 percent of $^{18}O_2$ was found in the acrolein formed. This result showed that only the catalyst oxide ions participate in the reaction and that

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[118] M. A. Accomazzo, K. Nobe, Ind. Eng. Chem. Proc. Des. Dev., 4, 425 (1965).

[119] Y. Moro-oka and A. Ozaki, J. Catalysis, 5, 116 (1966).

[120] K. Klier, J. Catalysis, 8, 14 (1967).

[121] G. W. Keulks, J. Catalysis, 19, 232 (1970).

the diffusion of oxide ions from the surface into the bulk and from bulk to the surface must be rapid. These experiments also indicated that the adsorption of the oxygen occurs on some portion of the catalyst other than the site for propene adsorption. Similar experiments were carried out by Wragg, *et al.*,[122] and their results and conclusions are in excellent agreement with the work of Keulks. These results were to be expected on the basis of the work of Schuit and coworkers[123] [124] who showed that the initial rates of the oxidation of 1-butene to butadiene were virtually independent of the presence of oxygen in the gas-phase and concluded that the oxidizing species were the oxygen ions of the catalyst. The gas-phase oxygen merely replenishes the anion vacancies created by the reduction of the catalyst surface. This work will be discussed in more detail in the following section.

b. Some Results Suggesting the Involvement of Adsorbed Diatomic Oxygen in Catalytic Oxidation. The work of Schuit and coworkers, briefly mentioned above, provided convincing evidence for the catalyst reduction-reoxidation mechanism but in addition indicated that adsorbed diatomic oxygen species may be important in catalytic oxidation reactions on some catalysts. These authors studied the oxidation 1-butene on various oxide catalysts whereby gaseous oxygen was excluded. Confirming the catalyst reduction-reoxidation mechanism, they showed that the catalysts were partially reduced and at the same time the 1-butene was oxidized to the same products as in the usual catalytic oxidation in which gaseous oxygen is present. The catalytic activities of the oxides could be correlated with a quantity Q_0 which is the heat of dissociation of 1/2 mole of oxygen from the oxide surface whereby reduction to the next lower oxidation state was considered. These Q_0 values are a measure of the metal-oxygen bond strength of the catalysts. Oxides with small Q_0 value such as for instance MnO_2 catalyze the complete oxidation of the 1-butene to carbon dioxide and water at relatively low temperatures. At intermediate Q_0 values (Fe_2O_3), maximum selectivity for conversion to butadiene was observed. On oxides with high Q_0 values (SnO_2, TiO_2, ZnO), oxidation was slow and isomerization took place.

When the oxide surfaces which were reduced by the interaction with 1-butene were reoxidized by admission of gaseous oxygen, an interesting phenomenon was discovered. Surfaces of oxides with low or medium Q_0 returned to their initial oxidizing capability, but oxides with a high Q_0 value became more oxidizing than initially. Schuit and coworkers proposed that this increased oxidation capacity is due to surface peroxides. This seems a reasonable suggestion since several groups of investigators found evidence for peroxide or superoxide type species on oxides such as TiO_2, ZnO, and

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[122] R. D. Wragg, P. G. Ashmore, and J. A. Hockey, J. Catalysis, 22, 49 (1971).

[123] Ph. A. Batist, C. J. Kapteijns, B. C. Lippens, and G. C. A. Schuit, J. Catalysis, 7, 33 (1967).

[124] TH. G. J. Simons, E. J. M. Verheijen, PH. A. Batist, and G.C.A. Schuit, "Oxidation of Organic Compounds: Advances in Chemistry Series 76," page 261, ACS 1968.

SnO_2.[125-130] Hauffe[131] described the chemisorption of oxygen on ZnO and suggested that the first step is the formation of a superoxide ion. Burwell[132,133] visualized the initial chemisorption of oxygen molecules on chromia to take place according to the reaction $Cr^{3+}_{\square} + O_2 \rightarrow Cr^{4+}O_2$. In this scheme, $Cr^{3+}_{\square}$ stands for a coordinatively unsaturated surface chromium (III) ion. These examples show that the occurrence of surface superoxides and peroxides during oxygen adsorption on oxides seems not to be disputed. The question is whether these surface peroxides do function as hydrocarbon oxidizing species or whether they are only intermediates in the reduction of oxygen molecules to oxide ions. Sachtler,[134] one of the main proponents of the catalyst reduction-reoxidation mechanism, believes that there is enough evidence to show that only the oxygen ions are the oxidizing species. However, the observation of Schuit and coworkers that the oxidizing capability of the high Q_0 oxides is greater after reoxidation than initially indicates that surface peroxides may be important in catalytic oxidation.[135] Schuit *et al.* interpreted these experimental results as follows: If the Q_0 value (M-O bond strength of the catalyst) is small, the mobility of the oxygen ions may be sufficient even at low temperatures to maintain a constant and fast supply of oxygen ions to the adsorbed hydrocarbon resulting in complete oxidation. On oxide catalysts with higher Q_0 values, the mobility of the oxygen ions will be decreased and, therefore, the oxidation will occur only at higher temperatures as compared with the small Q_0 catalysts. The average residence time of the adsorbed hydrocarbon will be reduced at the higher temperature, and the chances for complete oxidation become smaller and partial oxidation will occur. On oxides which have high Q_0 values, the reaction of adsorbed hydrocarbons with oxygen ions will be slow but here peroxide or superoxide ions take over in oxidation catalysis. Teichner and coworkers[136] found evidence for the involvement of superoxide ions in the oxidation of hydrocarbons on titanium dioxide catalysts which were irradiated with ultraviolet light.

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[125] R. J. Kokes, Proc. 3rd International Congress on Catalysis, Vol. 3, page 484, North-Holland Publishing Co., Amsterdam (1965).

[126] P. F. Cornaz, J. H. C. van Hooff, F. J. Pluijm, and G. C. A. Schuit, Disc. Faraday Soc., 41, 290 (1966).

[127] J. H. C. van Hooff and J. F. van Helden, J. Catalysis, 8, 199 (1967).

[128] J. H. C. van Hooff, J. Catalysis, 11, 277 (1968).

[129] R. D. Iyengar and R. Kellermann, J. Catalysis, 12, 107 (1968).

[130] P. Meriaudeau, C. Naccache, and A. J. Tench, J. Catalysis, 21, 208 (1971).

[131] K. Hauffe, Z. f. Elektrochemie, 65, 321 (1961).

[132] R. L. Burwell, G. L. Haller, K. C. Taylor, and J. F. Read, Advances in Catalysis, 20, 1 (1969).

[133] D. Cornet and R. L. Burwell, J. Am. Chem. Soc., 90, 2489 (1968).

[134] W. M. H. Sachtler, Catalysis Reviews, 4 (1), 27 (1970).

[135] TH. G. J. Simons, E. J. M. Verheijen, PH. A. Batist, and G. C. A. Schuit, "Oxidation of Organic Compounds: Advances in Chemistry Series 76," page 261, ACS 1968.

[136] M. Formenti, F. Juillet, P. Meriaudeau, and S. J. Teichner, Preprint 73, V. Intern. Congr. on Catalysis, Palm Beach, Florida (1972).

On the basis of general principles and in analogy to the coordination chemistry of the oxygen molecule in solution, Dowden[137] had previously suggested that peroxide complexes may be important in oxidation reactions. He proposed that an oxygen molecule and a hydrocarbon molecule may become coordinated to the same metal ion on the oxide surface. Interaction between these "ligands" may then lead to a rearrangement in which the oxygen molecule is inserted between the surface metal ion and the adsorbed hydrocarbon, thus forming an adsorbed hydrocarbon peroxide. Subsequent dehydration will lead to an aldehyde. Such a mechanism is favored also by Margolis[138] who stressed the importance of readily occurring rearrangements (isomerization) of the oxygen-hydrocarbon complexes on the catalyst surface.

In a recent paper, Margolis[139] summarized her work on hydrocarbon oxidation and proposed a mechanism in which the surface oxygen ions of oxide catalysts as well as adsorbed diatomic oxygen have essential functions. The experimental part of this paper describes the oxidation of ^{14}C labeled propene, acrolein, and acetaldehyde on a bismuth oxide-molybdenum oxide catalyst. The oxidation of propene led to the formation of acrolein, acetaldehyde, carbon monoxide, and carbon dioxide. The ^{14}C distribution in these oxidation products indicated that the reaction proceeds through a symmetric allyl type surface complex. This is a confirmation of the earlier work of Sachtler,[140] [141] Adams and Jennings,[142] [143] and of Voge *et al.*[144] The oxidation of ^{14}C labeled aldehydes, such as acrolein or acetaldehyde, resulted in the formation of formaldehyde, carbon monoxide, and carbon dioxide. The ^{14}C distribution in these products of the aldehyde oxidation showed that the formaldehyde stems from the aldehyde group and the carbon oxides from the vinyl or methyl group respectively. This result is interesting in conjunction with the observation of other investigators[145-148] who found that in

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[137] D. A. Dowden, Colloquio sobre Quimica Fisica de Procesos en Superficies Solidas, C.S.I.C. Madrid, page 177 (1965).

[138] L. Ya. Margolis, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 1, page 327.

[139] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[140] W. M. H. Sachtler, Rec. Tra. Chim., 82, 243 (1963).

[141] W. M. H. Sachtler and N. H. DeBoer, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 252, North-Holland Publishing Company, Amsterdam 1965.

[142] C. R. Adams and T. J. Jennings, J. Catalysis, 2, 63 (1963).

[143] C. R. Adams, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 240, North-Holland Publishing Company, Amsterdam (1965).

[144] H. H. Voge, C. D. Wagner, and D. P. Stevenson, J. Catalysis, 2, 58 (1963).

[145] C. Kemball and W. R. Patterson, Proc. Roy. Soc. (London), A(270), 219 (1962).

[146] W. R. Patterson and C. Kemball, J. Catalysis, 2, 465 (1963).

[147] H. R. Gerberich, N. W. Cant, and W. K. Hall, J. Catalysis, 16, 204 (1970).

[148] N. W. Cant and W. K. Hall, J. Catalysis, 16, 220 (1970).

oxidation of ethene on palladium some partial oxidation to acetaldehyde and acetic acid occurs and that this partial oxidation and the complete oxidation are not consecutive but parallel reactions. Apparently neither on oxide nor on metal catalysts does the complete oxidation of hydrocarbons proceed to a significant extent over aldehyde and carboxyl groups as intermediates. Margolis[149] also found that the oxidation rate of aldehydes which have a double bond is considerably smaller than the oxidation rate of aldehydes without a double bond. This observation led to the speculation that saturated aldehydes are bonded to the catalyst at the carbonyl bond and unsaturated aldehydes at the double bond via π-bonding.

Margolis and coworkers[150] [151] found that preadsorption of oxygen on oxides which catalyze partial propene oxidation results in higher hydrocarbon coverages. On the other hand, with oxides which catalyze the complete propene oxidation, preadsorption of hydrocarbon resulted in higher oxygen coverages. These findings can be understood on the basis of results, obtained in electron work function studies, which indicated that different oxygen-hydrocarbon complexes are formed on catalysts for partial and complete oxidation respectively. The oxygen-hydrocarbon complexes formed on catalysts for partial oxidation contain more carbon atoms than oxygen atoms and have a positive charge. The oxygen-hydrocarbon complexes formed on catalysts which facilitate the complete oxidation of hydrocarbons consist of more oxygen atoms than carbon atoms and their charge is negative. Margolis[152] pointed out that these findings may be useful for understanding why electronegative additives such as sulfur, phosphorus, selenium, tellurium oxides, or halides increase the catalyst selectivity for partial oxidation.[153] The electronegative additives may reduce the oxygen adsorption and hinder the formation of the negatively charged oxygen-rich oxygen-hydrocarbon complexes, all of which will lead to suppression of the complete oxidation.

Higher catalytic activity of mixed oxides as compared to individual oxides was often observed (which was previously discussed in this chapter). Smaller energies for oxygen release[154] or more favorable conditions for formation of anion vacancies[155] were

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[149] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[150] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[151] A. V. Krylova, L. Ya. Margolis, G. A. Vorob'eva, and O. I. Dokunina, Izv. Akad. Nauk. SSSR, Ser. Khim., 226 (1970).

[152] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[153] L. Ya. Margolis, Advances in Catalysis, 14, 429 (1963).

[154] W. M. H. Sachtler, G. J. H. Dorgelo, J. Fahrenfort, R. J. H. Voorhoeve, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, p. 453.

[155] PH. A. Batist, B. C. Lippens, and G. C. Schuit, J. Catalysis, 5, 55 (1966).

considered as explanations. Margolis and coworkers[156] [157] studied this subject with Mössbauer spectroscopy. The spectra indicated that on tin dioxide-molybdenum trioxide catalysts propene becomes bonded via oxygen to the tin ions which is accompanied by a decrease of the valency state of tin from four to two. However, on pure tin dioxide chemisorption of propene and oxygen brought about no change of the Mössbauer spectrum. These results prompted Margolis to suggest that, upon chemisorption of propene on tin dioxide-molybdenum trioxide catalysts, electrons are transferred from the molybdenum ions to the tin ions. Margolis believes that electron transfer between neighboring cations is generally important in catalytic oxidation on oxides and that a more complicated composition of the oxide catalyst and a greater number of components would make such electron exchanges easier.

On the basis of these experimental results and using the findings of other investigators, Margolis[158] proposed a mechanism of the propene oxidation on tin dioxide-molybdenum trioxide catalysts which is speculative. This mechanism will be sketched here and compared to a related mechanism proposed by Schuit and coworkers.[159] [160] The first step in the mechanism of Margolis is the dissociative chemisorption of propene under formation of a π-allyl intermediate whereby the abstracted hydrogen bonds to a surface oxygen ion, thus forming a hydroxide ion. At the same time, Mo(VI) ions are reduced to Mo(V) ions. So far, this mechanism is similar to the one proposed by Schuit and coworkers for the oxidation of butene to butadiene on a bismuth oxide-molybdenum oxide catalyst except that Schuit believes that an anion vacancy near the Mo(VI) ion is necessary. In Schuit's mechanism, the next step is an interaction of the molybdenum (V)-hydrocarbon complex with another surface oxygen ion resulting in the formation of butadiene, a second hydroxide ion, and a Mo(IV) ion. This is followed by a reaction between the two hydroxide ions to yield water and an oxide ion. Oxygen from the gas phase will reoxidize Mo(IV) to Mo(VI) which will restore the original state of the catalyst. In this mechanism, the only function of the oxygen molecules is the reoxidation of Mo(IV) to Mo(VI) and the filling of the oxygen ion vacancies created by the hydrocarbon oxidation, as generally assumed in the catalyst reduction-reoxidation mechanism. Margolis, however, suggests that oxygen molecules coordinate to the Mo(V) ions, which were formed in the first reaction step, in a similar way as observed with transition metal ions in solution. The resulting oxygen-hydrocarbon-molybdenum (V) complex reacts with a surface oxide ion which leads to the abstraction of another hydrogen from the hydrocarbon and the formation of a second surface hydroxide ion. Finally, the

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[156] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[157] A. A. Firsova, I. P. Suzdalev, A. D. Tsyganov, L. Ya. Margolis, Kinetica i Kataliz No. 4 (1971).

[158] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[159] Ph. A. Batist, B. C. Lippens, and G. C. Schuit, J. Catalysis, 5, 55 (1966).

[160] Ph. A. Batist, C. J. Kapteijns, B. C. Lippens, and G. C. A. Schuit, J. Catalysis, 7, 33 (1967).

oxygen-hydrocarbon-molybdenum (V) complex interacts with Sn(IV) to form an intermediate binuclear complex. Decomposition of this complex leads to acrolein desorption and restoration of the charges on the cations.

Recently Schuit and coworkers[161] [162] obtained new results on the oxidation of butene on the bismuth oxide-molybdenum oxide catalyst and proposed a modified mechanism. This mechanism seems well supported by experimental evidence. In this mechanism, diatomic oxygen is not involved in the hydrocarbon oxidation except for reoxidation of surface sites, i.e., the reduction-oxidation mechanism is supported. They studied the adsorption of butene, butadiene, water, and oxygen as a function of the degree of reduction of the catalysts and found that the adsorption of hydrocarbons decreased with increasing reduction; that of water or oxygen was zero on oxidized catalysts and increased with increasing reduction. The results of the adsorption experiments led to the assumption that there are two different kinds of adsorption sites, called A- and B-sites, which are believed to be oxygen ions distinguished by their crystallographic location. The rate of catalyst reduction depends on $(A) \cdot (B)^2$. In the proposed mechanism, the initial adsorption of the butene is on B-sites by σ-allyl adsorption which is accompanied by interaction of the abstracted hydrogen atom with another B-site to form a hydroxyl group as well as by the reduction of a neighboring Mo(VI) ion to Mo(IV). The allyl moves then to a vacancy near a bismuth atom leading to a bismuth-allyl entity and reoxidation of Mo(IV) to Mo(VI). Interaction with another B-site results in the abstraction of another hydrogen atom and butadiene desorption. The reoxidation of the surface starts at an A-site. The suggestion that the initial adsorption of the butene is on an oxygen site appears very reasonable. Adsorption of benzaldehyde on oxygen sites of vanadium pentoxide catalysts was conclusively demonstrated by Fahrenfort *et al.*[163] In the propene oxidation on tin oxide-molybdenum oxide catalysts, bonding of propene to tin ions via oxygen was found by Margolis[164] [165] in Mössbauer spectroscopy work. That hydrocarbon oxidation and oxygen adsorption take place at different locations could be concluded also by Keulks[166] on the basis of his studies with isotopically labeled oxygen.

Summarizing the discussions on heterogeneous catalytic oxidation presented so far, it can be concluded that the catalyst reduction-reoxidation mechanism is well

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[161] J. Matsuura and G. C. A. Schuit, J. Catalysis, 20, 19 (1971).

[162] J. Matsuura and G. C. A. Schuit, J. Catalysis, 25, 316 (1972).

[163] J. Fahrenfort and N. C. Rol, quoted by W. M. H. Sachtler, Catalysis Reviews, 4(1), 46 (1970).

[164] L. Ya. Margolis, J. Catalysis, 21, 93 (1971).

[165] A. A. Firsova, I. P. Suzdalev, A. D. Tsyganov, L. Ya. Margolis, Kinetica i Kataliz No. 4 (1971).

[166] G. W. Keulks, J. Catalysis, 19, 232 (1970).

established.[167-183] However, on oxides having high M-O bond strengths, where the oxidations via the reduction-reoxidation mechanism are slow, diatomically adsorbed oxygen appears to become important.[184] Diatomic oxygen is also involved in heterogeneously catalyzed liquid phase oxidations of hydrocarbons.[185, 186] In homogeneous oxidation catalysis, oxygen molecules as ligands are well known. Recent investigations[187, 188] indicate that on some catalysts water plays a role as oxydizing species in a similar way as in the electrocatalytic oxidations. These subjects will be discussed later.

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[174] Y. Moro-oka, Y. Morikawa, and A. Ozaki, J. Catalysis, 7, 23 (1967).

[175] Y. Moro-oka and A. Ozaki, J. Catalysis, 5, 116 (1966).

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[179] TH. G. J. Simons, E. J. M. Verheijen, PH. A. Batist, and G. C. A. Schuit, "Oxidation of Organic Compounds: Advances in Chemistry Series 76," page 261, ACS 1968.

[180] J. Matsuura and G. C. A. Schuit, J. Catalysis, 20, 19 (1971).

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c. **Some Aspects of the Catalytic Oxidation on Noble Metals.** Also in this field, there is some discussion whether adsorbed diatomic oxygen is or is not involved in catalytic oxidation of hydrocarbons. Several groups of investigators believe that the activity of silver for partial oxidation of ethene is due to adsorbed diatomic oxygen while the complete oxidations occurring on platinum are generally attributed to adsorbed atomic oxygen. Some investigations indicate that hydrogen abstraction may be rate determining in the oxidation of hydrocarbons on metal catalysts. In the following paragraphs, some studies will be discussed which dealt with these subjects.

(1) Catalytic oxidations on silver. The activity of silver for partial oxidation of ethene to ethene oxide was discovered in 1931.[189] Twigg[190] was the first to investigate the mechanism of this reaction in detail. His study indicated that oxygen was chemisorbed as atoms and that ethene was not chemisorbed. He proposed that ethene is oxidized to ethene oxide by reaction with one chemisorbed oxygen atom while interaction with two chemisorbed oxygen atoms results in products which rapidly oxidize further to carbon dioxide and water. The ethene oxide may also isomerize to acetaldehyde which was expected to be easily further oxidized. This mechanism accounted for the observed oxidation products and found much recognition. Relevant observations were made by Margolis[191] who found that ethene adsorbs only weakly and reversibly on silver and that fast, extensive and irreversible adsorption occurs after preadsorption of oxygen. However, the complete ethene oxidation via aldehydes, as discussed by Twigg, appears questionable since Margolis and Roginskii[192] showed that admixtures of aldehydes to ethene decrease the rates of complete ethene oxidation. This is analogous to the results obtained by other authors[193-196] in olefin oxidation on palladium who found that aldehydes are not intermediates in the complete oxidation of hydrocarbons. Several groups of investigators[197-200] believe that the oxidation of ethene

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[189] T. E. Lefort, French Patent 729,952 (1931).

[190] G. H. Twigg, Proc. Roy. Soc., A188, 92 (1946); Trans Faraday Soc., 42, 284 (1946).

[191] L. Ya. Margolis, Izvest. Akad. Nauk SSSR., Otdel Khim. Nauk No. 10, 1175 (1958); Advances in Catalysis, 14, 429 (1963).

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on silver can be better explained if interaction of the ethene with diatomic adsorbed oxygen is considered. Such a theory was first proposed by Worbs[201] and is supported by Voge and Adams[202] who emphasize that this theory is better suited to explain the often observed 80 percent maximum selectivity of silver catalysts. According to the reaction scheme presented in the paper of Voge and Adams, four diatomic adsorbed oxygen molecules will oxidize four ethene molecules leaving four adsorbed oxygen atoms at the surface. Four such oxygen atoms will oxidize one molecule of ethene to carbon monoxide and water. In summary, four ethene molecules are converted to ethene oxide and one to water and carbon monoxide. The carbon monoxide will be further oxidized to carbon dioxide by reaction with diatomic adsorbed oxygen. Thus, this mechanism permits an explanation of the maximal selectivity of 80 percent and also satisfies the expectation that atomically adsorbed oxygen would lead to complete oxidation.

Considerable time and effort were devoted to the elucidation of the mechanism of the oxidation of ethene on silver, but no generally agreed conclusions have been reached. Very recent investigations of Manara and Parravano[203] on the exchange of oxygen between ethene and ethene oxide on silver seem to indicate that ethene oxide can be formed by reaction of adsorbed atomic oxygen and ethene. Sachtler[204] favors the mechanism of Worbs and prepared a list of investigations which give some evidence for the existence of diatomic oxygen on silver surfaces. Some of these will be briefly discussed as follows. Vol and Shishakov[205] found that silver superoxide (AgO_2) was formed when oxygen of near atmospheric pressure reacted at 100-150°C with thin silver films. Electron diffraction studies showed that the silver superoxide lattice disappeared and the silver lattice reappeared when the superoxide film was exposed to ethene or propene. Czanderna[206] observed breaks in kinetically obtained curves of oxygen adsorption on silver and attributed them to the adsorption of diatomic and monoatomic oxygen. In a very recent paper, Sachtler and coworkers[207] showed that silver is an active catalyst in the liquid phase oxidation of cumene by gaseous oxygen to yield cumene hydroperoxide. In the presence of silver, the induction period characteristic of this free radical chain reaction was shortened, the rate increased, and the activation energy lowered. Copper and gold were inactive, but those silver-gold alloys which are known to be the

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[201] H. Worbs, Dissertation, Technische Hochschule Breslau (1942); U. S. OPB Rept. 98705.

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most selective for partial oxidation of ethene to ethene oxide[208] were also most active for the cumene hydroperoxide formation. These results support the mechanism which was proposed by DeBoer: $[\mathrm{Ag}] + \mathrm{O}_2 \rightarrow [\mathrm{Ag}]\,\mathrm{O}_2^{\cdot}$; $[\mathrm{Ag}]\,\mathrm{O}_2^{\cdot} + \mathrm{RH} \rightarrow [\mathrm{Ag}] + \mathrm{ROOH}$, with R standing for cumene and [Ag] for silver metal.[209] This mechanism is analogous to the mechanism of homogeneous liquid phase hydrocarbon oxidation,[210-214] but here the oxygen molecules are activated by the silver surface.

Two recent investigations to be discussed here provided quite conclusive evidence that diatomically adsorbed oxygen is involved in the partial oxidation of ethene on silver and thus confirmed the mechanism of Worbs. Herzog[215] reacted ethene on silver catalysts with oxygen and also with nitrous oxide. Although significant yields of ethene oxide were obtained with oxygen, the use of nitrous oxide, a source of atomic oxygen, led to complete oxidation of the ethene. Particularly conclusive were the results of Sachtler and coworkers.[216] Using labeled oxygen and infrared techniques, the adsorption of oxygen on silver in diatomic form was proven as well as a peroxide type intermediate ($\mathrm{CH_2\text{-}CH_2\text{-}O\text{-}O\text{-}Ag}$) in the ethene oxidation. It was also shown that there is rapid dissociative adsorption of oxygen on silver up to a coverage of 0.25. Further adsorption is non-dissociative. Preadsorption of chlorine increased the selectivity of the silver catalysts for ethene oxide formation. The results indicated that the selectivity is increased by the chlorine adsorption because the chlorine reduces the dissociative oxygen adsorption for which four adjacent silver atoms appear to be necessary.

(2) Catalytic oxidations on group VIII noble metals. The catalytic oxidation of ethene and other olefins on group VIII noble metals was studied by Kemball *et al.*[217] [218] using a static catalytic reactor. On platinum and rhodium, complete oxidation to carbon dioxide and water was the only reaction observed. With palladium, about 3 percent partial oxidation to acetaldehyde, acetic anhydride, and acetic acid was found in addition to the complete oxidation. Further oxidation of the acetic acid

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was extremely slow which indicated that the complete oxidation must proceed through other kinds of intermediates and that the partial oxidation occurs in a side reaction. Acetic anhydride and acetic acid were found to poison the catalyst. The kinetic results with the platinum catalysts indicated that also with this metal some poisoning occurred, i.e., there is some partial oxidation taking place even with platinum catalysts. The rates of olefin oxidation decreased in the sequences Pt > Pd > Rh > Au > W. It was pointed out that the order for the four transition metals may be correlated with the integral heats of adsorption of oxygen on the respective metals (M-O bond strength). Different reaction orders were found with different metal catalysts and reactant molecules, but this was not considered to be indicative of differences in reaction mechanisms but was attributed to different adsorption characteristics. Kemball *et al.* pointed out that judging on the basis of the initial heats of adsorption one can expect the oxygen to be more strongly adsorbed than olefins. However, there must be a very marked decrease in the heat of adsorption with coverage on platinum and palladium since Brennan, Hayward, and Trapnell[219] showed that only 63 percent of the surface of platinum and 74 percent of the surface of palladium were readily covered with oxygen. Therefore, Kemball *et al.* suggested that olefins may be more strongly adsorbed on the remaining portion of the surface of these metals than oxygen. The general conclusion was that the rate-determining step of the olefin oxidation involves an adsorbed olefin molecule, possibly on top of an oxygen-covered surface and a chemisorbed oxygen atom.

The olefin oxidation on group VIII noble metals and on gold was studied recently in greater detail by Hall and coworkers. These investigators[220-224] used a dynamic catalytic reactor which led to the observation that some of the noble metals have considerably greater selectivity for partial oxidation than previously believed. Selectivities up to 45% were observed. In the oxidation of ethene, palladium shows considerable selectivity; rhodium, ruthenium, and gold do not. In the oxidation of propene, the latter three metals are also selective. Platinum was found to be the least selective catalyst with all olefins, thus catalyzing mainly the total oxidation to carbon dioxide and water. Using ^{14}C labeled olefins, Hall and coworkers confirmed the conclusion of Kemball *et al.*[225,226] that partial and total oxidation are parallel and not consecutive reactions. Similar properties as catalysts were found with the silica supported and alumina supported metals as

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well as with metal sponges. Therefore, the observed catalytic properties are regarded as characteristic of the metals per se.

The specific activity for total oxidation of olefins on group VIII metals[227] decreased in the following sequence: platinum, palladium, iridium, ruthenium, rhodium. Three distinct types of pressure dependencies were found. With type I (platinum and palladium), the rates were repressed by olefin and were first order in oxygen. With type II (ruthenium), the rates were independent of olefin pressure and first order in oxygen. With type III (rhodium and iridium), the rates increased with olefin pressure and were weakly inhibited by oxygen pressure. The inverse olefin pressure dependence with platinum and palladium was also found by Moro-oka *et al.*,[228 229] while Kemball and coworkers[230 231] found it only with platinum. The observed pressure dependencies correspond well to observations in the field of electrocatalysis where it was found that, at the same potentials, the coverages with oxygen are low on platinum and palladium and high on iridium and rhodium, while the coverages with hydrogen are in the reverse order.[232 233] Also, coverage by oxygen begins to be appreciable at considerable lower potentials on rhodium and iridium than on platinum or palladium.[234]

The catalytic oxidation of ethene on palladium (type I pressure dependency) was studied in considerable detail.[235] In agreement with Kemball *et al.*,[236 237] it was found that the acetic acid formed is not easily further oxidized and constitutes a poison. This was confirmed in experiments in which acetic acid was intentionally added. It is interesting that formic acid, a species with only one carbon atom, is not a poison and was rapidly oxidized to carbon dioxide and water. Using deuterated ethene, only a small isotope effect was found which indicated that breaking of the carbon-hydrogen bond is not involved in the rate-determining step. The gross kinetics were the same for partial and for total oxidation and also the activation energies were the same, namely, 20 ± 2 Kcal/mole from the initial rate and 30 ± 2 Kcal/mole from the steady-state measurements.

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the difference reflecting poisoning. It was concluded that on palladium the rate-determining step is the same in partial and total oxidation and is likely to be the oxygen chemisorption. A related conclusion was reached in the electrocatalytic oxidation of ethene on platinum electrodes which will be discussed in a later section.[238, 239] High oxygen coverages on palladium as well as alloying palladium with gold resulted in increases in the selectivity for partial oxidation. The fact that alloying with gold (a metal with little dehydrogenation capability) as well as increasing the coverage with oxygen led to an increase in selectivity was considered an indication that the ability of metals to catalyze the total oxidation is related to the dehydrogenation ability of the metal. This idea is in agreement with the general view of Margolis[240] that strong hydrocarbon bonding to the catalyst and the presence of labile oxygen are required for total oxidation to occur. It is interesting to note here that oxygen coverages of more than 0.2 repress the electrocatalytic oxidation of olefins.[241-243] However, in the electrocatalytic oxidation in acid electrolytes, the oxidizing species are adsorbed hydroxyl groups stemming from the oxidative adsorption of electrolyte water; in this case adsorbed oxygen may not only reduce the dehydrogenation ability of the catalyst surface but also may hinder the water adsorption. In any event, research in electrocatalytic hydrocarbon oxidation has shown that strong bonding of hydrocarbons leading to dehydrogenation and to carbon-carbon bond breaking, i.e., to C_1 species, is an important step in the complete oxidation of hydrocarbons to carbon dioxide.[244-258] This will be discussed in detail in

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(Continued)

the section on electrocatalytic hydrocarbon oxidation.

In the oxidation of propene on surfaces of rhodium, ruthenium, iridium (type II and III pressure dependencies) and gold,[259-261] substitution of deuterium for hydrogen in the methyl group resulted in a considerable reduction of the rates. Thus, a large kinetic isotope effect was operative but only for deuterium in the methyl group. This isotope effect indicated that the abstraction of a hydrogen atom from the methyl group leading to a symmetric allylic intermediate was the rate-determining step. Such intermediates are well known in propene oxidation on oxide catalysts.[262-267] With rhodium, ruthenium, and gold, the oxidation led to considerable acrolein formation, but with iridium the acrolein is further oxidized because iridium is distinguished by a special activity in catalyzing the cleavage of double bonds. The single-carbon fragments formed by double-bond cleavage on iridium are rapidly converted to carbon dioxide and water, but the multiple-carbon fragments are stabilized by formation of aldehydes and acids. With ethene, this possibility does not exist and bond cleavage or attack of the molecule simultaneously on both ends results in total oxidation. Acetic acid is formed only as fast as an intramolecular shift of hydrogen can occur to form the methyl group. Evidence for the importance of hydrogen abstraction in the catalytic oxidation of hydrocarbons was also found by Wise *et al.*

(Continued)

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[267] H. H. Voge, C. D. Wagner, and D. P. Stevenson, J. Catalysis, 2, 58 (1963).

Wise *et al.*[268] [269] studied the catalytic oxidation of alkanes, alkenes, alcohols, and ketones on platinum and palladium. The principle of their experimental technique was the measurement of the ignition temperature as a function of reactant concentration of various hydrocarbon-oxygen mixtures or hydrocarbon-oxygen-carrier gas mixtures. The concentration of hydrocarbon was kept low, and oxygen was always in excess. Therefore, oxygen reaction orders could not be determined. The oxidation of alkanes, alcohols, and ketones were first-order reactions with respect to hydrocarbon pressure. In agreement with Moro-oka *et al.*,[270] [271] Kemball *et al.*,[272] [273] and Hall and coworkers,[274] an inverse fractional order was found with olefins on platinum catalysts. In the olefin oxidation on palladium, a first-order pressure dependency was observed which agrees with the work of Kemball *et al.* but not with the findings of Hall and coworkers.

Most extensively investigated was the oxidation of alkanes on platinum catalysts. The activation energy of the oxidation of ethane on platinum was found to be 27 Kcal/mole. However, with various n-alkanes having three or more carbon atoms, the activation energy was only 17 Kcal/mole. These observations led to the conclusion that in the oxidation mechanism of these alkanes an identical step is involved which is the hydrogen abstraction from a secondary carbon atom which energetically is less expensive than abstraction from a primary carbon atom. In line with this conclusion is the observation that the activation energy is even smaller with alkanes having a tertiary carbon atom such as isobutane (10 Kcal/mole) or substituted octane isomers (13 Kcal/mole). These results support the view that the oxidation process is initiated with dissociative chemisorption in which the weakest carbon-hydrogen bond is broken. This reactivity sequence of alkanes in oxidation is similar to the reactivity sequence of alkanes in hydrogen deuterium exchange reaction where dissociative chemisorption is also rate determining.[275] The results of Wise *et al.* indicated that the alkane adsorption takes place on the bare metal surface because the reactivity pattern of the alkanes could not possibly be rationalised if adsorption on top of adsorbed oxygen is considered.

Wise *et al.* suggested that the conditions for total oxidation may be most favorable when the metal surface has the highest ability to maintain fractional coverages with both the dissociatively chemisorbed hydrocarbons and oxygen. This condition appears

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[268] L. Hiam, H. Wise, and S. Chaikin, J. Catalysis, 10, 272 (1968).

[269] A. Schwarts, L. L. Holbrook, and H. Wise, J. Catalysis, 21, 199 (1971).

[270] Y. Moro-oka, Y. Morikawa, and A. Osaki, J. Catalysis, 7, 23 (1967).

[271] Y. Moro-oka and A. Osaki, J. Catalysis, 5, 116 (1966).

[272] C. Kemball and W. R. Patterson, Proc. Roy. Soc. (London), A(270), 219 (1962).

[273] W. R. Patterson and C. Kemball, J. Catalysis, 2, 465 (1963).

[274] N. W. Cant and W. H. Hall, J. Catalysis, 16, 220 (1970).

[275] G. C. Bond, "Catalysis by Metals," Academic Press, New York (1962).

to be best fulfilled with platinum. The lower activity of palladium for total oxidation is attributed to a greater tendency of palladium to form a surface oxide layer which is not active for the dissociative chemisorption of alkanes. This view gains support from the observation that strongly oxidized palladium surfaces are not active in alkane oxidation but retained the activity for olefin oxidation.

In context with the above discussions of hydrocarbon oxidation on group VIII noble metals, recent ultra-high vacuum work seems relevant and will be briefly discussed: Helium and deuterium beam shattering techniques as well as Auger electron spectroscopy and LEED were used. With these techniques Smith and Merrill[276] found that ethene adsorbs irreversibly on platinum (111), dissociating into an acetelenic species and mobile hydrogen atoms. This study indicated that four-site dissociative adsorption of ethene takes place and that the sticking coefficient is unity. Elevated surface temperatures result in further loss of hydrogen and formation of an amorphous residue which transforms into graphite at temperatures above 550°C. This graphite formation was also observed by other investigators.[277] [278] Merrill and coworkers[279-282] also showed that heating in vacuum is not sufficient to remove carbon from platinum surfaces. Heating in the presence of oxygen is required. Merrill's findings on ethene adsorption on platinum are in general agreement with earlier infrared work.[283]

It is interesting that a sticking probability of only 7×10^{-7} was found by Weinberg *et al.*[284] in the adsorption of oxygen on specially cleaned platinum (111). The sticking probability was independent of the oxygen pressure and of temperature. These results agree with the work of Morgan and Somorjai.[285] Thus, it seems likely that the higher

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[276] D. L. Smith and R. P. Merrill, J. Chem. Phys., 52, 5861 (1970).

[277] A. E. Morgan and G. A. Somorjai, J. Chem. Phys., 51, 3309 (1969).

[278] P. W. Palmberg, in "The Structure and Chemistry of Solid Surfaces," edited by G. A. Somorjai (Wiley, New York, 1969), 29-1.

[279] D. L. Smith and R. P. Merrill, J. Chem. Phys., 52, 5861 (1970).

[280] R. P. Merrill and D. L. Smith, Surface Science, 21, 203 (1970).

[281] D. L. Smith and R. P. Merrill, J. Chem. Phys., 53, 3588 (1970).

[282] A. G. Stoll, D. L. Smith, and R. P. Merrill, J. Chem. Phys., 54, 163 (1971).

[283] W. A. Pliskin and R. P. Eischens, J. Chem. Phys., 24, 482 (1956).

[284] W. H. Weinberg, R. M. Lambert, C. M. Comrie, and J. W. Linnett, Preprint No. 34, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[285] A. E. Morgan and G. A. Somorjai, Surface Science, 12, 405 (1968).

oxygen sticking probabilities found earlier[286] are typical for platinum contaminated with carbon, an impurity which is usually present on platinum. These investigations indicate that clean platinum has very little ability to adsorb oxygen, and it may be concluded that the reported[287] heats of oxygen adsorption on platinum pertain to carbon contaminated platinum. All of this led to the speculation that not platinum as such but carbon contaminated platinum is the effective catalyst for hydrocarbon oxidation.[288]

In connection with this influence of carbon impurities on platinum, it is interesting that, in a recent investigation,[289] a beneficial effect of carbonaceous residues on the rate of ethene hydrogenation over palladium was found. During the use as catalyst, the activity of palladium dropped to one-fiftieth of the original value. However, by adsorption of acetylene the activity of the palladium could be considerably increased. The adsorbed acetylene did not show any C-H vibration spectrum which suggests that the acetylene was adsorbed in a highly dissociated form, i.e., as a carbonaceous residue. It was concluded that the adsorbed acetylene did not act as a poison, as could have been expected, but stabilizes active sites for ethene hydrogenation. These are quite unexpected results. In the hydrogenation of ethene on platinum catalysts, carbonaceous residues were recently shown to be poisons.[290]

d. Water as Oxidizing Species in Heterogeneous Catalytic Oxidation. In the history of the study of heterogeneous oxidation catalysis, reaction mechanisms have been considered in which catalyst oxide ions or some forms of adsorbed oxygen were the oxidizing species. All of this has been discussed in some detail. However, recently, it was shown by Moro-oka *et al.*[291] and by T. Seiyama *et al.*[292] that with some catalysts and in some reactions water can function as an oxidizing species. Using isotopically labeled water, Moro-oka *et al.*[293] found that the ^{18}O of the water was incorporated into the oxidized product according to the following reaction in which A stands for olefin: $A + 1/2\,O_2 + H_2{}^{18}O \rightarrow A^{18}O + H_2O$. These studies were carried out in a flow system

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[286] C. W. Tucker, Jr., J. Appl. Phys., 35, 1897 (1964).

[287] D. Brennan, D. O. Hayward, and P. M. W. Trapnell, Proc. Roy. Soc. (London), A256, 81 (1960).

[288] W. H. Weinberg, R. M. Lambert, C. M. Comrie, and J. W. Linnett, Preprint No. 34, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[289] T. Yasumori, H. Shinohara, and Y. Inoue, Preprint No. 53, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[290] J. C. Schlatter and M. Boudart, J. Catalysis, 24, 482 (1972).

[291] Y. Moro-oka and Y. Takita, J. Catalysis, 27, 177 (1972); Preprint No. 74, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[292] T. Seiyama, N. Yamazoe, and M. Egashira, Preprint No. 72, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972); T. Seiyama, N. Yamazoe, J. Hojo, M. Hayakawa, J. Catalysis, 27, 177 (1972).

[293] Y. Moro-oka and Y. Takita, J. Catalysis, 27, 177 (1972); Preprint No. 74, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

at atmospheric pressures and with gas mixtures of propene, oxygen, water, and nitrogen. They will be discussed in the following paragraphs.

The oxidation of propene to acrolein over SnO_2 - MoO_3 and MoO_3 - Bi_2O_3 catalysts followed the mechanisms involving the catalyst oxide ion, thus confirming previous work by many authors in which allylic adsorption and reaction with oxide ions was established. However, the oxidation of propene to acetone over the SnO_2 - MoO_3 catalyst proceeded through the mechanism in which oxygen is taken from the water. This oxyhydration is favored at low temperatures, the formation of acrolein at higher temperatures. Thus, the selectivity of the catalysts for one or the other oxidation product could be attributed to the different modes of oxygen incorporation into the olefin molecule. For the acetone formation on the SnO_2 - MoO_3 catalyst, an adsorbed carbonium ion intermediate was suggested to be involved because the catalytic activity increased linearly with the concentration of acidic sites of the binary oxide catalyst.

In the oxidation of propene to acrolein on Pd-carbon catalysts, the water mechanism was found to be operative. Allylic adsorption, addition of a hydroxyl group (from the water), and removal of two hydrogen atoms to form the acrolein was suggested as the mechanism. Analogous results were obtained by Seiyama *et al.*[294] who contacted gaseous mixtures of olefins and oxygen with palladium in an aqueous suspension. Comparing the oxidation products of various olefins, it could be concluded that the first step is an allylic adsorption if three or more carbon atoms are present. With ethene, this is not possible and considerably lower oxidation rates were found. Then OH groups from the water are added to the surface complex which finally is transformed into aldehydes or ketones by losing two hydrogen atoms. The influence of water was established in gas-phase experiments using propene, oxygen, and water vapor mixtures and palladium as catalyst. In addition to palladium, platinum also showed activity in the liquid phase oxidation of propene but complete oxidation to carbon dioxide and water was strongly favored. The activities of rhodium and ruthenium were relatively small.

It is well known that oxyhydration is important in the homogeneous catalytic oxidation of olefins to aldehydes or ketones. The Wacker process using palladium chloride in aqueous solution as catalyst is a well known example.[295] The discovery of heterogeneous catalytic oxyhydration shows how similar the catalytic properties of metal atoms on surfaces of solids and those of the respective ions in solution are, i.e., how closely related heterogeneous catalysis and homogeneous catalysis are. The discovery that water can be the oxidizing species in gas-phase catalysis on noble metals is also interesting in view of the fact that adsorbed water is the oxidizing species in the electrocatalytic

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[294] T. Seiyama, N. Yamazoe, and M. Egashira, Preprint No. 72, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972); T. Seiyama, N. Yamazoe, J. Hojo, M. Hayakawa, J. Catalysis, 27, 177 (1972).

[295] J. Smidt *et al.*, Angew. Chem., 71, 176 (1959).

oxidation of organic compounds.

e. **Electrocatalytic Oxidation of Hydrocarbons.** Electrocatalysis is the term used for heterogeneous catalysis of charge-transfer reactions occurring at an electrode-electrolyte interface.[296] The rates of electrocatalytic reactions are influenced not only by the catalytic activity of the catalyst (electrode) but also by the presence of an electric field across the electrode-electrolyte interface and by the nature of the electrolyte.

Work on electro-organic oxidation had been carried out already in the 1920's, although at that time it was not presented in terms of electrocatalysis.[297] The term "electrocatalysis" was used for the first time in 1963.[298] Probably, this field emerged so late because most electrode processes were studied on mercury, as in polarography, and therefore the catalytic effects of different electrode materials were not observed. Another reason for the slow development of the field of electrocatalysis was that the relation between the electrode potential and the current density (Tafel equation) was written, in analogy to the Nernst equation, as $\eta = a - b \log i$ (η stands for the overpotential, i for current density, and a and b are constants). In this form of the Tafel equation, it was somewhat obscured that the overpotential is a kind of activation energy, as may be seen after converting into $i = \exp[(a - \eta)/b]$. When the potential-current density relationship is expressed in the later fashion, it is also more easily seen that the current density is a measure of the reaction rate.

Rates of electrocatalytic reactions can be changed orders of magnitude at one temperature by changing the potential. In the potential-current density relationship the researcher in electrocatalysis has a diagnostic criterion which is useful in searching for the rate-determining step.[299 300] In electrocatalysis, the active surface area can be determined by measuring the charge which is involved in hydrogen deposition from the electrolyte onto the electrode via the Volmer reaction ($H^+ + e^- \rightarrow H_{ads}$).[301-303] Coverages with strongly adsorbed organic species can be determined by measuring the charge

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[296] S. Srinivasan, H. Wroblowa, and J. O'M. Bockris, "Advances in Catalysis," 17, Chap. 6, Academic Press, Inc., New York (1967).

[297] E. Müller, Z. Electrochem., 28, 101 (1923); 29, 264 (1923).

[298] W. T. Grubb, Nature, 198, 883 (1963).

[299] J. O'M. Bockris, J. Chem. Phys., 24, 817 (1957).

[300] B. E. Conway and B. L. Bourgault, Can. J. Chem. 40, 1690 (1962); Trans Faraday Soc., 58, 593 (1962).

[301] T. Erdey-Gruz and M. Volmer, Z. Physik. Chem. A 150, 203 (1930).

[302] S. Gilman, J. Phys. Chem. 67, 78 (1963).

[303] M. W. Breiter, "Electrochemical Processes in Fuel Cells," page 60, Springer-Verlag, New York, Inc. (1969) and references therein.

required to oxidize the adsorbed material.[304-308] These methods are less involved than the equivalent measurements in regular catalysis. A disadvantage of electrocatalysis is that the requirements imposed upon the catalysts by the corrosive nature of the electrolyte, the potentials, and the need for electronic conductance are such, that the choice of materials is quite limited. With acid electrolytes, mainly platinum or some of the other noble metals are used.

In the last 10 years, considerable work was done in the field of electrocatalysis because of the great interest in the direct conversion of chemical into electrical energy by means of fuel cells. This led to many publications as well as a number of review papers and books on electrocatalysis.[309] [310] [311-315] [315a] To cover this field in this review in depth is not possible; therefore, only the field of electrocatalytic hydrocarbon oxidation in acid electrolyte systems will be briefly outlined.

Saturated hydrocarbons were expected to be inert electrochemically, except at high temperatures, until Heath and Worsham[316] reported on the spontaneous electrochemical oxidation of a saturated hydrocarbon yielding electrical energy. This result led to a great increase in interest in the field of electrochemical energy conversion because saturated hydrocarbons are readily available and cheaper than other fuels. Heath and Worsham worked with a potassium hydroxide electrolyte, but for a practical

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[304] M. W. Breiter, "Electrochemical Processes in Fuel Cells," p. 118, Springer-Verlag, New York, Inc. (1969) and references therein.

[305] T. O. Pavela, Ann. Acad. Sci. Fennicae, Series A, II, Chemica 59 (1954).

[306] M. W. Breiter and S. Gilman, J. Electrochem. Soc. 109, 622 (1962).

[307] S. Gilman and M. W. Breiter, J. Electrochem. Soc. 109, 1099 (1962).

[308] M. W. Breiter, Electrochim. Acta, 8, 457 (1963).

[309] S. Srinivasan, H. Wroblowa, and J. O'M. Bockris, "Advances in Catalysis," 17, Chap. 6, Academic Press Inc., New York (1967).

[310] M. W. Breiter, "Electrochemical Processes in Fuel Cells," Springer-Verlag, New York, Inc., 1969, chapter VI and references therein.

[311] "Progress in Electrochemistry," ed. A. N. Frumkin and A. B. Ershler, Plenum Press, London and New York, 1971.

[312] B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorption of Organic Compounds on Electrodes," Plenum Press, New York and London, 1971.

[313] J. O'M. Bockris and S. Srinivasan, "Fuel Cells: Their Electrochemistry," McGraw-Hill Book Co. (1969).

[314] B. J. Piersma and E. Gileadi, "The Mechanism of Electrochemical Oxidation of Organic Fuels," in *Modern Aspects of Electrochemistry*, No. 4, Edited by J. O'M. Bockris, Plenum Press, New York, 1966.

[315] A. S. Appleby, "Electrocatalysis and Fuel Cells," Catalysis Reviews 4, No. 2 (1970).

[315a] J. O'M. Bockris and H. Wroblowa, J. Electroanal. Chem., 7, 428 (1964).

[316] C. E. Heath and C. H. Worsham, 140th National Meeting of the A.C.S., Chicago (1961); Chap. 14, in G. J. Young (ed), "Fuel Cells," vol. 2, Reinhold Publishing Corp, New York (1963).

hydrocarbon fuel cell a carbon dioxide rejecting electrolyte would be necessary. A carbon dioxide rejecting system using phosphoric acid as an electrolyte and platinum black electrodes was described by W. T. Grubb and L. W. Niedrach,[317] and the performance of this system with propane as fuel was investigated by Grubb and Michalske.[318] Complete oxidations of the propane to carbon dioxide at temperatures of 150°-200°C were observed. The completeness of the reaction indicated that the intermediates of this reaction are more strongly adsorbed than the propane. Therefore, less complete oxidation was expected when fuels with a higher adsorbability than propane are used. This agrees with some observations in the electrocatalytic oxidations of propene and cyclopropane[319] available at that time and with later work.[320] A comparative study of the coverages of various saturated and unsaturated hydrocarbons on platinized platinum was made by Niedrach[321] using galvanostatic and volumetric techniques. In acid electrolytes, the coverages fall into three categories: low for methane; intermediate for saturated hydrocarbons such as ethane and propane; and high for unsaturated hydrocarbons. The rates of adsorption in the acid electrolyte were found to be reasonably high. However, in alkaline electrolytes, the adsorption of saturated hydrocarbons was exceedingly slow. In contrast, the adsorption of the unsaturated hydrocarbons was affected little by the electrolyte. This influence of the electrolyte on the adsorption of hydrocarbons is not well understood. A lower adsorbability and reactivity of methane as compared to ethane and other saturated hydrocarbons was often found in gas-phase catalysis.[322-324] This is generally attributed to a 5 Kcal/mole higher C-H dissociation energy of methane.[327, 328] However, the difference on adsorbability appears to be larger than to be expected on the basis of the lower dissociation energy alone. Therefore, it was suggested that the influence of the catalyst surface on both carbon atoms of ethane or higher hydrocarbons (1,2 diadsorption) is also responsible for the greater ease of

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[317] W. T. Grubb and L. W. Niedrach, J. Electrochem. Soc., 110, 1086 (1963).

[318] W. T. Grubb and C. J. Michalske, J. Electrochem. Soc., 111, 1015 (1964).

[319] W. T. Grubb and L. W. Niedrach, Proc. 17th Annual Power Sources Conference, Atlantic City, New Jersey, May 1963, p. 69.

[320] E. Luksha and E. Y. Weissman, J. Electrochem. Soc., 116, 118 (1969).

[321] L. W. Niedrach, J. Electrochem. Soc., 111, 1309 (1964).

[322] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., 58, 1445, 1795 (1936).

[323] K. Morikawa, N. R. Trenner, and H. S. Taylor, J. Am. Chem. Soc., 59, 1103 (1937).

[324] B. M. W. Trapnell, Trans. Faraday Soc., 52, 1618 (1956).

[325] P. G. Wright, P. G. Ashmore, and C. Kemball, Trans. Faraday Soc., 54, 1692 (1958).

[326] G. C. Bond, "Catalysis by Metals," Academic Press (1962), page 183.

[327] P. G. Wright, P. G. Ashmore, and C. Kemball, Trans. Faraday Soc., 54, 1692 (1958).

[328] G. C. Bond, "Catalysis by Metals," Academic Press (1962), page 183.

hydrogen dissociation from these hydrocarbons as compared to methane.[329]

The electrocatalytic oxidation of hydrocarbon was studied by Gilman[330-332] and by Niedrach[333-336] using the multipulse potentiodynamic technique. Although Gilman worked with smooth platinum electrodes and Niedrach with Teflon-bonded platinum black electrodes, very similar results were obtained. The electrodes were held at 0.4 volt in hydrocarbon saturated electrolytes. With a cathodic pulse, the charge involved in the saturation hydrogen coverage, i.e., the remaining free surface, was determined. The hydrocarbon coverage was obtained with an anodic pulse, i.e., by determining the charge associated with the oxidation of the adsorbed species. A linear relationship between these two quantities was obtained which allowed one to estimate the composition of the adsorbed molecules. It was concluded that dissociative adsorption occurs, and Gilman suggested that the average composition of adsorbed ethane was C_2H_2. The degree of dehydrogenation is greater the higher the temperature and the longer the adsorption time. Carbon-hydrogen ratios of 1:2 and 1:1 were also found by Burshtein *et al.*[337] In the oxidation of the adsorption layer of saturated hydrocarbons such as ethane, propane, or butane, both Niedrach[338-341] and Gilman[342-344] found two oxidation waves upon the application of a linear anodic sweep. The first wave was a distinct, well-defined peak and occurred at potentials below 0.8 volt. The second wave is more diffuse and extends from 0.8 volt well into the oxygen evolution potentials. The comparatively

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[329] P. G. Wright, P. G. Ashmore, and C. Kemball, Trans. Faraday Soc., 54, 1692 (1958).

[330] S. Gilman, Trans. Farad. Soc., 61, 2546, 2561 (1965).

[331] S. Gilman, J. Electrochem. Soc., 113, 1036 (1966).

[332] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349.

[333] L. W. Niedrach, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 377.

[334] L. W. Niedrach, S. Gilman, and J. Weinstock, J. Electrochem. Soc., 112, 1161 (1965).

[335] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[336] L. W. Niedrach and M. Tochner, J. Electrochem. Soc., 114, 17 (1967).

[337] R. Kh. Burshtein, A. G. Pshenichnikov, and V. S. Tyurin, Dokl. Akad. Nauk. SSSR, 160, 629 (1965).

[338] L. W. Niedrach, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 377.

[339] L. W. Niedrach, S. Gilman, and J. Weinstock, J. Electrochem. Soc., 112, 1161 (1965).

[340] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[341] L. W. Niedrach and M. Tochner, J. Electrochem. Soc., 114, 17 (1967).

[342] S. Gilman, Trans. Faraday Soc., 61, 2546, 2561 (1965).

[343] S. Gilman, J. Electrochem. Soc., 113, 1036 (1966).

[344] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349.

oxidation-resistant species giving rise to the second wave can be hydrogenated and desorbed as various saturated hydrocarbons by application of a cathodic pulse. This shows that the adsorbed compounds oxidized in wave 2 (designated type II) consist of partially dehydrogenated hydrocarbon species. With methane, only the wave I was found which corresponds to a species which is much more easily oxidized.[345] Consequently, it was concluded that the species of wave I is a C_1 species. This so-called type I species resists cathodic desorption[346-348] or is only partially desorbable[349-352] all of which indicates that it is a partially oxygenated species. This conclusion gains support from the fact that the single oxidation wave of methane, as well as the wave I of ethane, propane, and butane, is in the same potential range as the oxidation waves of formic acid, the "CO-like" species of Niedrach,[353] and the reduced CO_2 of Giner.[354] In addition, Grubb and Lazarus[355] showed that the non-desorbable species must contain oxygen. They found that the maximum rate of carbon dioxide formation was higher than could be produced by a 4 electron reaction from the total 10 ma galvanostatic current employed. This could occur only if the surface species is already partially oxidized. From all this, it transpired that the formation of the type II material on fuel cell electrodes is undesirable because it will block adsorption sites and limit the fuel cell performance. The desirable path is the cracking of the carbon chain to form the more readily oxidized C_1 species. At not too high current densities, the oxidation of the C_1 species to CO_2 is the rate-limiting factor.[356] Using similar techniques, Russian workers[357-359] obtained related results. In their terminology, the initially chemisorbed hydrocarbon is called "particle

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[345] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[346] S. Gilman, Trans Faraday Soc., 61, 2546, 2561 (1965).

[347] S. Gilman, J. Electrochem. Soc., 113, 1036 (1966).

[348] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349.

[349] L. W. Niedrach, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 377.

[350] L. W. Niedrach, S. Gilman, and J. Weinstock, J. Electrochem. Soc., 112, 1161 (1965).

[351] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[352] L. W. Niedrach and M. Tochner, J. Electrochem. Soc., 114, 17 (1967).

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[354] J. Giner, Electrochim. Acta, 8, 857 (1963).

[355] W. T. Grubb and M. E. Lazarus, J. Electrochem. Soc., 114, 360 (1967).

[356] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[357] A. G. Pshenichnikov, A. M. Bograchev, and R. Kh. Burshtein, Soviet Electrochemistry, 5, No. 9, 993 (1969); 5, No. 12, 1369 (1969).

[358] V. S. Tyurin, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry, 5, No. 10, 1103 (1969).

[359] A. M. Bograchev, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry, 7, No. 6, 871 (1971).

II" which is cathodically desorbable and which cracks to C_1 fragments (particle I). These are rapidly transformed into oxidized species.

Considering ethene and acetylene as subsystems to ethane, Gilman[360 361] also investigated the reactions of these unsaturated hydrocarbons on platinum electrodes. The adsorption at 0.4 volt from perchloric acid at 30°C and 60°C is extremely rapid at zero coverage and remains diffusion controlled throughout most of the range of surface coverages. Ethene adsorption was accompanied by an anodic current indicating dissociative adsorption while, with acetylene, only associative adsorption appears to take place. Consequently, the average composition of the adsorbed species is believed to be C_2H_2 as was found with ethane. At higher temperatures and potentials, more extensive dehydrogenation occurs. A very interesting observation was that with these unsaturated hydrocarbons wave I was not found which indicates that the more readily oxidizable type I species is not formed. This may well be due to the high coverages occurring with unsaturated hydrocarbons which will tend to promote polymerization rather than cracking and oxidation. Polymerization of ethene to C_4 species was found long ago in gas phase catalysis work[362] and was repeatedly observed in infrared studies.[363-365] In agreement with Gilman's studies, Russian workers[366-368] did not find any formation of C_1 species when the ethene pressure was high. However, at pressures of 10^{-2} atm and below, C_2 and C_1 fragments were found. Therefore, essentially the same reaction steps as with saturated hydrocarbon were suggested to take place with the unsaturated hydrocarbon.

Dissociative adsorption of saturated hydrocarbon on metals is widely observed in the gas phase work.[369-382] It is the only mode of adsorption which can be imagined with a species having only σ bonds such as a saturated hydrocarbon. The dissociative

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[360] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349.

[361] S. Gilman, Trans. Faraday Soc., 62, 446 (1966).

[362] K. Morikawa, N. R. Trenner, and H. S. Taylor, J. Am. Chem. Soc., 59, 1103 (1937).

[363] B. A. Morrow and N. Sheppard, J. Phys. Chem., 70, 2406 (1966).

[364] J. B. Peri, Disc. Faraday Soc., 41, 121 (1966).

[365] B. A. Morrow and N. Sheppard, Proc. Roy. Soc., A311, 391 (1969).

[366] V. S. Tyurin, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry, 5, No. 10, 1103 (1969).

[367] V. S. Tyurin, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry, 5, No. 12, 1365 (1969).

[368] A. A. Michri, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry 8, No. 2, 270 (1972); 8, No. 3, 347 (1972).

[369] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., 58, 1445, 1795 (1936).

[370] K. Morikawa, N. R. Trenner, and H. S. Taylor, J. Am. Chem. Soc., 59, 1103 (1937).

[371] B. M. W. Trapnell, Trans. Faraday Soc., 52, 1618 (1956).

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adsorption of methane, ethane, and higher saturated hydrocarbon on metal surfaces was conclusively shown by several authors by determining the hydrogen formed and by hydrogen-deuterium exchange experiments.[383-387] Also magnetic studies[388] on adsorption of ethane on nickel showed that dissociative adsorption is taking place. After the initial dissociative adsorption, further dehydrogenation occurs on many metals resulting in multiple bonded hydrocarbon species. At slightly higher temperatures, carbon-carbon bond breaking occurs.[389-395] Some of the surface species react with hydrogen on the surface. This self-hydrogenation leads to the desorption of methane or some other saturated hydrocarbon. If excess hydrogen is present, extensive desorption of methane or other hydrocarbons of smaller chain length than the original one takes place which

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[372] P. G. Wright, P. G. Ashmore, and C. Kemball, Trans. Faraday Soc., 54, 1692 (1958).

[373] G. C. Bond, "Catalysis by Metals," Academic Press (1962), page 183.

[374] A. Cimino, M. Boudart, and H. Taylor, J. Phys. Chem., 58, 796 (1954).

[375] C. Kemball, Adv. Catalysis, 11, 223 (1959).

[376] J. J. Rooney, Chemistry in Britain, 2, 242 (1966).

[377] C. Kemball, Catalysis Reviews, 5(1), 33 (1971).

[378] G. C. Bond, "Catalysis by Metals," Academic Press, London, New York (1962), page 395.

[379] J. H. Sinfelt, Catalysis Reviews, 3(2), 175 (1969).

[380] A. K. Galway and C. Kemball, Trans. Faraday Soc., 55, 1959 (1959).

[381] J. R. Anderson and B. G. Backer, Proc. Roy. Soc., A271, 402 (1963).

[382] R. W. Roberts, Trans. Faraday Soc., 58, 1159 (1962).

[383] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., 58, 1445, 1795 (1936).

[384] K. Morikawa, N. R. Trenner, and H. S. Taylor, J. Am. Chem. Soc., 59, 1103 (1937).

[385] B. M. W. Trapnell, Trans. Faraday Soc., 52, 1618 (1956).

[386] P. G. Wright, P. G. Ashmore, and C. Kemball, Trans. Faraday Soc., 54, 1692 (1958).

[387] A. K. Galway and C. Kemball, Trans. Faraday Soc., 55, 1959 (1959).

[388] P. W. Selwood, J. Am. Chem. Soc., 79, 3346 (1957).

[389] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., 58, 1445, 1795 (1936).

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[391] G. C. Bond, "Catalysis by Metals," Academic Press, London, New York (1962), page 395.

[392] J. H. Sinfelt, Catalysis Reviews, 3(2), 175 (1969).

[393] A. K. Galway and C. Kemball, Trans. Faraday Soc., 55, 1959 (1959).

[394] J. R. Anderson and B. G. Baker, Proc. Roy. Soc., A271, 402 (1963).

[395] R. W. Roberts, Trans. Faraday Soc., 58, 1159 (1962).

process is known as hydrogenolysis.[396] [397] Such processes occur also in the adsorption of hydrocarbons on electrocatalysts in electrocatalytic systems. Upon adsorption of ethane, propane, and n-butane on platinum electrodes desorption of methane, ethane, and of the original hydrocarbon was observed, i.e., dissociative adsorption, cracking, and self-hydrogenation occurred.[398-400] When cathodic reduction (electrochemical hydrogenation and hydrogenolysis) of adsorbed propane was carried out, the desorption products consisted of propane, ethane, methane, and some butane indicating also that some polymerization is taking place.[401] In propane adsorption, a dependence of the ratio of the desorbed quantities of methane and ethane on the potential of adsorption was found.[402] In gas-phase catalysis, very much information on the reactions of hydrocarbons on metal surfaces was obtained by investigating hydrogen-deuterium exchange reactions.[403-405] Frequently, the fully deuterated species is the major product, followed by the singly deuterated species while products of intermediate degree of deuteration are formed only to a much smaller extent. Such studies were also performed in an electrocatalytic system, and analogous results were obtained.[406] In the electrocatalytic work, the percentage of the fully deuterated product was even higher than in the gas-phase studies. A slight dependence of the percentage of the fully deuterated product on the potential was also observed. These results suggested that C-H and C-catalyst bonds are made and broken easily and that the rate-determining step in the electrocatalytic oxidation of hydrocarbons can be expected to be some reaction step which is closer to the end product, carbon dioxide.

The adsorption and oxidation of saturated hydrocarbons on platinum electrodes was also extensively investigated by Brummer and coworkers.[407-411] From

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[396] G. C. Bond, "Catalysis by Metals," Academic Press, London, New York (1962), page 395.

[397] J. H. Sinfelt, Catalysis Reviews, 3 (2), 175 (1969).

[398] W. T. Grubb, Nature 198, 883 (1963).

[399] W. T. Grubb and L. W. Niedrach, J. Electrochem. Soc., 110, 1086 (1963).

[400] L. W. Niedrach, J. Electrochem. Soc., 111, 1309 (1964).

[401] L. W. Niedrach, J. Electrochem. Soc., 111, 1309 (1964).

[402] H. J. Barger and M. L. Savitz, J. Electrochem. Soc., 115, 686 (1968).

[403] C. Kemball, Adv. Catalysis, 11, 223 (1959).

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[406] H. J. Barger and A. J. Coleman, J. Phys. Chem., 72, 2285 (1968); 74, 880 (1970); 75, 3715 (1971), 77, 2783 (1973).

[407] S. B. Brummer, J. I. Ford, and M. J. Turner, J. Phys. Chem., 69, 3424 (1965).

[408] S. B. Brummer and M. J. Turner in "Hydrocarbon Fuel Cell Technology," B. S. Backer, Ed., Academic Press, Inc., New York (1965), page 409.

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anodic charging curves the charge required to oxidize the adsorbed material was determined. From cathodic galvanostatic pulses the extent to which the electrode was covered with irreversibly adsorbed material was found. The measurements also permitted the determination of the number of electrons per adsorption site which are involved in the oxidation of the adsorbate. These investigations showed that in the electrocatalytic oxidation of hydrocarbons on platinum there are three types of intermediates which were designated as CH-α, CH-β, and O-type. CH-α can be cathodically desorbed. It is believed to consist of adsorbed alkyl radicals. The amount of CH-α increases with increasing molecular weight of the hydrocarbon. There is no CH-α formation when methane is adsorbed. The CH-β material is not cathodically desorbable, and its amount is greater the higher the molecular weight of the hydrocarbon. CH-β is unreactive toward oxidation and is believed to be a carbonaceous polymer. The O-type species is the major constituent of the adsorption layer in terms of coverage. Its oxidation state and the fact that it cannot be cathodically desorbed indicate that it is an oxygenated species and is believed to be similar to reduced CO_2.[412] In the case of methane adsorption, CH-α is not formed but only the O-type. This shows that the C_1 species, once formed, is rapidly transformed into the O-type. In this context, it is worthwhile to mention that recent ultra-high-vacuum studies indicate that very clean platinum surfaces have little ability to adsorb oxygen, but carbon-contaminated platinum adsorbs oxygen readily.[413] [414] After this comment, let us return to the discussion of Brummer's work. In their early papers, Brummer and coworkers were under the impression that the coverage by O-type species is insensitive to the hydrocarbon pressure. This led to the conclusion that the O-type species was a posion which lowers the availability of catalyst surface for a main oxidation process. It is quite probable that the O-type species corresponds to Gilman's[415-417] and Niedrach's[418-426] type I species. Consequently, viewing

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[409] S. B. Brummer and M. J. Turner, J. Phys. Chem. 71, 2825 (1967); *ibid.*, 71, 3494 (1967); *ibid.*, 71, 3902 (1967).

[410] S. B. Brummer in "Advances in Chemistry Series 90," American Chemical Society (1969), page 223.

[411] A. H. Taylor and S. B. Brummer, J. Phys Chem., 72, 2856 (1968), *ibid.*, 73, 2397 (1969).

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[416] S. Gilman, J. Electrochem. Soc., 113, 1036 (1966).

[417] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349.

[418] L. W. Niedrach, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 377.

[419] L. W. Niedrach, S. Gilman, and J. Weinstock, J. Electrochem. Soc., 112, 1161 (1965). (Continued)

the O-type as a poison was incompatible with the earlier findings of Gilman and Niedrach. However, Brummer and coworkers[427, 428] found later that the O-type coverage is dependent on the hydrocarbon pressure and suggested that the following reaction steps take place at potentials below 0.35 volt: Hydrocarbon $\rightarrow CH_a$, $CH_a \rightarrow$ O-type, O-type $\rightarrow CO_2$ with the oxidation of O-type being the rate-determining step. At higher potentials, the adsorption of the hydrocarbon was suggested to be rate determining.

Bockris *et al.*[429] investigated the electrocatalytic oxidation of saturated hydrocarbons by determining current potential relationships as well as the rates of oxidation as a function of hydrocarbon pressure and of the water concentration in the electrolyte. Linear Tafel lines were found for the region from 0.28-.048 volt having a slope of F/RT, as well as first-order dependence on hydrocarbon pressure and zero-order dependence on the water concentration. Upon admission of the hydrocarbon, a current was found to pass across the electrode, indicating dissociative adsorption, followed by oxidation of the dissociated hydrogen atoms to protons. Bockris *et al.* derived the kinetic parameters of 15 possible reaction schemes and compared them with the observed ones. Considering that a Tafel slope of F/RT excludes any reaction step as the rate-determining step which is during or after the third electron transfer and also taking the reaction orders into account, it was concluded that the cracking (C-C bond cleavage) of the dissociatively desorbed hydrocarbon is the rate-determining step. This conclusion is not in agreement with the work of Gilman,[430-432] Niedrach,[433-436] and Brummer[437-441] who

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[420] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[421] L. W. Niedrach and M. Tochner, J. Electrochem. Soc., 114, 17(1967).

[422] R. Kh. Burshtein, A. G. Pshenichnikov, and V. S. Tyurin, Dokl. Akad. Nauk. SSSR 160, 629 (1965).

[423] J. Giner, Electrochim. Acta, 8, 857 (1963).

[424] W. T. Grubb and M. E. Lazarus, J. Electrochem. Soc., 114, 360 (1967).

[425] A. G. Pshenichnikov, A. M. Bograchev, and R. Kh. Burshtein, Soviet Electrochemistry, 5, No. 9, 993 (1969); 5, No. 12, 1369 (1969).

[426] V. S. Tyurin, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry, 5, No. 10, 1103 (1969).

[427] S. B. Brummer in "Advances in Chemistry Series 90," American Chemical Society (1969), page 223.

[428] A. H. Taylor and S. B. Brummer, J. Phys. Chem., 72, 2856 (1968), *ibid.*, 73, 2397 (1969).

[429] J. O'M. Bockris, E. Gileadi, and G. E. Stoner, J. Phys. Chem., 73, 427 (1969).

[430] S. Gilman, Trans. Faraday Soc., 61, 2546, 2561 (1965).

[431] S. Gilman, J. Electrochem. Soc., 113, 1036 (1966).

[432] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349.

[433] L. W. Niedrach, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 377.

[434] L. W. Niedrach, S. Gilman, and J. Weinstock, J. Electrochem. Soc. 112, 1161 (1965). (Continued)

found that the oxidation of a partially oxidized C_1 species is the rate-determining step. Bockris[442] feels that it is not clear why different results were found by him and the other workers. Brummer[443] sees no conflict between his results and those of Bockris *et al.* because his work refers to the potential region below 0.35 volt while much of the work of Bockris refers to the region above 0.35 volt where the coverage by adsorbed hydrocarbons becomes low.

The electrocatalytic oxidation of unsaturated hydrocarbons was studied extensively by Bockris and coworkers[444-448] by determining current-potential relationships. These investigations were carried out with sulfuric acid and with sodium hydroxyde as electrolytes at 80°C. The highest exchange current densities were obtained with platinum, and the electrocatalytic oxidation of 8 different unsaturated hydrocarbons was studied on this metal.[449] This will be discussed in the following paragraph. Subsequently, the investigations of ethene oxidation on other noble metals will be described.[450,451]

With platinum electrocatalysts, the faradaic efficiency for oxidation to carbon dioxide was found to be 100% with ethene and nearly 100%, or quite high, with the other unsaturated hydrocarbons. The activation energies for the unsaturated hydrocarbons

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[435] L. W. Niedrach, J. Electrochem. Soc., 113, 645 (1966).

[436] L. W. Niedrach and M. Tochner, J. Electrochem. Soc., 114, 17 (1967).

[437] S. B. Brummer, J. I. Ford, and M. J. Turner, J. Phys. Chem., 69, 3424 (1965).

[438] S. B. Brummer and M. J. Turner in "Hydrocarbon Fuel Cell Technology," B. S. Backer, Ed., Academic Press, Inc., New York (1965), page 409.

[439] S. B. Brummer and M. J. Turner, J. Phys. Chem., 71, 2825 (1967); *ibid.*, 71, 3494 (1967); *ibid.*, 71, 3902 (1967).

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[442] J. O'M. Bockris, "From Electrocatalysis to Fuel Cells," G. Sandstede, Ed., published for Battelle Seattle Research Center by the University of Washington Press, Seattle and London, page 81.

[443] S. B. Brummer in "Advances in Chemistry Series 90," American Chemical Society (1969), page 223.

[444] H. Dahms and J. O'M. Bockris, J. Electrochem. Soc., 111, No. 6, 728 (1964).

[445] J. O'M. Bockris and H. Wroblowa, J. Electroanal. Chem., 7, 428 (1964).

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[447] H. Wroblowa, Bernard J. Piersma, and J. O'M. Bockris, J. Electroanal. Chem., 6, 401 (1963).

[448] A. T. Kuhn, H. Wroblowa, and J. O'M. Bockris, Trans. Faraday Soc., 63, 1458 (1967).

[449] J. O'M. Bockris, H. Wroblowa, E. Gileadi, and B. J. Piersma, Faraday Soc. Trans., 61, 2531 (1965).

[450] A. T. Kuhn, H. Wroblowa, and J. O'M. Bockris, Trans. Faraday Soc., 63, 1458 (1967).

[451] K. W. Johnson, S. C. Lai, and W. J. James, Electrochimica Acta., 15, 1511 (1970).

investigated were in the range between 20 and 24 Kcal/mole. Linear Tafel lines were found in the region from about 0.3 volt up to 0.75 volt. Above 0.75 volt, a limiting current was reached. At potentials higher than 0.95 volt, the current decreased with increasing potential which was attributed to passivation of the electrode due to the formation of an oxygen layer. Experiments at different hydrocarbon pressures led to the interesting result that the current density (rate) decreased with increasing hydrocarbon pressure (negative reaction order). From the observed Tafel slope, it could be concluded that a first-charge transfer step should be the rate-determining step. The negative hydrocarbon pressure dependency indicated that the rate-determining step involves a substance other than the hydrocarbon, namely, the oxidizing species which could be water or hydroxide ions. Since the dependence of the current density on the pH was found to be linear in the pH range from 0.3 to 12.5, the hydroxide ion could be excluded. Consequently, the conclusion was drawn that the discharge of water ($H_2O \rightarrow OH_{ads} + H^+ + e$) was the rate-determining step in the electrocatalytic oxidation of unsaturated hydrocarbon on platinum electrodes. Kinetic isotope effect studies with D_2O and D_2SO_4 as electrolyte support this conclusion.[452]

In addition to platinum, the electrocatalytic oxidation of ethene was studied with palladium, rhodium, iridium, ruthenium, gold, and noble metal alloy electrodes. Except with gold, the linear Tafel regions were shorter because the limiting current region was reached at lower potentials. At the same potentials, oxygen coverage begins which is fairly good evidence that the limiting current densities are reached because of the oxygen layer formation. In contrast to platinum, a positive dependence of the current density on the hydrocarbon pressure was found. This indicated that the ethene is involved in the rate-determining step. Investigations of isotope effects using D_2O and D_2SO_4 as electrolyte indicated that the oxidizing species is also involved in the rate-determining step.[453] Consequently, it was proposed that the surface reaction between adsorbed ethene and dissociatively adsorbed water, i.e., adsorbed hydroxyl groups, was the rate-determining step on the metals other than platinum. With palladium and gold, considerable partial oxidation of ethene to acetaldehyde, aceton, and propionaldehyde was found, while rhodium and iridium catalyzed mainly the complete oxidation to carbon dioxide.

The electrocatalytic oxidation of ethene on gold electrodes was investigated also by Johnson *et al.*[454] In strongly acidic electrolytes, they observed only acetaldehyde and no carbon dioxide formation and did not find a pH effect. They suggested that these results could be understood with a mechanism in which the rate-determining

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[452] A. T. Kuhn, H. Wroblowa, and J. O'M. Bockris, Trans. Faraday Soc., 63, 1458 (1967).

[453] A. T. Kuhn, H. Wroblowa, and J. O'M. Bockris, Trans. Faraday Soc., 63, 1458 (1967).

[454] J. W. Johnson, S. C. Lai, and W. J. James, Electrochimica Acta, 15, 1511 (1970).

surface reaction is preceded by an electron transfer leading to an adsorbed carbonium ion, as considered previously by Dahms and Bockris.[454a] It was suggested that the carbonium ion formation may occur due to the high positive potentials at which oxidation takes place on gold anodes.

Bockris and coworkers rationalized the electrocatalytic activity of the noble metals and their alloys in ethene oxidation by considering competition between water and ethene for adsorption sites and by taking into account the adsorption strengths of ethene and the hydroxyl groups, i.e., of metal-carbon and metal oxygen bonds.[455] The bond strengths were calculated, following Eley,[456] with the Pauling equation[457] whereby one-sixth of the heats of sublimation of the metals were taken as the values for the metal-metal bond strengths. A volcano curve resulted with gold on the ascending branch due to small coverages particularly in hydroxyl groups while iridium, rhodium, and ruthenium were on the descending branch because of high coverages in hydroxyl groups and relatively higher metal-oxygen and metal-carbon bond strengths. With platinum, the coverages with both ethene and hydroxyl groups as well as the bond strengths are at an optimum and, therefore, the surface reaction becomes so fast that water discharge takes over as the rate-determining step.

In the interpretation of their results, associative adsorption of the unsaturated hydrocarbons was assumed by Bockris and coworkers. Associative adsorption was indicated by the fact that different kinetics was found in the electrocatalytic oxidation of ethene and acetylene.[458] If ethene would adsorb dissociatively, the adsorbed species would resemble acetylene and similar kinetics could be expected. Calculations also made it likely that in electrocatalytic systems associative chemisorption of unsaturated hydrocarbons should be thermodynamically more favorable than dissociative adsorption.[459] Another argument for associative chemisorption was that a transient current was found upon chemisorption of saturated hydrocarbons (electrons due to the reaction $H_{ads} \rightarrow H^+ + e$) but not with ethene.[460] Gilman,[461] [462] however, did find transient currents upon adsorption of ethene and concluded that ethene is dissociatively adsorbed

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[461] S. Gilman, J. Electrochem. Soc., 113, 1036 (1966).

[462] S. Gilman, Trans. Faraday Soc., 62, 446 (1966).

forming an acetylenic residue. He reached this conclusion also on the basis of the similarity of the traces of anodic sweeps of ethene and acetylene adsorbed on platinum electrodes. However, Niedrach[463] did not observe any wave in the oxidation curves which could be attributed to hydrogen which indicates that under his experimental conditions little or no dissociative ethene adsorption occurred. On the other hand, the volumetric measurements of Niedrach showed that some of the ethene adsorbed was hydrogenated to ethane which is only possible if some dissociative ethene adsorption had taken place. The question whether associative or dissociative adsorption of olefins is taking place on electrocatalysts seems undecided. Also, in regular gas-phase catalysis, the mode of adsorption of unsaturated hydrocarbons was very much discussed for a long time.[464-469] Infrared work indicates that both associative and dissociative adsorption take place. Which kind of adsorption dominates depends on the temperature, preadsorption of hydrogen, and the relative activity of the catalyst.[470 471]

f. Comparison of Some Results in the Gas Phase and Electrocatalytic Oxidation of Hydrocarbons. Before the 1960's, the oxidation of hydrocarbons on group VIII noble metal catalysts was not studied to a great extent probably because the complete oxidation to carbon dioxide and water was the only reaction found.[472 473] After Kemball and coworkers[474 475] observed that some partial oxidations also occur, interest increased and several research groups investigated this subject during the last 10 years.[476-484] In the same period, the field of electrocatalysis emerged. This term was

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used for the first time in 1963.[485] Because of the interest in fuel cells, considerable effort was devoted to the electrocatalytic oxidation of hydrocarbons.[486-517] The gas phase

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[487] W. T. Grubb and L. W. Niedrach, J. Electrochem. Soc., 110. 1086 (1963).

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[492] S. Gilman, "Hydrocarbon Fuel Cell Technology," ed. S. Baker, Academic Press, New York-London (1965), p. 349

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[505] A. A. Michri, A. G. Pshenichnikov, and R. Kh. Burshtein, Soviet Electrochemistry 8, No. 2, 270 (1972); 8, No. 3, 347 (1972).

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(Continued)

and electrocatalytic work on hydrocarbon oxidation led to related results and conclusions, but few correlations were made. It is the purpose of this section to correlate some of the results found in these areas of investigation. Since the results are not conclusive in the gas phase or in the electrocatalytic oxidation, it can be hoped that an increased exchange of ideas between these fields will further the understanding of the processes involved.

Before discussing these subjects in some detail, let us compare the gas phase and electrocatalytic oxidation of hydrocarbons in a general way. In electrocatalytic systems such as fuel cells, oxygen is brought in contact with the electrocatalyst at the cathode. There, adsorption and reduction of the oxygen takes place whereby water is formed in systems having acid electrolytes. The hydrocarbons are brought in contact with the electrocatalyst at the anode and are, after adsorption, oxidized by adsorbed water from the electrolyte. Thus, the electron receiving and producing processes are completely separated and much of the energy released in the hydrocarbon oxidation can be gained as electrical energy. In gas phase catalysis, the hydrocarbon and oxygen adsorb and react on the same catalyst surface. Often, the reduction-oxidation mechanism was found to take place.[518-534] This mechanism was established mainly with oxide catalysts but

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applies also to metal catalysts. According to this mechanism, the oxygen becomes adsorbed and reduced at some surface sites while the hydrocarbon adsorbs and reacts at other sites. Thus, in gas-phase catalysis, electron receiving and producing reaction steps are separated as well, but in a microscopic scale. Since there is a "chemical short circuit" in this case, the energy is evolved as heat, but mechanistically there is considerable analogy between such a hydrocarbon oxidation process and the electrocatalytic oxidation in fuel cells.

Now, let us discuss some of the results in gas phase and electrocatalytic oxidation of hydrocarbons on group VIII noble metals and gold. Kemball and coworkers[535-536] and Hall and coworkers[537-541] studied the catalytic gas-phase oxidation of olefins on such catalysts and found that, in addition to the complete oxidation to carbon dioxide and water, partial oxidation can occur. With ethylene the partial oxidation results in

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the formation of some acetic acid which is not further oxidized and poisons the catalyst. This inertness of the adsorbed acetic acid against oxidation indicated that the acetic acid is not an intermediate in the oxidation process which leads to carbon dioxide and water and, thus, partial and complete oxidation are not consecutive but parallel reactions.

Very little was known about the reaction mechanism of the complete oxidation process but recently some observations were made in gas phase work[542] which support the idea that the formation of single carbon fragments is a very important step. For instance, while acetic acid poisons the catalyst, formic acid, a C_1 species, was found to be rapidly and completely oxidized.[543] Recent work in the oxidation of propylene supports this idea.[544] On rhodium, ruthenium, and gold, considerable partial oxidation to acrolein was found, but with iridium mainly carbon dioxide and acetic acid were formed. Experiments with ^{14}C labeled propylene showed convincingly that, on iridium, cleavage of the double bond occurs. The C_1 fragments formed by breaking of the double bond are then rapidly oxidized to carbon dioxide and water, while the multiple carbon fragments are more difficult to oxidize and can become stabilized by the formation of the acetic acid.

These observations and conclusions agree with a large body of information obtained in the electrocatalytic oxidation of hydrocarbons in systems with acid electrolytes. Using the multipulse potentiodynamic technique, Gilman,[545-547] Niedrach and coworkers,[548-551] and Burshtein *et al.*[552-554] observed that the oxidation of hydrocarbons on platinum electrodes takes place in two different potential regions, one below and one above 0.8 volt (vs. the reversible hydrogen reference electrode). With ethane,

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propane, or higher hydrocarbons, a well-defined oxidation peak at potentials below 0.8 volt and a more diffuse peak at higher potentials were found. With methane, a C_1 hydrocarbon, only the peak at low potentials was observed. These findings, as well as the coincidence of the position of the well-defined oxidation wave in the lower potential region with the oxidation waves of C_1 species such as formic acid and "reduced CO_2,"[555] led to the conclusion that the easily oxidized species giving rise to the wave at low potentials is a C_1 species which was termed type I.[556-561] This type I species is believed to be partially oxidized because it was found to be not[562] or not as readily[563] desorbable by a cathodic pulse as the adsorbed species which gives rise to the wave at potentials above 0.8 volt. The latter species is referred to as "type II." This type II species can be completely desorbed by a cathodic pulse which led to the conclusion that it consists of partially dehydrogenated, multiple-carbon hydrocarbons. Also work by Brummer and coworkers[564-568] indicated that a partially oxidized C_1 species, termed "O-type," plays an important role in the electrocatalytic oxidation of hydrocarbons.

The electrocatalytic oxidation of unsaturated hydrocarbon was studied extensively by Bockris and coworkers[569-573] by determining current potential relationships. The

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results obtained and conclusions made are similar to those in gas-phase catalytic oxidation of unsaturated hydrocarbons.[574-584] This will be briefly outlined in the following paragraphs. In both fields, a negative dependence of the rates on the olefin pressure was observed in the case of platinum catalysts or electrocatalysts respectively. Consequently, it was concluded in gas phase as well as electrocatalysis that coverage by olefins on platinum is extensive and that the rate-determining step on this metal involves the oxidizing species only. Thus, for the electrocatalytic olefin oxidation, the oxidative adsorption of water from the electrolyte to yield an adsorbed hydroxyl group was suggested to be rate determining.[585-589] In the gas-phase studies, the adsorption of oxygen was proposed to be the rate-determining step with catalysts like platinum or palladium where negative reaction orders in olefin were found.[590,591] The activation energies for the oxidations of various olefins were found to be in the range from 20-24 Kcal/mole in the electrocatalytic and from 17-23 Kcal/mole in the gas-phase work.[592-607] The

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similarity of the activation energy values in these two areas is surprising considering that different oxidizing species are believed to be involved. In contrast to the results with platinum, positive dependencies of the rates on the olefin pressure were found with rhodium and iridium in gas phase as well as electrocatalytic work.

The selectivities of catalysts in olefin oxidation are quite similar in gas phase and electrocatalysis. Platinum is always very little selective, i.e., it promotes mainly the complete oxidation.[608-623] Palladium is quite selective in the gas phase as well as

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electrocatalysis.[624-630] With gold, a somewhat higher selectivity was found in electrocatalysis than in the gas-phase work. Rhodium was found in both fields to be quite unselective in the oxidation of ethylene;[631,632] however, in propylene oxidation, rhodium as well as ruthenium and gold showed considerable selectivity in gas-phase work. This selectivity in the case of propylene oxidation appears to be due to the formation of a symmetric allylic intermediate which is evidenced by kinetic isotope effects observed with deuterated propylenes.[633,634] Such intermediates are, of course, not possible with ethylene. No data on electrocatalytic oxidation of propylene on noble metals other than platinum were found in the open literature. The selectivity of palladium for catalytic gas-phase oxidation of ethylene was found to increase with the oxygen coverage of the catalyst.[635] In connection with this observation, it is interesting that in the electrocatalytic oxidation of ethylene on palladium a higher selectivity, i.e., more of the partial oxidation products, was found when the experiments were carried out at 0.8 volt than at 0.6 volt.[636] Since palladium is more oxidized at 0.8 volt than at 0.6 volt, it seems possible that the different selectivities are also in the electrocatalytic oxidation due to the oxygen coverages.

In gas phase catalysis, so-called moderators are used when it is desired to suppress the complete oxidation of hydrocarbons and obtain a better yield in partially oxidized products. This subject was reviewed by several authors.[637-639] Electronegative species like chlorine, bromine, iodine, sulfur, selenium, and tellurium or their compounds have moderating effects. In the oxidation of ethene to ethene oxide on silver catalysts,

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moderators have a great technological importance. It was shown that the moderators are preferentially adsorbed and affect the oxygen adsorption.[640] Too much of the moderator will destroy the catalytic activity of the surface. The oxidation of methane on platinum group catalysts usually leads to complete oxidation. However, in the presence of halomethanes some partial oxidation to formaldehyde was recently observed.[641] These halomethanes adsorb dissociatively on the catalyst surface thus forming adsorbed halogens.[642] These occupy sites otherwise available for oxygen adsorption and may cause oxygen deficiencies near hydrocarbon oxidation sites. Furthermore, the adsorption of such electronegative species will increase the work function of the catalyst which will adversely affect the oxygen adsorption.

Analogous observations were made in electrocatalysis. The presence of anions such as halides reduced the rates of electrocatalytic oxidation of fuels such as hydrogen,[643] methanol,[644] carbon monoxide,[645] and ethane.[646] The influence of these anions depends on the adsorbability; thus, with platinum electrodes iodide is more effective than bromide which in turn is more effective than chloride.[647] In actual fuel cells, the specific adsorbability of the electrolyte anions was found to have an influence on the fuel-cell performance. Thus, higher current densities were found in the electrocatalytic oxidation of ethane when perchloric acid was used as electrolyte instead of phosphoric acid.[648] Best results were obtained with hydrofluoric acid,[649-651] but Russian workers did not confirm this.[652] Double-layer effects and fuel solubility in the electrolyte will contribute to the influences asserted by the electrolyte on the rates. (These subjects are not included in this discussion because they have no counterpart in gas phase catalysis.)

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[652] B. I. Podlochenko and E. A. Kolyadko, Soviet Electrochemistry 8, Nr. 1, 137 (1972).

The similarities between gas phase and electrocatalytic hydrocarbon oxidation, outlined above, are remarkable considering that different oxidizing species are believed to be involved in these two areas. Also, the state of the catalyst surfaces is different. In the gas phase catalytic oxidation, there is considerable coverage of the noble metal catalysts by oxygen and the chemisorbed oxygen is generally believed to be the oxidizing species. In the electrocatalytic oxidation, the surfaces of the noble metal electrocatalysts are not covered by oxygen at the potentials where most of the hydrocarbon oxidation occurs, and adsorbed water is the oxidizing species. Water is known to play a role as oxidizing species not only in the electrocatalytic oxidation but also in certain biochemical oxidation reactions. However, it has not been considered in the past as an oxidizing species in gas-phase heterogeneous catalytic oxidation. Therefore, it is interesting that recently two research teams[653] [654] found strong indications that water is involved in the heterogeneous catalytic oxidation of hydrocarbons on palladium and platinum. Seiyama *et al.*[655] showed that the rate of the vapor phase oxidation of mixtures of propane, oxygen, water, and nitrogen at 100°C is strongly dependent on the partial pressure of water. These authors also recognized that water plays a role in the oxidation of olefins on palladium and platinum catalysts suspended in aqueous solutions. Platinum catalyzed mainly the complete oxidation, while with palladium partial oxidation also was found. Moro-oka *et al.*[656] investigated the oxidation of propylene on palladium using mixtures of propylene, oxygen, and ^{18}O labeled water. They found that the oxidation of this olefin on a palladium catalyst took place according to the following reaction scheme in which A stands for olefin: $A + 1/2\ O_2 + H_2O^* \rightarrow AO^* + H_2O$. These authors demonstrated that exchange reactions are not responsible for the fact that the oxygen from the water appeared on the olefin. Therefore, it was concluded that the water oxidized the olefin and gas-phase oxygen was reduced to water. Thus, a mechanism of heterogeneous catalytic gas-phase oxidation was found which corresponds to the mechanism of electrocatalytic hydrocarbon oxidation in which, as discussed before, the hydrocarbons are oxidized on the anode by adsorbed water and the oxygen is reduced on the cathode whereby water is formed. Confirmation of these findings of Seiyama *et al.* and Moro-oka *et al.* by other investigators would be desirable.

In hydrocarbon oxidation without intentionally added water, a related mechanism can be visualized. On catalysts such as platinum and palladium, dissociative adsorption of alkanes has been widely observed. Infrared spectroscopy work shows that at the

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[653] Y. Moro-oka and Y. Takita, J. Catalysis, 27, 177 (1972); Preprint No. 74, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[654] T. Seiyama, N. Yamazoe, and M. Egashira, Preprint No. 72, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972); T. Seiyama, N. Yamazoe, J. Hojo, M. Hayakawa, J. Catalysis, 27, 177 (1972).

[655] T. Seiyama, N. Yamazoe, and M. Egashira, Preprint No. 72, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972); T. Seiyama, N. Yamazoe, J. Hojo, M. Hayakawa, J. Catalysis, 27, 177 (1972).

[656] Y. Moro-oka and Y. Takita, J. Catalysis, 27, 177 (1972); Preprint No. 74, V. Intern. Congress on Catalysis, Palm Beach, Florida (1972).

temperatures under consideration extensive dissociative adsorption of olefins can be expected also.[657] [658] The adsorbed hydrogen atoms formed by dissociative adsorption of the hydrocarbons will react with adsorbed oxygen at considerably higher rates than with the adsorbed hydrocarbons. This can be concluded from the low temperatures at which hydrogen oxidation occurs on the surfaces of platinum metals,[659] as well as from the fact that selfhydrogenations such as observed under nonoxidizing conditions do not occur during oxidation reactions.[660] The reaction between the adsorbed hydrogen atoms and adsorbed oxygen will result in surface hydroxyl groups which may play a role in the oxidation of hydrocarbons as is the case in the electrocatalytic oxidation. The formation of hydroxyl groups on platinum by reactions of oxygen with hydrogen adsorbed on platinum was recently shown with infrared techniques.[661] Activity of these hydroxyl groups in the oxidation of ethene was recently observed.[662]

The results discussed in this chapter lead to the conclusion that the reaction mechanisms of gas-phase and electrocatalytic oxidation of hydrocarbons may be more closely related than assumed in the past. Before closing, it seems pertinent to discuss the question of dissociative adsorption of water. In electrocatalysis, the oxidizing species is formed on the anode by adsorption of water ($H_2O \rightarrow OH + H^+ + e$). This reaction is thermodynamically more favorable than the dissociative adsorption of water from the gas phase because the solvation energy of the proton is high. Dissociative adsorption of water from the gas phase was observed on tungsten.[663] With platinum, the results are not conclusive. Changes of the surface potential of atomically clean (110)-oriented platinum films upon exposure to water are believed to be due to dissociative adsorption of water leading to a coverage by hydroxyl groups and hydrogen evolution.[664] Eley *et al.*[665] used the concept of dissociative adsorption of water on platinum in the interpretation of some infrared results. However, Darensbourg and Eischens[666] investigated this problem in more detail using both H_2O and D_2O. Very similar bands were obtained

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[657] R. P. Eischens and W. A. Pliskin, Advances in Catalysis, 10, 1 (1958).

[658] B. A. Morrow and N. Sheppard, Proc. Roy. Soc., A311, 391 (1969).

[659] T. J. Jennings, H. H. Voge, and W. E. Armstrong, J. Cat., 24, 493 (1972).

[660] N. W. Cant and W. K. Hall, J. Catalysis, 16, 220 (1970).

[661] B. A. Morrow and P. Ramamurthy, Canadian Journal of Chemistry, 49, Nr. 20, 3409 (1971).

[662] B. A. Morrow and P. Ramamurthy, J. Phys. Chem. 77, 3052 (1973).

[663] H. Imai and C. Kemball, Proc. Roy. Soc., A302, 399 (1968).

[664] C. W. Jowett, P. J. Dobson, and B. J. Hopkins, Surface Science, 17, 474 (1969).

[665] D. D. Eley, D. M. Moran, and C. H. Rochester, Trans. Faraday Soc., 64, 2168 (1968).

[666] D. J. Darensbourg and R. P. Eischens, Preprint No. 21, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972).

with H_2O and D_2O which indicated that the infrared bands were not due to dissociative chemisorption of water. They could be attributed to impurity carbon monoxide. On the other hand, on the basis of deuterium water exchange reactions on platinum catalysts, dissociative water adsorption seems likely.[667]

4. Some Problems in Catalysis on Metals.

a. Recent Work Supporting the Localized Bonding and Molecular Orbital Approach in Catalysis. The renaissance of purely chemical concepts in catalysis, exemplified by the work on formic acid decomposition,[668] in which it was shown that chemical interaction between catalyst surface atoms and formic acid was important rather than interaction with delocalized levels of the metal catalysts, led to new interest in catalytic studies with alloys. As discussed, alloys between group VIII and IB metals received considerable attention because the number of holes in the *d*-band of these alloys depends on the alloy composition. Sachtler and co-workers reinvestigated the copper-nickel system in great detail and obtained quite interesting results.[669-673] Their work indicated that copper and nickel are only at high temperatures miscible in all proportions. At low temperatures, thin films or small crystals consist of two coexisting phases. One is an alloy with 80% copper and 20% nickel and the other is an alloy with 2% copper and 98% nickel. This is indicated by the free energies of alloying and is substantiated by x-ray analysis and other techniques. In bulk samples, equilibrium is not established quickly at low temperatures, but in thin alloy films prepared in high vacuum, equilibrium can be achieved within several hours. Copper has a higher rate of surface diffusion which gives rise to the envelopment of nickel or the high nickel content alloy with the 80% copper - 20% nickel alloy. The result is a surface of constant composition regardless of the overall copper-nickel ratio. This conclusion is supported by photoelectric work function measurements which indicate that copper-nickel alloys of widely differing bulk composition have the same work function. Analogous results were obtained with platinum-gold alloys.[674] Hydrogen adsorption studies showed that one hydrogen atom is adsorbed per nickel atom and that the chemisorption of hydrogen is

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[667] G. C. Bond, "Catalysis by Metals," Academic Press, London and New York (1962), page 217 and references therein.

[668] J. Fahrenfort, L. L. Van Reijen, and W. M. H. Sachtler, Z. f. Elektrochemie 64, 216 (1960); "The Mechanism of Heterogeneous Catalysis," J. H. DeBoer et al., Ed, Elsevier Publ. Co., Amsterdam, p. 23.

[669] W. M. H. Sachtler and G. J. H. Dorgelo, J. Catalysis, 4, 654 (1965).

[670] W. M. H. Sachtler and R. Jongepier, J. Catalysis, 4, 665 (1965).

[671] P. van der Plank and W. M. H. Sachtler, J. Catalysis, 7, 300 (1967).

[672] P. van der Plank and W. M. H. Sachtler, J. Catalysis, 12, 12 (1968).

[673] W. M. H. Sachtler and P. van der Plank, Surface Science, 18, 62 (1968).

[674] R. Bouman and W. M. H. Sachtler, Jr., Catalysis, 19, 127 (1970).

controlled by the composition of the surface phase and not by the copper to nickel ratio of the whole alloy. Copper does not chemisorb appreciable quantities of hydrogen; the copper-nickel alloy does. Since the 80% copper - 20% nickel surface phase has no holes in the *d*-band, it appears that the holes in the *d*-band are not a controlling factor in this reaction. Local interaction between the surface nickel atoms and hydrogen atoms is indicated by the fact that the nickel concentration of the surface can be titrated with reasonable accuracy by hydrogen chemisorption. The hydrogenation of benzene on copper-nickel alloys was also investigated. The activity pattern was analogous to the hydrogen chemisorption. Sachtler's results on copper-nickel alloys gain support from work by Cadenhead *et al.*[675]

These experimental results indicate that a model relying mainly on the collective electronic properties such as holes in the *d*-band may not be sufficient for describing chemisorption and catalysis on metals. The experiments support the modern trend of quantum mechanical description of chemisorption and catalysis as discussed, for instance, by Dowden[676, 677] and by Bond.[678] Dowden points out that chemisorption leads to surface complexes having single or double bonds of σ, π, etc. type using orbitals appropriate to the local symmetry. The surface orbitals of clean metal surfaces are similar in kind and arrangement to those of the interior, and the broken bond model appears to give good account of the surface energies. The infrared spectra of adsorbates indicate the approximate nature of the bonds within the surface ligands, but the metal-ligand bonds must be described in terms of the semi-empirical system devised by Goodenough[679] following the lead of Pauling.[680] Goodenough's analysis led to the conclusion that in transition metals there are collective and localized 3*d* electrons. Goodenough, Dowden, and Bond discussed particularly the electronic structure of face-centered cubic metals. This structure is believed to result from the overlap of each of the twelve lobes of the t_{2g} (i.e. d_{xy}, d_{xz}, d_{yz}) orbitals with one lobe projecting from a near neighbor. Thus, the coordination number 12 is obtained and the t_{2g} electrons occupy a collective (metallic) band. The remaining *d*-electrons occupy e_g (i.e. d_{z^2}, $d_{x^2-y^2}$) orbitals directed toward but not bonding with those from the next-nearest neighbors along the Cartesian axes. The e_g electrons are, therefore, localized and exist in two

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[675] D. A. Cadenhead, N. J. Wagner, and R. L. Thorp, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 2, p. 453.

[676] D. A. Dowden, Colloquio sobre Quimica Fisica de Procesos en Superficies Solidas, Ed. C.S.I.C. Madrid (1965), p. 177.

[677] D. A. Dowden, J. Res. Inst. Catalysis, Hokkaido Univ., 14, 1 (1966).

[678] G. C. Bond, Disc. Faraday Soc., 41, 200 (1966).

[679] J. B. Goodenough, Phys. Rev. 120, 67 (1960); "Magnetism and the Chemical Bond," Interscience Publ. Co., New York (1963).

[680] L. Pauling, Phys. Rev., 54, 899 (1938); Proc. Roy. Soc. (London), A 196, 343 (1949).

energy levels as a result of intra-atomic exchange splitting (Hund's rule). The 0·55 d-electron holes of nickel were divided between the t_{2g} band (0·41) and the e_g band (0·14). On the basis of this theory, Dowden as well as Bond predicted the direction of emergence of the two kinds of orbitals at various faces of face-centered cubic metals and discussed adsorption in terms of σ- and π-bond formation utilizing these orbitals. In Bond's discussion, the inequality of different crystal faces for chemisorption and catalysis emerges clearly as a consequence of the geometry of the orbitals. The interaction of the surface metal atoms with the adsorbed atoms must lead to a weakening of the metal-metal bond at the surface. This was discussed by Grimley[681] who states that chemisorption cannot be described properly when the metal is treated simply as a donor-acceptor whose electronic structure is little altered in chemisorption. Formation of a surface compound having weak remnant interaction with the metallic continuum appears to be a better model.

The molecular orbital approach provides a better basis for understanding some phenomena in chemisorption which are incompatible with the collective model such as the difference in adsorption behavior of different crystal faces, the de-metallization of the surface atoms upon chemisorption as derived from measurements of resistance and superparamagnetism and the surface reconstruction upon chemisorption as observed by means of field ion microscopy and LEED.

Weinberg and Merrill[682] used the molecular orbital model in conjunction with the bond energy bond order correlation of gas-phase kinetics[683] to describe the interaction of hydrogen with the platinum (111) plane. The experimentally observed adsorption states with heats of adsorption of 17 and 31 Kcal/mole[684-687] could be predicted with good accuracy if it were assumed that the low-energy state represents molecular hydrogen adsorption and the high-energy state, atomic hydrogen adsorption. Molecular adsorbed hydrogen on platinum has not been found by infrared techniques[688] but was postulated in the interpretation of surface potential and electrical conductivity changes

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[681] T. B. Grimley, "Molecular Processes on Solid Surfaces," E. Drauglis, R. D. Gretz, R. I. Jaffee, Ed., Battelle Institut Materials Science Colloquia, McGraw-Hill Book Co., 1969, p. 299.

[682] W. H. Weinberg and R. P. Merrill, Presented at the California Catalysis Society, Santa Barbara, 1970.

[683] H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, N. Y., 1966.

[684] G. B. Taylor, G. B. Kistiakowski, and J. H. Perry, J. Phys. Chem., 34, 799 (1930).

[685] G. B. Maxted and N. J. Hassid, J. Chem. Soc., 3313 (1931).

[686] T. Kwan, Advances in Catalysis, 6, 67 (1954).

[687] H. Chon, R. A. Fisher, and J. G. Aston, J. Am. Chem. Soc., 82, 1055 (1960).

[688] W. A. Pliskin and R. P. Eischens, Z. Phys. Chem., 25, 69 (1960).

upon hydrogen adsorption on platinum,[689] [690] as well as in an investigation of the temperature programmed desorption of hydrogen from platinum.[691] Hydrogen adsorption on platinum in a weakly and strongly adsorbed form was also observed in electrochemical work.[692-694]

Before returning to the discussion of alloy systems, let us discuss some recent work on surface valencies of metal atoms. Plummer and Rhodin[695] measured the binding energies of simple adatoms of the period-6 transition metals on atomically perfect single-crystal planes of tungsten by utilizing low-temperature, pulse-field desorption in an ultra-high-vacuum field ion microscope. The binding energies increased from hafnium over tantalum and tungsten to rhenium where a maximum is reached and decreased in the sequence osmium, iridium, platinum, and gold. These results could be explained in terms of the number of bonding and antibonding *d* electrons and the additional assumption that in some cases the surface-adatom interaction is sufficiently large to change the ground state configuration of the adatom. The higher the number of electrons contributing to bonding, which can be considered an effective surface valency, the higher is the binding energy. The effective surface valency is 7 for rhenium, 6 for tungsten and osmium, and 5 and 4 for tantalum and hafnium. For platinum and iridium, the results indicate that these metals have two different effective surface valencies, namely, 5 and 4 for iridium and 4 and 3 for platinum. For gold, a variable surface valency is indicated by the exceptional low energy for promotion of *d* electrons to *s* levels and also by some experimental results.[696]

Now, let us proceed to the discussion of alloy systems other than nickel-copper. In contrast to nickel-copper and platinum-gold alloys, there is complete miscibility of palladium and silver and palladium and gold at all temperatures.[697-699] However, even in this case, the alloy composition on the surface is not exactly the same as in the bulk because the alloy component which lowers the surface energy more will be enriched in

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[689] J. C. P. Mignolet, J. Chem., Phys., 54, 19 (1957).

[690] R. Suhrmann, Advances in Catalysis, 7, 303 (1955).

[691] S. Tsuchiya, Y. Amenomiya, and R. J. Cvetanovic, J. Cat., 19, 245 (1970); J. Catalysis, 20, 1 (1971).

[692] W. Bold and M. Breiter, Z. f. Elektrochemie, 64, 897 (1960).

[693] F. G. Will, J. Electrochem. Soc., 112, 451 (1965).

[694] M. Breiter, "Electrochemical Processes in Fuel Cells," Springer Verlag, New York, Inc., 1969, page 68.

[695] E. W. Plummer and T. N. Rhodin, J. Chem. Phys., 49, 3478 (1968).

[696] P. W. Palmberg and T. N. Rhodin, J. Chem. Phys., 49, 134 (1968).

[697] E. G. Allison and G. C. Bond, Catalysis Reviews, 7 (2), 233 (1972).

[698] R. Bouwman, G. C. M. Lippits, and W. M. H. Sachtler, J. Catalysis, 25, 350 (1972).

[699] H. R. Geberich, N. W. Cant, and W. K. Hall, J. Catalysis, 16, 204 (1970).

the surface.[700] Also chemisorption of gases such as carbon monoxide leads to a reconstruction of the surface with enrichment in the surface of the group VIII metal component.[701] [702] This enrichment upon adsorption of carbon monoxide is a consequence of the higher bond strength of the carbon monoxide to palladium or platinum as compared to silver or gold. These observations show the high mobility of atoms in the surface. With nickel-copper alloys, indications were obtained that also exposure to hydrogen at temperatures above 100°C can cause nickel enrichment in the surface.[703] It is consistent with the above ideas on the causes of surface reconstruction that no surface reconstruction was found with platinum-ruthenium alloys.[704]

Alloys of platinum and ruthenium were found to be more active catalysts for hydrogenation reactions[705] [706] and the electrocatalytic oxidation of methanol[707] [708] than platinum itself. This is rather surprising since pure platinum is a better hydrogenation as well as oxidation catalyst than ruthenium. This synergistic effect did not find any satisfactory explanation for some time but recent work[709] on the platinum-ruthenium alloy system seems quite promising to lead to a better understanding. It was found that the platinum-ruthenium system has a miscibility gap like nickel-copper, but in this case the surface is not covered by one phase but by different platinum-ruthenium phases. It was suggested[710] that the catalytic anomalies of the platinum-ruthenium system might be due to the grain boundaries between the crystals of the different alloy phases.

An unresolved problem of heterogeneous catalysis is the marked difference in selectivity between similar metals in interconversion of hydrocarbons. Even such closely related metals as nickel, palladium, and platinum exhibit very strong differences with respect to hydrogenolysis, isomerization, and dehydrocyclization. Very recent work on nickel-copper alloys[711] [712] sheds some light on this problem. In these studies, it was

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[700] R. Bouwman, G.C.M. Lippits, and W. M. H. Sachtler, J. Catalysis, 25, 350 (1972).

[701] R. Bouwman, G. C. M. Lippits, and W. M. H. Sachtler, J. Catalysis, 25, 350 (1972).

[702] R. Bouwman and W. M. H. Sachtler, J. Catalysis, 19, 127 (1970).

[703] W. K. Hall, J. Catalysis, 6, 314 (1966).

[704] R. Bouwman and W. M. H. Sachtler, J. Catalysis, 26, 63 (1972).

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[706] G. C. Bond and D. E. Webster, Proc. Chem. Soc., 398, December 1964.

[707] O. A. Petry, B. I. Podlovchenko, A. N. Frumkin, and Hira Lal, J. Electroanal. Chem., 10, 253 (1965).

[708] H. Binder, A. Kohling, and G. Sandstede "From Electrocatalysis to Fuel Cells," G. Sandstede ed., The University of Washington Press, Seattle and London, page 43.

[709] R. Bouwman and W. M. H. Sachtler, J. Catalysis, 26, 63 (1972).

[710] R. Bouwman and W. M. H. Sachtler, J. Catalysis, 26, 63 (1972).

[711] V. Ponec and W. M. H. Sachtler, J. Catalysis, 24, 250 (1972).

[712] V. Ponec and W. M. H. Sachtler, Preprint Nr. 44, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972).

found that for reactions involving C-H bond rupture such as hydrogen-deuterium exchange the rates per available nickel surface remains essentially constant on alloying of nickel with copper but hydrogenolytic reactions are affected strongly. In other words, alloying influences the C-H rupture to a much lesser extent than reactions where C-C bonds are broken or formed. These results were interpreted as indicative that reactions involving C-H rupture occur on single nickel surface atoms while for hydrogenolysis to occur, multiple nickel sites (nickel ensembles) are necessary. Recent data on homogeneous catalysts[713] indeed show that C-H bond reactions are probably occurring on isolated atoms whereas there is general consensus that hydrogenolytic splitting requires several adjacent adsorption sites. Alloys with 47 to 63% copper show in addition to the dilution effect an energy effect, namely changes in the activation energy of the catalytic reactions.[714-715] This is an indication that nickel atoms surrounded by copper atoms are modified by the presence of the copper atoms.

b. Hydrogenolysis and Isomerizations of Hydrocarbons on Metals. The catalytic hydrogenolysis of hydrocarbons refers to reactions involving the rupture of carbon-carbon bonds by interactions of the hydrocarbon with hydrogen. An example is the hydrogenolysis of ethane to yield methane as product. The kinetics of hydrogenolysis of simple hydrocarbons over metal catalysts was studied by Hugh Taylor and coworkers[716-719] who found that the reaction was strongly inhibited by hydrogen. The explanation of these results was given in the paper by Cimino, Boudart, and Taylor.[720] According to their kinetic analysis, the first step in the reaction involves 1,2 adsorption and dehydrogenation to an unsaturated surface species followed by an attack of the unsaturated species by hydrogen resulting in the rupture of the carbon-carbon bond to form monocarbon fragments which are then, in the case of ethane, hydrogenated to methane. Since deuterium exchange with ethane occurs more readily than the hydrogenolysis,[721] it was concluded that the rate of hydrogenolysis was limited by the rupture of the carbon-carbon bond. More recent work by Sinfelt and coworkers[722-723] has confirmed the

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[713] R. Ugo, La Chim. e L'Industria, 51 (1969) 1319; Engelhard Ind. Techn. Bull. 11, 45 (1970).

[714] V. Ponec and W. M. H. Sachtler, J. Catalysis, 24, 250 (1972).

[715] V. Ponec and W. M. H. Sachtler, Preprint Nr. 44, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[716] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., 58, 1445, 1795 (1936).

[717] K. Morikawa, N. R. Trenner, and H. S. Taylor, J. Am. Chem. Soc., 59, 1103 (1937).

[718] A. Cimino, M. Boudart, and H. Taylor, J. Phys. Chem., 58, 796 (1954).

[719] C. Kemball, H. S. Taylor, J. Am. Chem. Soc., 20, 345 (1946).

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[722] J. H. Sinfelt, J. Phys. Chem., 68, 344 (1964).

[723] J. H. Sinfelt, W. F. Taylor, D. J. C. Yates, J. Phys. Chem., 69, 95 (1965). (Continued)

findings of Taylor and his school. Extensive data on the activities of all group VIII metals and rhenium were obtained by these authors whereby differences of seven orders of magnitude in the specific activities were found. The VIII$_1$ metals showed maximum specific activity, while the activities of VIII$_3$ metals were lowest. The activity trends of the group VIII noble metals could be correlated with the percentage *d*-bond character of the metallic bond, but nickel, cobalt, and iron were in a different range. Work by J. H. Wood[726] supports Pauling's views on bonding of metals which may be one of the reasons why correlations with the percentage *d*-bond character were again made. In any event, it is reasonable to expect a dependence of the adsorption strengths of the hydrocarbon residues and herewith a dependence of the catalytic activity on the percentage *d*-bond character of the metal bond.

Anderson and Avery[727] studied the hydrogenolysis on platinum and palladium films and found that the reactivity of ethane in hydrogenolysis was considerably smaller than the reactivity of n-butane, isobutane, neopentane, and isopentane. Since 1,2 adsorption is impossible in the case of neopentane, the above observation led to the conclusion that ethane is 1,2 adsorbed while the other molecules which show the higher reactivity are 1,3 adsorbed. It is now widely believed that 1,3 adsorption is important in hydrogenolysis reactions. Sachtler's recent work with alloys,[728] [729] discussed above, is interesting in this context. Cycloalkanes are hydrogenolized as readily as neopentane and the other multi-carbon hydrocarbons.[730] [731] Since 1,3 adsorption is not possible with cycloalkanes due to steric reasons, it was suggested that in addition to 1,2 adsorbed and 1,3 adsorbed dehydrogenated surface species also π-allylic surface species play a role in hydrocarbon hydrogenolysis.[732] [733]

An interesting development of the last 10 years was the finding that on platinum not only hydrogenolysis but also isomerization of hydrocarbons takes place.[734-738]

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[724] J. H. Sinfelt and D. J. C. Yates, J. Catalysis, 8, 82 (1967); *ibid.* 10, 362 (1968).

[725] D. J. C. Yates and J. H. Sinfelt, J. Catalysis, 14, 182 (1969).

[726] J. H. Wood, Physical Review, 117, 714 (1960).

[727] J. R. Anderson and N. R. Avery, J. Catalysis, 5, 446 (1966).

[728] V. Ponec and W. M. H. Sachtler, J. Catalysis, 24, 250 (1972).

[729] V. Ponec and W. M. H. Sachtler, Preprint Nr. 44, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972).

[730] Y. Barron, G. Maire, D. Cornet, and F. G. Gault, J. Catalysis, 2, 152 (1963).

[731] Y. Barron, G. Maire, J. M. Muller, and F. G. Gault, J. Catalysis, 5, 428 (1966).

[732] Y. Barron, G. Maire, D. Cornet, and F. G. Gault, J. Catalysis, 2, 152 (1963).

[733] Y. Barron, G. Maire, J. M. Muller, and F. G. Gault, J. Catalysis, 5, 428 (1966).

[734] J. R. Anderson and B. G. Baker, Proc. Roy. Soc., A271, 402 (1963).

(Continued)

Formerly, hydrocarbon isomerization was known to occur only on acid site catalysts such as silica alumina. In the platinum catalyzed hydrocarbon isomerization, two types of isomerization mechanisms were found, namely, the C-C bond shift mechanism which probably occurs via a 1,3 adsorbed intermediate and a mechanism which proceeds through a carbocyclic intermediate. Both mechanisms will be briefly discussed in the following paragraphs.

With neopentane and butanes, Anderson and Avery[739] showed that hydrogenolysis and isomerization reactions have activation energies and frequency factors that are very similar and concluded that these reactions are mechanistically related in that the slow step in both involves the conversion of a 1,3 adsorbed species into a bridged intermediate. If the bridged intermediate is attacked by hydrogen, hydrogenolysis results; if not, skeletal isomerization takes place. It was shown that the energy criterion for isomerization is favorable on catalysts and sites where there is partial electron transfer from the hydrocarbon residue to the surface metal atom. This is possible for finite overlap when a double bond with a surface metal atom is formed.[740] Consequently, one of the carbon-platinum bonds of the 1,3 adsorbed species is expected to be a double bond. The theory on the bridged intermediate is an extension of the general theory of carbonium ion, free radical, and carbanium rearrangements as discussed by Zimmerman and Zweig.[741]

Gault and coworkers[742] [743] studied the reactions of hexanes and methylpentanes on platinum. From the products formed, it could be concluded that the isomerization reaction proceeds to and over cyclic products, and it was suggested that, in the C_6 series, isomerization proceeds via an adsorbed C_5 carbocyclic intermediate. Recent work on isomerization of dimethylbutanes on platinum indicated that both the bond shift mechanism and the mechanism in which cyclic intermediates are formed do take place consecutively.[744] J. R. Anderson *et al.*[745] reported that on ultra-thin platinum films,

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[735] J. R. Anderson and N. R. Avery, J. Catalysis, 5, 446 (1966).

[736] Y. Barron, G. Maire, D. Cornet, and F. G. Gault, J. Catalysis, 2, 152 (1963).

[737] Y. Barron, G. Maire, J. M. Muller, and F. G. Gault, J. Catalysis, 5, 428 (1966).

[738] J. R. Anderson and N. R. Avery, J. Catalysis, 2, 542 (1963).

[739] J. R. Anderson and N. R. Avery, J. Catalysis, 5, 446 (1966).

[740] J. R. Anderson and N. R. Avery, J. Catalysis, 7, 315 (1967).

[741] H. E. Zimmerman and A. Zweig, J. Am. Chem. Soc., 83, 1196 (1961).

[742] Y. Barron, G. Maire, D. Cornet, and F. G. Gault, J. Catalysis, 2, 152 (1963).

[743] Y. Barron, G. Maire, J. M. Muller, and F. G. Gault, J. Catalysis, 5, 428 (1966).

[744] J. M. Muller and F. G. Gault, V Intern. Congress on Catalysis, Palm Beach, Florida (1972), Preprint Nr. 51.

[745] J. R. Anderson, R. J. MacDonald, and Y. Shimoyama, J. Catalysis, 20, 147 (1971).

i.e., on very small platinum particles, the selectivity for formation of cyclic products is greater than on catalysts consisting of larger platinum particles. This selectivity pattern was interpreted as follows: On the very small platinum particles, low coordinated corner atoms are present in a higher proportion and these corner atoms favor the formation of adsorbed π-bonded carbocyclic reaction intermediates. These intermediates can lead to cyclic reaction products and provide a path for isomerization. Hydrogenolysis as well as isomerization by the bond shift mechanism, however, require three adjacent atoms and will, therefore, be more prevalent on larger catalyst particles. This subject was discussed again more recently.[746]

Boudart and Ptak[747] investigated the reactions of neopentane on all group VIII metals as well as on copper and gold. These authors found that not only platinum but also iridium and gold catalysts promote some isomerization in addition to hydrogenolysis. They suggested that the high electronegativity of the noble metals which will promote electron transfer from the hydrocarbon to the metal is an important factor. They also speculated that the variable surface valency which is exhibited only by platinum, iridium, and gold[748] [749] may explain the isomerization activity of these three metals.

Matsumoto *et al.*[750] postulated that not only partial electron transfer to the metal is important in the platinum catalyzed hydrocarbon isomerization, but proposed a more extensive electron transfer leading to a carbonium ion intermediate. These authors studied the hydrogenolysis of saturated hydrocarbons over nickel and platinum catalysts. In agreement with the results of Taylor and coworkers,[751-754] and Sinfelt *et al.*,[755-758] nickel catalyzed α-scission which leads to the formation of methane and a hydrocarbon which has lost one carbon atom. With platinum, isomerization also occurred, and the reaction products indicated that β-scission of carbonium ions was taking place.

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[746] J. R. Anderson and Y. Shimoyama, V International Congress on Catalysis, Palm Beach, Florida, 1972, Preprint 48.

[747] ., Boudart and L. D. Ptak, J. of Catalysis, 16, 90 (1970).

[748] E. W. Plummer and T. N. Rhodin, J. Chem. Phys., 49, 3478 (1968).

[749] P. W. Palmberg and T. N. Rhodin, J. Chem. Phys., 49, 134 ((1968).

[750] H. Matsumoto, Y. Saito, and Y. Yoneda, J. Catalysis, 19, 101 (1970).

[751] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Am. Chem. Soc., 58, 1445, 1795 (1936).

[752] K. Morikawa, N. R. Tremer, and H. S. Taylor, J. Am. Chem. Soc., 59, 1103 (1937).

[753] A. Cimino, M. Boudart, and H. Taylor, J. Phys. Chem., 58, 796 (1954).

[754] C. Kemball, H. S. Taylor, J. Am. Chem. Soc., 20, 345 (1946).

[755] J. H. Sinfelt, J. Phys. Chem., 68 344 (1964).

[756] J. H. Sinfelt, W. F. Taylor, D. J. C. Yates, J. Phys. Chem., 69, 95 (1965).

[757] J. H. Sinfelt and D. J. C. Yates, J. Catalysis, 8, 82 (1967); *ibid.*, 10, 362 (1968).

[758] D. J. C. Yates and J. H. Sinfelt, J. Catalysis, 14, 182 (1969).

Matsumoto *et al.*[759] suggested that the carbonium ions are produced on the platinum surface as a result of heterolytic elimination of the hydride ion from the starting molecule. They also suggested that the high affinity of platinum, being a soft acid,[760-762] for the hydride ion and the high stability of the platinum hydride ion coordination may be the reason for the carbonium ion formation on platinum. Matsumoto's interpretation of platinum metal catalyzed hydrocarbon isomerization may have been influenced by work in homogeneous catalysis in which it was shown that transition metal hydrides play a key role in the catalytic homogeneous isomerization of olefins.[763] The homogeneous reactions function through hydrogen abstraction from the coordinated olefin and subsequent addition on another part of the hydrocarbon molecule. The theory of Matsumoto *et al.* on the platinum-catalyzed hydrocarbon isomerization is not proven and is in conflict with some results of Barron *et al.*[764] which indicate that complete electron transfer to the metal leading to carbonium ion formation may not take place.

Isomerization of hydrocarbons was found also in the field of electrocatalysis.[765] [766] A 1,2 dimethylcyclopentene isomerized upon adsorption on a platinum electrocatalyst to give an equilibrium mixture of 1,2 and 2,3 dimethylcyclopentene. This isomerization occurred with and without application of a potential. On raising the potential to +0.5 volt vs. the hydrogen reference electrode, an additional isomerization reaction occurred, namely, a ring expansion to a six-carbon system. This was clearly indicated by the formation of cyclohexane and methylcyclohexane upon cathodic pulsing following adsorption periods at +0.5 volt. This influence of the potential on hydrocarbon isomerization is quite interesting in view of the above discussed theories in which partial electron transfer from the hydrocarbon to the platinum is considered to be important in the catalysis of isomerization reactions.

c. Hydrogen-Deuterium Exchange in Hydrocarbons. To understand the mechanism of catalytic reactions, it is important to know the nature of the adsorbed intermediates. A fruitful method of learning more about the intermediates which hydrocarbons form on catalysts has been the study of hydrogen-deuterium exchange. The pattern of products formed in the initial stages of an exchange reaction is determined

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[759] H. Matsumoto, Y. Saito, and Y. Yoneda, J. Catalysis, 19, 101 (1970).

[760] R. G. Pearson, Chem. Com. (1968), 65.

[761] R. G. Pearson and J. Songstad, J. Am. Chem. Soc., 89, 1827 (1967).

[762] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, London, Sidney (1967).

[763] M. Orchin, Advances in Catalysis, 16, 1 (1966).

[764] Y. Barron, G. Maire, J. M. Muller, and F. G. Gault, J. Catalysis, 5, 428 (1966).

[765] H. J. Barger, Jr., G. W. Walker, and R. J. York, J. Electrochem. Soc., 118, 1713 (1971).

[766] H. J. Barger, Jr., G. W. Walker, and R. J. York, J. Am. Chem. Soc., 93, 2800 (1971).

by the nature of the intermediates and their reactivity. In some cases, only a single hydrogen atom is replaced on one visit of the hydrocarbon to the catalyst surface; in other cases, a range of isotopic products is formed. Hydrogen-deuterium exchange with methane on tungsten is an example for the first case, exchange on nickel, for the second.[767] [768] In the first case, mainly CH_3D is formed, in the second CD_4. It can be concluded that a high activation energy is required for the dissociation of a second hydrogen atom of methane on tungsten, while a considerably smaller energy is required on nickel. Extensive deuteration was also found in hydrogen-deuterium exchange studies in electrocatalytic work on platinum fuel cell catalysts.[769] These studies were mentioned in the section on electrocatalysis. The hydrogen-deuterium exchange was studied extensively by Kemball and coworkers.[770-775] With relatively small molecules such as ethane, the experimentally found deuterium distributions could be explained by assuming an interconversion of monoadsorbed and 1,2-diadsorbed ethane formed by step-wise dissociative chemisorption of ethane. This mechanism is referred to as $\alpha\beta$ process. The exchange reaction with methane[776] and neopentane[777] showed that two-point attachment at one carbon atom to the metal surface ($\alpha\alpha$ process) is also possible but took place at temperatures much higher than those required for the $\alpha\beta$ process. Similarly, the exchange of neopentane on rhodium films[778] demonstrated that 1,3-diadsorbed species ($\alpha\gamma$ process) can also form but less easily than the other intermediates. The importance of 1,3 diadsorbed species in the isomerization of hydrocarbons was discussed in a previous section. Extensive deuteration was also observed with cyclic molecules. The interpretation of the results with these molecules required the assumption of multiadsorbed species. It was then realized that the formation of such species becomes difficult if only σ-bonding is considered since each additional carbon atom bonded to the surface utilizes one additional metal atom. The geometrical restrictions imposed by such a model were considered to be too severe; therefore, chemisorption was thought of in terms of variable multicentered bonding to the same metal atom. In other words,

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[767] C. Kemball, Proc. Roy. Soc., A207, 539 (1951).

[768] C. Kemball, Proc. Roy. Soc., A217, 376 (1953).

[769] H. J. Barger and A. J. Coleman, J. Phys. Chem., 72, 2285 (1968); 74, 880 (1970); 75, 3715 (1971). 77, 2783 (1973).

[770] C. Kemball, Proc. Roy. Soc., A207, 539 (1951).

[771] C. Kemball, Proc. Roy. Soc., A217, 376 (1953).

[772] J. R. Anderson and C. Kemball, Proc. Roy. Soc., A223, 361 (1954).

[773] C. Kemball, Advances in Catalysis, 11, 223 (1959).

[774] C. Kemball, Proc. Chem. Soc., 269, August 1960.

[775] C. Kemball, Trans. Faraday Soc., 50, 1344 (1954).

[776] C. Kemball, Proc. Roy. Soc., A207, 539 (1951).

[777] C. Kemball, Trans. Faraday Soc., 50, 1344 (1954).

[778] C. Kemball, Trans. Faraday Soc., 50, 1344 (1954).

it was proposed that intermediates may undergo step-wise interconversion as σ- and π-bonded ligands to one atomic center in the metal surface.[779-782] Such an αβ process involving σ-bonded alkyl and π-bonded olefin is still restricted to cis elimination or addition. In order to explain the initial exchange of all ten hydrogen atoms in cyclopentane on palladium surfaces, a π-allyl mechanism was proposed in which alternations between π-olefin and π-allyl complexes facilitate the complete exchange of all hydrogen atoms in one sojourn of the molecule on the catalyst.[783-785] The formation of the π-allyl intermediate requires a chain containing a minimum of three non-quarternery carbon atoms. This condition is not satisfied in 1,1,3,3 tetramethylcyclopentane, and with this molecule the initial exchange is limited to a pair of hydrogen atoms on one side of the ring in agreement with the expectations from an αβ process. In compounds satisfying the above condition, initial exchange of the maximal possible number of hydrogen atoms was found.[786] The idea of π-bonding of hydrocarbons to metal surfaces is very appealing, but some caution is warranted since infrared spectroscopy so far has not yielded evidence for olefins π-bonded to metal surfaces, as pointed out recently by Dent and Kokes.[787] However, Bond[788] stressed that there is much indirect evidence for intermediates π-bonded to metal surfaces.

Much work on metal catalyzed hydrogen-deuterium exchange reactions was carried out also by Burwell and coworkers.[789-798] These workers had considerable success by

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[779] J. J. Rooney, F. G. Gault, and C. Kemball, Proc. Roy. Soc., 407, December 1960.

[780] F. G. Gault, J. J. Rooney, and C. Kemball, J. Catalysis, 1, 255 (1962).

[781] J. J. Rooney, J. Catalysis, 2, 53 (1963).

[782] J. J. Rooney, Chemistry in Britain, 2, 242 (1966).

[783] F. G. Gault, J. J. Rooney, and C. Kemball, J. Catalysis, 1, 255 (1962).

[784] J. J. Rooney, J. Catalysis, 2, 53 (1963).

[785] J. J. Rooney, Chemistry in Britain, 2, 242 (1966).

[786] F. G. Gault, J. J. Rooney, and C. Kemball, J. Catalysis, 1, 255 (1962).

[787] A. L. Dent and R. J. Kokes, J. Am. Chem. Soc., 92, 6709 (1970).

[788] G. C. Bond, Disc. Faraday Soc., 41, 251 (1966).

[789] R. L. Burwell and W. S. Briggs, J. Am. Chem. Soc., 74, 5096 (1952).

[790] R. L. Burwell, Chem. Rev., 57, 895 (1957), and references therein.

[791] H. C. Rowlinson, R. L. Burwell, and R. H. Tuxworth, J. Phys. Chem., 59, 225 (1955).

[792] R. L. Burwell, B. K. C. Shim, and H. C. Rowlinson, J. Am. Chem. Soc., 79, 5142 (1957).

[793] J. Newham and R. L. Burwell, J. Phys. Chem., 66, 1438 (1962).

[794] K. Schrage and R. L. Burwell, J. Am. Chem. Soc., 88, 4555 (1966).

[795] R. L. Burwell and K. Schrage, Disc. Faraday Soc., 41, 215 (1966).

(Continued)

studying the exchange reactions of relatively complicated hydrocarbon molecules but with carefully chosen structures so that the pattern of products from the initial stages of the reaction can be related to the groupings and positions of the hydrogen atoms in the hydrocarbon. Burwell[799] believes that metal surfaces have enough free valencies to provide an ideal opportunity for formation of polynuclear complexes in which one adsorbed molecule is bonded to different surface atoms. With this in mind, Burwell prefers to interpret his results on hydrogen-deuterium exchange also in the case of cycloalkanes by assuming alternation between monoadsorbed and diadsorbed alkanes. To account for the exchange of the cycloalkane hydrogen atoms which are pointed away from the catalyst surface, it was proposed that 1,2 diadsorbed cycloalkanes may roll over from one side to the other.[800-802]

5. Analogies Between Heterogeneous Catalysis, Transition Metal Complex Chemistry, and Homogeneous Catalysis. Concepts such as crystal field, ligand field, and molecular orbital theory brought about remarkable advances in inorganic chemistry, particularly in the areas of transition metal complex chemistry and homogeneous catalysis. At the same time, many organometallic compounds such as ferrocene or various transition metal olefin π-complexes were discovered and their structure was determined. It was natural to apply all this information to heterogeneous catalysis and to search for correlations between the properties of such transition metal complexes and the properties of organic molecules adsorbed on metal surfaces. Rooney and Webb[803] were among the first to emphasize a relationship of transition metal complex chemistry and heterogeneous catalysis and pointed out that heterogeneous catalysis may be gaining considerably by looking at these fields rather than looking mainly at theoretical physics. Rooney and Webb were led to this conclusion by the experimental studies on the transition metal catalyzed hydrogen-deuterium exchange in hydrocarbons described in the previous chapter. These authors emphasized that there are striking similarities between the heterogeneous reactions on transition metal surfaces and the homogeneous reactions of π-bonded ligands in corresponding transition metal complexes. They suggested that heterogeneous and homogeneous catalysis are intimately related and that the ability of individual metal atoms and ions in the surface of solids to form π-bonded complexes

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(Continued)

[796] J. A. Roth, B. Geller, and R. L. Burwell, J. Res. Inst. Catalysis, Hokkaido Univ., 16, 221 (1968).

[797] R. L. Burwell, Accounts of Chemical Research, 2, Nr 10, 289 (1969).

[798] R. L. Burwell, Disc. Faraday Soc., 41, 249 (1966).

[799] R. L. Burwell, Disc. Faraday Soc., 41, 249 (1966).

[800] K. Schrage and R. L. Burwell, J. Am. Chem. Soc., 88, 4555 (1966).

[801] R. L. Burwell and K. Schrage, Disc. Faraday Soc., 41, 215 (1966).

[802] J. A. Roth, B. Geller, and R. L. Burwell, J. Res. Inst. Catalysis, Hokkaido Univ., 16, 221 (1968).

[803] J. J. Rooney and G. Webb, J. Catalysis, 3, 488 (1966).

with organic ligands is the origin of their catalytic activity. An investigation by Garnett *et al.*[804] added to the experimental basis of these ideas. These authors studied the hydrogen-deuterium exchange with monosubstituted benzenes, polycyclic aromatic hydrocarbons, and alkylbenzenes. In one series of experiments, group VIII metals were the catalysts for the exchange. In another series of experiments, the exchange was catalyzed by group VIII metal ions in solution. A remarkable similarity in the catalytic properties of the respective heterogeneous and homogeneous catalysts was observed.

Already, at the 3rd International Congress on Catalysis in 1964, the relation between heterogeneous catalysis and transition metal complex chemistry was a major discussion topic.[805] [806] This subject was also reviewed by Bond[807] in a comprehensive paper on the mechanism of the hydrogenation of unsaturated hydrocarbons on transition metals. The discovery of complexes with metal-to-metal bonds having similar bond lengths as the respective solid metals may contribute to an increase of interest in correlations between transition metal complex chemistry and heterogeneous catalysis by metals. In this context, it is interesting that Hume-Rothery[808] [809] suggested that transition metal atoms have the same valency as in their common compounds. This question was dealt with also by Nyholm[810] who assumes that nickel, palladium, and platinum have a valency of two and a d^8 configuration.

a. Applications of the Molecular Orbital Theory in Catalysis. In transition metal complex chemistry, the molecular orbital theory is now widely used. That is, a bond is formed by the combination of two atomic orbitals to give a bonding and an antibonding molecular orbital. In the case of octahedral environment, σ bonds are formed with s, p, d_{z^2}, and $d_{x^2-y^2}$ orbitals (e_g). The d_{xy}, d_{xz}, d_{yz} orbitals (t_{2g}) remain non-bonding. The combination of d-orbitals, the p-orbitals, and the s-orbital with the six ligand orbitals forms a system of six bonding orbitals, six antibonding orbitals, and three non-bonding orbitals. The bonding orbitals are filled with the ligand electrons, and the cation d-electrons are in the non-bonding and antibonding orbitals derived from

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[804] J. L. Garnett, R. J. Hodges, W. A. Sollich-Baumgartner, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for the Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 1, page 1.

[805] J. Halpern, Proc. 3rd International Congress on Catalysis, Vol. I, page 146, North Holland Publishing Co., Amsterdam (1965).

[806] R. S. Nyholm, Proc. 3rd International Congress on Catalysis, Vol. I, p. 25, North Holland Publishing Co., Amsterdam (1965).

[807] G. C. Bond, Advances in Catalysis, 15, 91 (1964).

[808] W. Hume-Rothery, H. Irving, and R. J. Williams, Proc. Roy. Soc. (London), A208, 431 (1951).

[809] W. Hume-Rothery, "Atomic Theory for Students of Metallurgy." 4th revised reprint (Institute of Metals, London, 1962). Structure of Metals and Alloys (Institute of Metals, London, 1956).

[810] R. S. Nyholm, Proc. 3rd International Congress on Catalysis, Vol. I, p. 25, North Holland Publishing Co., Amsterdam (1965).

the e_g-set. If the ligands also have orbitals with another orientation, such as, for instance, perpendicular to the axis cation-ligand, these orbitals may combine with the d_{xy}, d_{xz}, d_{yz} orbitals of the metal atom and form π-type molecular orbitals.

To illustrate the application of the molecular orbital theory to problems of heterogeneous catalysis, let us consider the theory of Cossee[811] for the Ziegler-Natta reaction, i.e., the polymerization of olefins under the influence of a catalyst system consisting of solid $TiCl_3$ and $Al(C_2H_5)_3$ in hydrocarbon solvents. Cossee postulated an active entity consisting of an octahedrally coordinated Ti^{3+} ion carrying in its coordination sphere four chloride ions, one C_2H_5 group obtained by ligand exchange with the $Al(C_2H_5)_3$, and one vacant octahedral position. This vacant position facilitates the attachment of an ethylene molecule by a π-bond so that the Ti^{3+} ion is then six-coordinate. The energy separation between the filled σ molecular orbital involved in the alkyl-Ti bond and the initially empty d_{yz} orbital is relatively small when the ethylene is coordinated. This d_{yz} orbital has the required symmetry for overlap with the antibonding $p\pi^*$ orbital of the ethylene molecule. As a result, it is easy to promote an electron from the $Ti\text{-}C_2H_5$ bonding orbital to the $d_{yz}\text{-}p\pi^*$ molecular orbital of the complex. Thereby, a four-center transition state is formed which facilitates a reaction between two ligands leading to the insertion of the ethylene between the Ti atom and the alkyl group and reformation of a vacant site. Repetition of this process leads to ethylene polymerization.

The electron withdrawal discussed above is reminiscent of the Volkenstein model. However, there is no need of electron transfer from other sites. The reaction remains strictly localized at the particular Ti^{3+} site. Also, at no time is there an organic radical present which could be detected by electron spin resonance spectroscopy. The reactivity is arrived at by more subtle changes of bond properties and bond energy levels.

Recently, the molecular orbital symmetry conservation rules of Woodward and Hoffman[812] were applied to catalytic reactions.[813, 814] Woodward and Hoffman interpreted the course of certain organic reactions by correlating the molecular orbitals of reactants and products with respect to symmetry. The Woodward and Hoffman rules divide molecular transformations into allowed and forbidden categories which has proven a powerful tool for understanding a large body of chemistry. Mango[815, 816] observed that symmetry forbidden reactions such as the fusion of two olefin molecules to a

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[811] P. Cossee, J. Catalysis, 3, 80 (1964).

[812] R. B. Woodward and R. Hoffman, J. Am. Chem. Soc., 87, 395, 2046, 2511, 4388, 4389 (1965).

[813] F. D. Mango and J. H. Schachtschneider, J. Am. Chem. Soc., 89, 2486 (1967); *ibid.*, 91, 1030 (1969).

[814] F. D. Mango, Advances in Catalysis, 19, 291 (1969).

[815] F. D. Mango and J. H. Schachtschneider, J. Am. Chem. Soc., 89, 2486 (1967); *ibid.*, 91, 1030 (1969).

[816] F. D. Mango, Advances in Catalysis, 20, 291 (1969).

ground state cyclobutane do occur in the presence of transition metals and proposed that transformations of this kind can become allowed through a catalytic process in which metal and olefin ligands exchange electron pairs giving a set of occupied molecular orbitals of the symmetry required for an allowed reaction path. The theory is supported by some transition metal catalyzed valence isomerizations. Recent work by Halpern and coworkers[817] casts doubt on Mango's theory. These authors studied in detail the catalysis by rhodium (I) of the valence isomerization of cubane and its derivatives to the corresponding syntricyclooctadienes which are symmetry forbidden reactions. Instead of a concerted mechanism, Halpern *et al.* found evidence that the rate-determining step involves the opening of only one carbon-carbon bond through an oxidative addition reaction.

b. Some Examples of Homogeneous Catalysis with Relevance to Heterogeneous Catalysis. In the following paragraphs, a few of the results in homogeneous catalysis which did inspire the workers in the field of heterogeneous catalysis will be briefly sketched. Reactions of transition metal compounds with gaseous covalent molecules play a vital role in life and are important in industry. Oxygen transport by hemoglobin or the oxidation of ethene to acetaldehyde homogeneously catalyzed by palladium (II) chloride in aqueous solution are examples. The mechanism by which metalloenzymes function is not known in detail. However, considerable progress toward a better understanding was made through the discovery of d^8 metal complexes which add reversibly covalent molecules to their coordination sphere (oxidative addition reaction). Molecules which add to these complexes include oxygen, hydrogen, acetylenes, olefins, alkyl halides, metal halides, halides, and others.[818-822] A vacant coordination site is considered the most important property which enables these d^8 complexes to add molecules and also to function as homogeneous catalysts. In other words, latent coordination sites are not only necessary to activate molecules by bringing them into the coordination sphere but also enable these complexes to be reactive in migration and oxidative-addition reactions. The d^8 complex which shows the most tendency to add covalent molecules is $[IrCl(CO)((C_6H_5)_3P)_2]$. It was discovered by Vaska.[823]

As discussed in the chapter on heterogeneous catalytic oxidation, there is some evidence that oxygen is adsorbed on certain oxide surfaces as a peroxide radical

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[817] L. Cassar, P. E. Eaton, J. Halpern, J. Am. Chem. Soc., 92, 3515 (1970).

[818] L. Vaska and J. W. DiLuzio, J. Am. Chem. Soc., 83, 2784 (1961).

[819] L. Vaska, Science, 140, 809 (1963).

[820] P. B. Chock and J. Halpern, J. Am. Chem. Soc., 88, 3511 (1966).

[821] J. P. Collman and J. W. Kang, J. Am. Chem. Soc., 89, 844 (1967).

[822] L. Vaska, Accounts of Chem. Res., 1, 335 (1968).

[823] L. Vaska and J. W. DiLuzio, J. Am. Chem. Soc., 83, 2784 (1961).

ion.[824-830] Dowden[831] suggested that surface peroxides may be important in heterogeneous oxidation of hydrocarbons. He proposed that oxygen molecules and hydrocarbons may become bonded to the same metal site on the oxide surface. Insertion of the oxygen molecule between the hydrocarbon and the metal site may follow, thus forming a hydrocarbon peroxide complex as the intermediate in the oxidation reaction. This proposed mechanism for heterogeneous oxidation reactions is analogous to a better known mechanism in homogeneous catalytic oxidation which will be briefly outlined here. As mentioned above, oxygen molecules are bonded as ligands to certain d^8 complexes. In these complexes, the oxygen molecules are bonded to the metal ion in a triangular structure $\mathrm{M}\!<\!\begin{array}{c}\mathrm{O}\\|\\\mathrm{O}\end{array}$ and the O–O bond distance is greatly increased as compared with free O_2.[832] This coordinated oxygen has a greater reactivity toward reductants than free oxygen. Much work in this field was done by Collman *et al.*[833-835] who reported that atom-transfer redox reactions can be catalyzed by metal ions which hold both reductant and oxidant in adjacent coordination sites. These processes go through discrete steps: oxidative addition, migratory insertion, and reductive elimination.

A striking example for the relationship between the catalytic activity of metal complexes and the catalytic activity of the respective metals is the homogeneous, palladium(II) catalyzed ethylene oxidation[836] (Wacker process) and the same reaction carried out in a fuel cell with palladium electrodes.[837] Rooney[838] pointed out that palladium appears to have a greater ability to form olefinic or allylic π-bonded intermediates

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[824] TH. G. J. Simons, E. J. M. Verheijen, PH. A. Batist, and G. C. A. Schuit, "Oxidation of Organic Compounds: Advances in Chemistry Series 76," page 261, ACS 1968.

[825] R. J. Kokes, Proc. 3rd International Congress on Catalysis, Vol. 3, page 484, North-Holland Publishing Co., Amsterdam (1965).

[826] P. F. Cornaz, J. H. C. van Hooff, F. J. Pluijm, and G. C. A. Schuit, Disc. Faraday Soc., 41, 290 (1966).

[827] J. H. C. van Hooff and J. F. van Helden, J. Catalysis, 8, 199 (1967).

[828] J. H. C. van Hooff, J. Catalysis, 11, 277 (1968).

[829] R. D. Iyengar and R. Kellermann, J. Catalysis, 12, 107 (1968).

[830] P. Meriaudeau, C. Naccache, and A. J. Tench, J. Catalysis, 21, 208 (1971).

[831] D. A. Dowden, Colloquio sobre Quimica Fisica de Procesos en Superficies Solidas, C.S.I.C. Madrid, page 177 (1965).

[832] A. McGinnety, N. C. Payne, and J. A. Ibers, J. Am. Chem. Soc., 91, 6301 (1969).

[833] J. P. Collman, Accounts Chem. Res., 1, 136 (1968).

[834] J. P. Collman, M. Kubota, and J. W. Hosking, J. Am. Chem. Soc., 89, 4809 (1967).

[835] J. Valentine, D. Valentine, and J. P. Collman, Inorg. Chem., 10, 219 (1971).

[836] J. Smidt *et al.*, Angew. Chem., 71, 176 (1959).

[837] M. Takahashi and T. Yanagihara, J. Electrochem. Soc., Japan, 34, 55 (1966).

[838] J. J. Rooney, Chemistry in Britain, 2, 242 (1966).

than, for instance, nickel or platinum. He stressed that palladium shows this property whether a reaction takes place on a solid palladium metal surface or on a palladium complex in solution. Rooney stated that palladium has a greater desire to fill the *d*-orbital than nickel or platinum. Since in olefinic and allylic π-complexes partial electron transfer to the metal takes place, such complexes will be particularly favored on palladium.

c. **Supported Homogeneous Catalysts.** One of the advantages of the homogeneous catalysis lies in its high specificity.[839] An interesting trend of recent times is to combine the advantages of homogeneous and heterogeneous catalysis by making catalysts in which homogeneous catalysts are supported by high-surface-area supports or by polymers. Examples are the ethylene oxidation by air on a catalyst consisting of palladium salts adsorbed on charcoal,[840] isomerization of butenes on palladium chloride on silica,[841] or a catalyst for the hydrolysis of p-nitrophenyl acetate consisting of silica gel supported imidazole.[842] The surface silanol groups of the silica gel provide the points of attachment of the catalyst to the silica gel. Similarly, functional groups of polymers are capable of bonding to transition metals. With rhodium bonded to a polymer, a catalyst for the oxidation of ethylene to aldehydes and alcohols was developed.[843]

d. **The Principle of Hard and Soft Acid and Base (HSAB Principle).** This principle, mainly proposed by Pearson,[844, 845] is sometimes used for the interpretation of catalytic reactions and the activity of catalysts and will be discussed here. Any inorganic or organic species can be mentally broken down into a generalized (Lewis) acid fragment and a generalized (Lewis) base fragment. Such generalized acids or bases can be classified as hard or soft. The terms "hard" or "soft" are related to the polarizability of the respective chemical entities. A soft base is one in which the donor atom is of high polarizability, has a low electronegativity, and is easily oxidized or is associated with empty, low-lying orbitals. Hard bases have the opposite properties. In a soft acid, the acceptor atom is of low positive charge and large size and has several easily excited outer electrons. In a hard acid, the acceptor atom has small size, high positive charge, and has no outer electrons which are easily excited. Typical hard acids are H^+, alkali, and earth alkali metal ions, Al^{3+} or Cr^{3+}. Typical soft acids are Cu^+, Ag^+, Au^+, Hg^+, Pd^{2+}, Pt^{2+}, Pt^{4+}, metal atoms, and bulk metals. Examples for hard bases are H_2O, OH^-, F^-, or

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[839] E. Stern, Catalysis Reviews, 1, 73 (1967).

[840] K. Fujimoto and T. Kunugi, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972), Preprint Nr. 28.

[841] E. Tijero, F. Castano, and E. Hermana, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972), Preprint Nr. 33.

[842] R. L. Burwell, Abstracts of the 165th National Meeting of the American Chemical Society, Dallas, Texas, Coll. 022.

[843] W. O. Haag and D. D. Whitehurst, 5th Intern. Congress on Catalysis, Palm Beach, Florida (1972), Preprint 30.

[844] R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963); Science, 151, 172 (1966).

[845] R. G. Pearson and J. Songstad, J. Am. Chem. Soc., 89, 1827 (1967).

CH_3COO^-; for soft bases H^-, I^-, CN^-, CO^-, C_2H_4, or C_6H_6. On the basis of the data of many different authors, Pearson[846] [847] formulated the principle that hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases. This principle refers to thermodynamic stabilities of the products of the acid base reaction. The HSAB principle is, however, also valid in kinetics: Hard acids react rapidly with hard bases and soft acids react rapidly with soft bases. An example of the application of the HSAB principle in catalysis is the interpretation of the platinum catalyzed isomerization of hydrocarbons via carbonium ions proposed by Matsumoto *et al.*[848] Platinum metal is a very soft acid; the hydride ion is a very soft base. Matsumoto *et al.* suggested that the stability gained by such a soft-soft interaction results in an abstraction of a hydride ion from the hydrocarbon and carbonium ion formation.

The softness or hardness of an acid is influenced by the softness or hardness of the bases associated with it. Soft bases tend to make an acid softer, hard bases harder. In other words, the electron density of the acid is influenced by the bases bonded to it. This effect permits an understanding of the stabilization of low or zero valent oxidation states of metal ions by ligands. Replacing H atoms by alkyl groups in the methyl carbonium ion (CH_3^+) leads to progressively harder carbonium ions. Apparently, the replacing of hydrogen atoms by alkyl groups results in the removal of some negative charge from the carbon atom of the CH_3^+. (Carbon is a more electronegative element than hydrogen.)

The classification of metal ions in hard and soft acids coincides with the older, less-general classification in class A and Class B metal ions.[849] [850] Pearson stressed very much that the HSAB principle is not a theory but a statement about experimental facts. Accordingly, an explanation of some observation in terms of soft and hard acid or base does not invalidate other more theoretical explanations.

6. Acid Site Concept, Dual-Functional Catalysis, Spillover and Catalysis on Metal Salts.

a. Acid Site Concept. Much research has been done with silica-alumina and related catalysts since it was first observed that alumina-silicates can be effective catalysts for hydrocarbon cracking. It is generally accepted that the catalytic activity of these insulator materials is due to their acid character. The origin of the acidity was

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[846] R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963); Science, 151, 172 (1966).

[847] R. G. Pearson and J. Songstad, J. Am. Chem. Soc., 89, 1827 (1967).

[848] H. Matsumoto, Y. Saito, and Y. Yoneda, J. Catalysis, 19, 101 (1970).

[849] G. Schwarzenbach, Experentia Suppl., 5, 162 (1956); Advan. Inorg. Radiochem., 3 (1961).

[850] S. Ahrland, J. Chatt, N. R. Davis, Quart. Rev. London, 12, 265 (1958).

recognized some 20 years ago in the isomorphic replacement of Si(IV) in a tetrahedral environment by Al (III).[851] [852] This results in aluminum ions with an unoccupied orbital, i.e., a Lewis acid. If water is present, it will be bound to these sites which then become proton donors, i.e., Brönsted acid sites. When hydrocarbons come in contact with Lewis acid sites, donation of electrons to these sites leads to the formation of carbonium ions which then proceed to subdivide according to the rules laid down by Whitmore[853] and applied to catalytic cracking by Greensfelder.[854] Interaction of hydrocarbons with the protons of Brönsted acid sites can also result in carbonium ion formation. Experimental proof of carbonium ion formation on silica-alumina catalysts was obtained by Hall *et al.*[855] [856] who observed that the triphenylcarbonium ion formed spontaneously from triphenylmethane on these catalysts. The concentration of acid sites can be determined by titration with gaseous ammonia or quinoline or by titration with n-butylamine of catalyst suspensions in non-aqueous media.[857-859] By using these techniques, it was found that the catalytic activity for hydrocarbon cracking is directly related to the amount of chemisorbed bases, i.e., to the acidity.[860]

For some reactions, alumina can be catalytically as active as silica-alumina. However, it is more easily poisoned by water.[861] The activity of aluminas is attributed to Lewis acid sites which form when aluminas are heat treated. Upon heat treatment, two surface hydroxyl groups, which aluminas are known to possess,[862] react to form water. This leaves an aluminum ion with an uncompleted coordination sphere, i.e., a Lewis acid site.[863] [864] The catalytic activity of alumina is enhanced by treatment with hydrofluoric acid[865-867] which appears to be due to an increase in acidity of the Lewis acid

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[851] C. L. Thomas, Ind. Eng. Chem., 41, 2564 (1949); J. Am. Chem. Soc., 66, 1586 (1944).

[852] M. W. Tamele, Disc. Faraday Soc., 8, 270 (1950).

[853] F. C. Whitmore, J. Am. Chem. Soc., 54, 3274 (1932).

[854] B. S. Greensfelder, "Chemistry of Petroleum Hydrocarbons," Vol II, Chap. 27, Reinhold Publishing Co., New York, 1955.

[855] H. P. Leftin and W. K. Hall, Actes Congr. Intern. Catalyse, 2^e, Editions-Technip, 1, 1353 (1961).

[856] Ching Yong Wu, W. K. Hall, J. Catalysis, 8, 394 (1967).

[857] M. W. Tamele, Disc. Faraday Soc., 8,270 (1950).

[858] A. G. Oblad, T. H. Milliken, and G. A. Mills, Advances in Catalysis, 3, 199 (1951).

[859] H. A. Benesi, J. Am. Chem. Soc., 78, 5490 (1956).

[860] A. G. Oblad, T. H. Milliken, and G. A. Mills, Advances in Catalysis, 3, 199 (1951).

[861] W. K. Hall, F. E. Lutinski, and H. R. Gerberich, J. Catalysis, 3, 512 (1964).

[862] O. Glemser and G. Rieck, Angew. Chem., 68, 182 (1956), Z. anorg. Chem., 297, 175 (1958).

[863] Y. Trambouze and M. Perrin, Compt. Rend. Acad. Sci., 236, 1261 (1953).

[864] W. K. Hall, F. E. Lutinski, and H. R. Gerberich, J. Catalysis, 3, 512 (1964).

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sites caused by the fluoride ion. Ammonia adsorption on hydrofluoric acid treated alumina does not result in adsorbed ammonium ions which indicates that the ammonia is adsorbed on Lewis acid sites and not on Brönsted acid sites.

Interesting work was done by Turkevich and coworkers[868-871] with molecular sieves of zeolite type which have the general formula $Na_x(AlO_2)_x(SiO_2)_y\ ZH_2O\ x<y$. So-called decationated zeolites were prepared by exchanging the sodium of Na-zeolites with ammonium and subsequent decomposition of the NH_4-zeolite at 340°C ($NH_4^+ \rightarrow NH_3 + H^+$), thus producing Brönsted acid sites. At temperatures above 480°C, the protons left the zeolite framework as water whereby Lewis acid sites were produced. The number of acid sites was determined by quinoline adsorption and corresponded well to the number of exchanged sodium ions, i.e., to the number of decationated sites. This is an interesting result. It may be considered to be the first quantitative identification of a catalytically active center with the molecular structure of the catalyst. Evidence was obtained that cumene cracking is facilitated by Brönsted acid sites and hydrogen-deuterium exchange by Lewis acid sites. The cracking of 2,3-dimethylbutane appears to require Lewis acid-Brönsted base dual sites. The existence of such dual sites was indicated by electron spin resonance work which showed that the electron donor and electron acceptor properties of such zeolites changed in the same fashion.

Na-zeolites as such show very little catalytic activity for hydrocarbon cracking, but high activity was found after replacing part or all of the sodium ions by multivalent cations.[872] The order of activity for bivalent cations is Mg>Ca>Sr>Ba, i.e., cations with smaller radius cause the greater activity. This result led Pickert *et al.*[873] to suggest that the high electrostatic field of these cations is the cause of the activity of these catalysts. The multivalent cations can exert their field very well, it is argued, because they are incompletely coordinated with structural oxygen ions and, therefore, easily accessible for

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(Continued)

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[867] A. G. Oblad, J. V. Messenger, and H. T. Brown, Ind. Eng. Chem., 39, 1462 (1947).

[868] D. Stamires and J. Turkevich, J. Am. Chem. Soc., 86, 757 (1964); *ibid.*, 85, 2557 (1963).

[869] J. Turkevich, "Catalysis Reviews," 1, No. 1, p. 1 (1967).

[870] J. Turkevich and Y. Ono, Advances in Catalysis, 20, 135 (1969).

[871] J. Turkevich and S. Ciborowski, J. Phys. Chem., 71, 3208 (1967).

[872] J. A. Rabo, P. E. Pickert, D. N. Stamires, and J. E. Boyle, Actes du Deuxième Congrès International de Catalyse, p. 2055, Editions Technip, Paris (1961).

[873] P. E. Pickert, J. A. Rabo, E. Dempsey, and V. Schomaker, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 714, North-Holland Publishing Company, Amsterdam (1965).

reactant molecules. Plank *et al.*[874] arrived at a different conclusion. They observed that zeolites with multivalent cations lose their high catalytic activity when dehydrated and regain it after admission of water. On the basis of these observations, Plank proposed that the multivalent cations promote Brönsted acid site formation by binding water as OH, thus freeing protons. Smaller cations having greater electrostatic fields will be more effective in promoting Brönsted acid site formation than larger cations. In this theory, not the cations but the Brönsted acid sites are the centers of the catalytic activity. Perturbation of hydroxyl groups by the polarizing effect of cations leading to increased acidity was considered by Hirschler[875] and by others.

Another interpretation of the catalytic activity of zeolites containing multivalent cations was offered for discussion by Schwab.[876] He considered the bipolar character of the surface of these catalysts as important. Schwab proposed that the Lewis acid sites (produced by the replacement of Si(IV) by Al(III)) accept electrons and cause carbonium ion formation while the electron rich sites (produced by the substitution of sodium by multivalent cations) transmit negative charge to another part of the hydrocarbon molecule.

Similar ideas were expressed by Pines *et al.*[877] [878] who studied extensively the dehydration of alcohols over alumina catalysts. An interesting case is the dehydration of menthol to 2 menthene which involves a trans-elimination. The trans-elimination can take place if a basic site of the alumina attacks the hydrogen from one side while the hydroxyl group is removed from the opposite side by an acidic site of the alumina. It was suggested that this may be possible if the reaction occurs within pores of the alumina having molecular dimensions.

b. Dual-Functional Catalysis. Naturally occurring alumina-silicates as well as synthetic silica-alumina or hydrofluoric acid treated alumina were used on a huge scale as catalysts for hydrocarbon cracking. These catalysts not only facilitate cracking but also catalyze, via carbonium ion intermediates, isomerization reactions which results in a product consisting of more highly branched hydrocarbons. These are better fuels for the internal combustion engine than straight-chain hydrocarbons. Now, most fuels for propulsion are produced using dual-functional reforming catalysts such as platinum on silica-alumina. The principal function of the metal is to catalyze dehydrogenation of

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[874] C. J. Plank, Proc. 3rd International Congress on Catalysis, Vol. 1, p. 727, North-Holland Publishing Company, Amsterdam (1965).

[875] A. E. Hirschler, J. Catalysis, 2, 428 (1963).

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[877] H. Pines and C. N. Pillai, J. Am. Chem. Soc., 83, 3270 (1961).

[878] H. Pines and J. Manassen, Advances in Catalysis, 16, 49 (1966).

saturated hydrocarbons to olefins. Subsequently, the olefins are isomerized on the acid sites of the silica-alumina and return to the metal to be rehydrogenated or further dehydrogenated. On these dual-functional catalysts occur hydrocarbon isomerizations, dehydrogenations, cyclizations, hydrogenolysis, and cracking. The metal and the acid sites fulfill their functions independently of each other. This was demonstrated in experiments in which platinum on nonacidic support and silica-alumina were mixed and used as dual-functional catalysts.[879] [880] The subject of hydrocarbon reforming and dual-functional catalysis was extensively investigated, particularly in industry, and also repeatedly reviewed.[881-888]

c. **Spillover.** Sinfelt and Lucchesi[889] observed that mixtures of platinum on silica with alumina were much more active in ethene hydrogenation than mixtures of platinum on silica with silica. This was surprising since alumina by itself is no catalyst for this reaction under the conditions of the experiment. This result suggested that hydrogen atoms are capable of diffusing from the platinum to the alumina and are active there in the hydrogenation of the ethene. Similar observations have been made by Sancier.[890] These results indicated that there may be a new kind of dual-functional catalysis in which active species like hydrogen atoms are formed on the metal and spill over onto the support, thus making the support catalytically active. It is now well known that spillover does occur and plays a role in reducing of supporting oxides. However, it is not clear whether catalytic activity is induced into the support by the spilled over species or not. Recent work by Schlatter and Boudart[891] indicates that Sinfelt and Lucchesi's[892] results were not due to the catalytic activity of the alumina acquired by spillover but by impurity effects.

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[879] S. G. Hindin, S. W. Weller, and G. A. Mills, J. Phys. Chem., 62, 244 (1958).

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[881] A. G. Oblad, T. H. Milliken, and G. A. Mills, Advances in Catalysis, 3, 199 (1951).

[882] V. Haensel, U. S. Patents 2,479,109 and 2,470,110 (1949).

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[885] J. H. Sinfelt, H. Hurwitz, and J. C. Rohrer, J. Phys. Chem., 64, 892 (1960).

[886] J. H. Sinfelt, Advances in Chem. Engineering, 5, 1 (1964).

[887] P. B. Weisz, Advances in Catalysis, 13, 137 (1962).

[888] J. E. Germain, Bull. Soc. Chim. France, page 23 (1966).

[889] J. H. Sinfelt and P. J. Lucchesi, J. Am. Chem. Soc., 85, 3365 (1963).

[890] K. M. Sancier, J. Catalysis, 20, 106 (1971).

[891] J. C. Schlatter and M. Boudart, J. Catalysis, 24, 482 (1972).

[892] J. H. Sinfelt and P. J. Lucchesi, J. Am. Chem. Soc., 85, 3365 (1963).

The phenomenon of spillover of hydrogen from metal specks to the support is now well known. For instance, hydrogen is adsorbed in appreciably larger quantities on platinum supported on carbon than on the corresponding amounts of platinum and carbon taken separately.[893] The most convincing illustration of spillover is that with platinum black and tungsten trioxide.[894] The reduction of WO_3 by hydrogen to the blue form (hydrogen tungsten bronze H_xWO_3) proceeds readily above 400°C. If the WO_3 powder is mixed with platinum black, reduction will start below 100°C. If some adsorbed water is present, the reduction takes place even at room temperature. These experiments indicated that hydrogen atoms formed by dissociative adsorption on the platinum spills over to the WO_3 and causes the reduction of the WO_3 at unusually low temperatures. The acceleration by water can be ascribed to an increase in the diffusion rate of the hydrogen atoms. Similarly, in work with platinized carbon, it was found that carbon impurities on the platinum can function as bridges which increase the diffusion of hydrogen atoms to the carbon support.[895]

d. **Catalysis on Metal Salts.** Another group of catalysts with acid sites are partially dehydrated metal sulfates which were studied by Tanabe *et al.*[896-898] and others. Much work was done with nickel sulfate. At room temperature, this salt crystalizes with 7 moles of water. Most of this water is lost quickly upon heating. At temperatures around 350°C, the water content is reduced to about one-half mole. Near this composition, Tanabe *et al.* found maximum acidity. In this intermediate state between monohydrate and the anhydrous salt, the nickel ion is coordinated to only 5 oxygen atoms (sulfate and water oxygens). The sixth position is vacant (an unoccupied sp^3d^2 orbital) and is able to accept an electron pair. This explains the Lewis acid nature of this partially dehydrated nickel sulfate. Brönsted acidity arises from the tendency of nickel ions to coordinate water through the oxygen atom, thus partially freeing a hydrogen ion.[899] Metal sulfates exhibit smaller acid strengths than silica alumina catalysts. Therefore, metal sulfates are more effective catalysts for those isomerization and polymerization reactions which require acid sites of moderate strength. Another point is that on metal sulfate catalysts basic sites are plentiful which may facilitate acid site/basic site/dual site catalysis. The considerably higher catalytic activity of metal sulfates as compared to silica alumina for the depolymerization of paraldehyde was attributed to such an acid site/basic site reactant interaction.

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[893] A. J. Robell, E. V. Ballou, and M. Boudart, J. Phys. Chem., 68, 2448 (1964).

[894] J. E. Benson, H. W. Kohn, and M. Boudart, J. Catalysis, 5, 307 (1966).

[895] M. Boudart, A. W. Aldag, and M. A. Vannice, J. Catalysis, 18, 46 (1970).

[896] K. Tanabe and M. Shokubai, Shokubai (Tokyo), 14, 1 (1957).

[897] K. Tanabe and R. Ohnishi, J. Res. Inst. Catalysis, Hokkaido Univ., 10, 229 (1962).

[898] K. Tanabe and T. Takenshita, Advances in Catalysis, 17, 315 (1967).

[899] T. Takenshita, R. Ohnishi, T. Matsui, and K. Tanabe, J. Phys. Chem., 69, 4077 (1965).

Two-point interaction between catalyst and reactant seems to be essential in elimination reactions such as the elimination of HCl from chlorohydrocarbons to form olefins. This is indicated by the fact that these reactions are catalyzed by polar compounds (salts or oxides) but not by metals. Apparently for elimination reactions, the catalyst must have electron accepting (acidic) sites, i.e., cations as well as electron donating (basic) sites, i.e., anions. Some 20 years ago, Schwab and Karatzas[900] worked in this field of catalysis which was in the meantime extensively studied by Noller and coworkers.[901-904] These investigators found that the activation energies for elimination reactions decreased with increasing ionic charge of the salt-catalyst ions and that the distance between cation and anion was important. In a recent investigation, the elimination of HCl from meso and DL 2,3-dichloro-butane catalyzed by various salts was studied.[905] The cation interacts with chlorine bound to the C_α carbon atom of the reactant; the anion interacts with the substituents on the C_β carbon atom. If these two interactions were of comparable strength, the catalyst was highly stereoselective and Cl^- and H^+ were abstracted simultaneously in a concerted reaction. When the salt catalyst consisted of a cation with high acceptor strength and an anion with low donor strength (basicity), the reaction path was different. In this case, the interaction of the catalyst cation and chlorine atom of the reactant is much stronger than the interaction of the anion with the substituents on the C_β carbon atom. A carbonium ion is formed which is converted to the olefin in a subsequent step. It was found that the stereoselective catalysts always gave trans-elimination. In homogeneous liquid-phase reactions, trans-elimination is the favored mechanism for concerted elimination reactions which is attributed to the higher stability of the staggered conformation. On the surface of a solid, the reactant is contacted on one side only and it is surprising that trans-elimination is the preferred mechanism also in this case.

7. The Role in Catalysis of Surface Heterogeneity, Lattice Defects, Coordinative Unsaturated Ions, Unusual Valency States, and Small Particle Size. The concept of "active center" was introduced more than 40 years ago by H. S. Taylor.[906] In all sections of this review, light was shed on this concept from various points of view. In this

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[901] H. Noller and K. Ostermeier, Z. f. Elektrochemie, 60, 951 (1956); 63, 191 (1959).

[902] H. Noller, H. Hantsche, and P. Andréu, J. Catalysis, 4, 354 (1965), and references therein.

[903] H. Noller, P. Andréu, E. Schmitz, A. Zahlout, and R. Ballesteros, Z. phys. Chem. N.F., 49, 299 (1966).

[904] H. Noller, P. Andréu, E. Schmitz, S. Serain, O. Neufang, J. Girón, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 4, page 1469.

[905] H. Noller, P. Andréu, E. Schmitz, S. Serain, O. Neufang, J. Girón, 4th International Congress on Catalysis, Moscow 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 4, page 1469.

[906] H. S. Taylor, Proc. Roy. Soc., A 108, 105 (1925).

chapter, this concept is discussed in its most direct meaning. First, work with oxides will be discussed and then work with metals.

a. **Investigations With Oxide Catalysts.** A voluminous literature exists on the role of lattice defects in semiconductor catalysis. Frequently, the function of these defects was interpreted in terms of the electronic theories on catalysis. However, there is evidence that catalytic reactions are often more influenced by modifications in the surface heterogeneity of catalysts than by changes in their properties as semiconductors. Extensive investigations of Garner, Stone, and coworkers[907] and of others led to this conclusion. Particularly emphasized was this point by Teichner and coworkers.[908-910] Teichner studied simple catalytic reactions such as the carbon monoxide oxidation, nitrous oxide decomposition, and ethylen hydrogenation on very finely divided nickel oxide and zinc oxide catalysts which were prepared by decomposition of the respective hydroxides at moderate temperatures and under vacuum. Nickel oxide prepared at 200°C and 250°C had the same conductivity but quite different catalytic activities. This difference between NiO (200°) and NiO (250°) was the subject of detailed investigations. On NiO (250°), oxygen was found to adsorb with a smaller heat of adsorption (bond energy) than on NiO (200°). It is believed that the smaller heat of adsorption on NiO (250°) is due to a recession of nickel ions which are in a more exposed position in the NiO (200°). The different energies of these nickel sites result in different mechanisms for the carbon monoxide oxidation. The less strongly bound oxygen on the NiO (250°) presents a greater reactivity toward carbon monoxide, and gaseous carbon dioxide is directly formed by this interaction. In contrast, on Ni (200°) the same interaction produces adsorbed carbon dioxide exclusively which inhibits the catalyst. Here, another mechanism takes place which involves the intermediate formation of a CO_3-(ads) complex. The higher catalytic activity of the NiO (250°) as compared to the NiO (200°) is not only explained by the different energies of the cationic adsorption sites (recessed and exposed nickel ions) but also by the presence of anionic vacancies on NiO (250°), which are known to form at 250°C but not at 200°C. When oxygen is adsorbed on high-energy anionic vacancies, the interaction with carbon monoxide yields the intermediate CO_3-(ads) ions. On less energetic anionic sites, the same interaction leads to adsorbed carbon dioxide. Doping of NiO with Li^+ and Ga^{3+} resulted, as expected, in samples having very different conductivities, but the differences in catalytic activities were smaller than the differences in catalytic activities caused by different thermal treatments. Incorporation of Li^+ in vacuo resulted in an increase of the number and energy of anionic sites. Oxygen adsorbed on these sites on NiO(Li) (250°) has small reactivity,

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[907] F. S. Stone, Advances in Catalysis, 13, 1 (1962), and references therein.

[908] P. C. Gravelle and S. J. Teichner, Advances in Catalysis, 20, 167 (1969), and references therein.

[909] G. El Shobaky, P. C. Gravelle, and S. J. Teichner, J. Catalysis, 14, 4 (1969).

[910] F. Bozon-Verduraz and S. J. Teichner, J. Catalysis, 11, 7 (1968).

and the mechanism involving intermediate CO_3-(ads) complexes takes place. Incorporation of Ga^{3+} causes the formation of cationic vacancies which are inactive toward oxygen. Consequently, the activity of NiO(Ga) (250°) is very similar to the activity of NiO (250°) and the same mechanism takes place on the Ga^{3+} doped and undoped nickel oxide. All of this led to the conclusion that the catalytic activity and the course of the catalytic reactions is primarily determined by the nature, concentration, and energy of lattice defects in the surface (energy spectrum of the surface). These, in turn, depend on the chemical nature of the catalyst, its previous history, and on the course of the catalytic reaction itself. The energy spectrum of the active surface is of paramount importance, and correlations with collective and bulk properties of the catalyst are not considered to be promising.

Extensive investigations with chromia catalysts were carried out by Burwell and coworkers.[911-915] The chromia catalysts were prepared by controlled heating of chromia gels. Burwell and coworkers attributed the catalytic activity of heat-treated chromia to coordinatively unsaturated sites which are generated by condensation of hydroxyl groups to yield oxygen ions plus water which evaporizes ($2OH^- \rightarrow O^{2-} + H_2O$). According to the gel structure and mode of heat treatment, the water loss can result in sites of different geometry, different degrees of coordinative unsaturation, and of different numbers of exposed chromium (III) ions. The coordinatively unsaturated chromium ions will have the properties of a generalized acid (acid site). The oxide ion formed at the surface during the dehydration of the chromia gel will be more basic than a bulk oxide ion. On coordinatively unsaturated chromium (III) ions, any Lewis base such as H_2O, CO, or dimethylether will be adsorbed. Lewis acids such as carbon dioxide will adsorb on coordinatively unsaturated oxygen ions. Burwell believes that there is a clear conceptional interrelationship between homogeneous and heterogeneous catalysis and applies the concept of strong and weak generalized acids and bases. Chromium (III) is a hard acid, the oxygen ion, a hard base. Therefore, one expects water or ammonia, which are hard bases, to adsorb on Chromium (III) sites more strongly than carbon monoxide or ethylen. The strength of bonding of ethylen or carbon monoxide to chromium should be augmented upon reduction of chromium (III) to the softer chromium (II). Burwell[916] imagines the reductive adsorption of hydrogen to occur in the following fashion: $Cr_{III}\ O^{2-}\ O^{2-}\ Cr_{III} \xrightarrow{H_2} Cr_{II}\ OH^-\ OH^-\ Cr_{II}$. Reduction of chromium (III) to chromium (II) in bulk would be disfavored by the crystal field stabilization energy. However, reduction of coordinatively

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[911] R. L. Burwell, A. B. Littlewood, M. Cordew, G. Pass, and C. T. H. Stoddart, J. Am. Chem. Soc., 82, 6272 (1960).

[912] R. L. Burwell and C. J. Loner, Proc. 3rd Intern. Congr. Catalysis, Vol. 2, p. 804, North-Holland Publ., Amsterdam 1965.

[913] R. L. Burwell, K. C. Taylor, and G. L. Haller, J. Phys. Chem., 71, 4580 (1967).

[914] D. Cornet and R. L. Burwell, J. Am. Chem. Soc., 90, 2489 (1968).

[915] R. L. Burwell, G. L. Haller, K. C. Taylor, and J. F. Read, Advances in Catalysis, 20, 1 (1969).

[916] R. L. Burwell, G. L. Haller, K. C. Taylor, and J. F. Read, Advances in Catalysis, 20, 1 (1969).

unsaturated chromium (III) ions should be much easier. Reduction of chromium (III) to chromium (II) by dry hydrogen was shown to occur readily at 500°C with chromia on silica or alumina.[917]

Burwell[918] [919] suggested that adsorption of hydrogen may involve heterolytic dissociative adsorption on adjacent pairs of coordinatively unsaturated chromium (III) and oxide ions. In this adsorption, formally, the H-H bond undergoes heterolytic fission with the proton going to the coordinatively unsaturated oxide ion and the hydride ion to the coordinatively unsaturated chromium (III) ion: $(HO^- Cr^{3+}\ O^{2-} \xrightarrow{H_2} HO^- \overset{H^-}{Cr^{3+}}\ OH^-)$. Electron sharing would probably occur and reduce the actual charge on the H^-. This adsorbed hydrogen is expected to be important in ethylene hydrogenation on chromia according to the following scheme in which the question of whether the acidic sites are chromium (III) or chromium (II) is ignored: $Cr\ O^{2-} \xrightarrow{H_2} \overset{H^-}{Cr}\ OH^- \xrightarrow{C_2H_4(g)} \overset{C_2H_5^-}{Cr}\ OH^- \rightarrow C_2H_{6(g)} + Cr\ O^{2-}$. Burwell[920] stressed that this scheme of ethylene hydrogenation on chromia is remarkably similar to the homogeneous catalytic hydrogenation of olefins at certain ruthenium complexes which coordinate hydrogen as hydride ion.[921] Burwell[922] also pointed out that the concept of coordinative unsaturation is of first ranking importance in the whole field of catalysis.

In the early 1950's, it was found that oxygen treatments of zinc oxide poison its catalytic activity for ethylene hydrogenation.[923] Such treatments also reduce the semiconductivity of zinc oxide because they render it more stoichiometric. This was one of the experiments which supported the theory that semiconductivity and catalytic activity are closely related. However, recently Dent and Kokes[924] found that oxygen treatments do not poison zinc oxide for room temperature ethylene hydrogenation provided the oxygen is free of any water. Their conclusion was that neither semiconductivity nor nonstoichiometry are related to the catalytic activity of zinc oxide. Dent and Kokes' results provided a basis for their proposal that zinc ion-oxygen ion pairs are the active sites. However, not zinc ions in regular lattice positions but zinc ions imbedded in the

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[920] R. L. Burwell, G. L. Haller, K. C. Taylor, and J. F. Read, Advances in Catalysis, 20, 1 (1969).

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close packed oxygen ion layers are expected to be catalytically active. Infrared studies indicated that hydrogen is dissociatively adsorbed on zinc and oxygen ion sites. For ethylene, no indications for opening of the double bond were found. Accordingly, it was assumed that chemisorption occurs by interaction of the π-bond with the surface. For steric reasons, it is not expected that ethylene could approach the imbedded zinc ions of the active sites close enough for interaction. Hence, it is believed that the ethylene is π-bonded to oxygen ion sites. The interaction of this π-bonded ethylene with hydrogen atoms bonded to zinc sites is expected to lead to ethane monoadsorbed on zinc sites through σ-bonds. Further interaction with a hydrogen atom bonded to a neighbor oxygen site may lead to free ethane.

There is considerable evidence that catalysis on transition metal compounds is often a question of the presence of ions in uncommon valency states, such as chromium (II), chromium (V), vanadium (IV), or nickel (III). Well known are vanadia catalysts for their ability to form vanadium (IV) ions as well as for forming a coordinatively unsaturated surrounding by losing one oxygen atom.[925] In the case of vanadia, this is probably due to the fact that one vandium-oxygen bond is considerably longer and weaker than the others. Also in chromia, uncommon valency states such as chromium (II) and chromium (V) were found by various authors.

Chromia gel and supported chromias are well known catalysts for dehydrogenation reactions of hydrocarbons. The first information on the nature of the active sites on these catalysts was provided by Weller and Voltz[926] who measured the uptake of hydrogen and oxygen by chromia at 500°C and arrived at the conclusion that Cr(II) ions had been formed. Detailed investigations were carried out by Burwell *et al.*[927] who studied the activity of chromia catalysts for deuteration, deuterium exchange, and isomerization reactions of hydrocarbons. Their results are consistent with a mechanism in which the hydrocarbon is adsorbed dissociatively, the alkyl group being bound to a chromium (II) ion on the catalyst surface and the hydrogen atom by one of the oxygen neighbors. In other words, a chromium (II) and an adjacent oxide ion form a pair site. In the adsorbed state, the alkyl group attains a carbanion character. Using electron spin resonance and other techniques, Van Reijen *et al.*[928] investigated chromia catalysts and their activity for cyclohexane dehydrogenation. Their results confirmed that the catalytically active chromia catalysts contain chromium (II) ions. These active sites are very reactive at room temperature toward oxygen and water. This, as well as results on carbon monoxide adsorption, indicated incomplete coordination of the chromium (II).

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[925] L. L. Van Reijen and P. Cossee, Disc. Faraday Soc., <u>41</u>, 277 (1966).

[926] J. W. Weller and S. E. Voltz, J. Am. Chem. Soc., <u>76</u>, 4695, 4701 (1954).

[927] R. L. Burwell, G. L. Haller, K. C. Taylor, and J. F. Read, Advances in Catalysis, <u>20</u>, 1 (1969).

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Incomplete coordination seems quite plausible for chromium (II). Being a d^4 system, chromium (II) is known to favor tetragonal Jahn-Teller distortion of its surroundings. This facilitates the formation of a pentacoordinated metal ion with one vacant octahedral site. From the measured reaction order and activation entropy of cyclohexane dehydrogenation, it was concluded that the adsorption step is rate determining. Van Reijen *et al.* also pointed out that a catalytically active cation site should have incomplete coordination and sufficiently extended, partly filled *d*-orbitals of the correct symmetry type to interact with the antibonding orbital of the C-H bond which has to be broken, and it should form a sufficiently stable metal-carbon bond. All these requirements are best fulfilled when the metal ion has low effective nuclear charge.

Uncommon valency states appear to be important for ethylene polymerization on supported chromia catalysts consisting mainly of Cr_2O_3 and CrO_3 (Phillips process). Several authors attributed the catalytic activity of chromia for this reaction to partial reduction of chromium (VI) to chromium (V).[929-931] Direct evidence for this was found by Boreskov *et al.*[932] The most detailed investigation was performed by Van Reijen and Cossee[933] who studied silica and alumina supported chromia and vanadia catalysts with electron spin resonance techniques. The formation of chromium (V) and vanadium (IV) was confirmed, and it was also observed that the coordination of these ions changes after contact of the catalyst with gases and vapors such as H_2O, air, CO, C_2H_4, HCl, or NH_3. The coordination was so flexible that contact at room temperature was sufficient to cause a change, and Van Reijen and Cossee suggested that this flexibility—encountered particularly with chromia/silica—is a prerequisite for catalytic activity. The results of this work indicated that chromium (V) is the active entity for ethylene polymerization provided it is in tetrahedral coordination. A mechanism was proposed according to which, in the initiation step of the polymerization, the coordination number is increased from four to five. An empty sixth coordination site may then be available to accommodate ethylene monomers. Previously, the coordination of the chromium (V) was not considered, and the catalytic activity could not be quantitatively related to the chromium (V) concentration. The above mechanism also explains the fact that silica-supported chromia is a better catalyst than alumina-supported chromia: Tetrahedral sites are provided by silica but not by alumina. Also Kasansky *et al.*[934-937] arrived at the conclusion that chromium (V) with tetrahedral

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[929] P. Cossee and L. L. Van Reijen, Actes du Deuxième Congrès International de Catalyse, p. 1679, Editions Technip, Paris (1961).

[930] V. B. Kasansky and Y. I. Pecherskaya, Kinetics and Catalysis, USSR, 2, 417 (1961).

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(Continued)

coordination is the active site.

b. **Investigations With Metal Catalysts.** The number of studies relating surface heterogeneity and catalytic activity is smaller for metals than for oxides but the evidence is convincing. Early work by Rienäcker[938] and by Eckell[939] indicated that cold working of metals increases the catalytic activity. Robertson *et al.*[940-942] found that nickel or copper wires have a very much increased catalytic activity after cooling suddenly from temperatures near the melting point. By rapid cooling, the dynamic disorder existing at high temperatures is preserved. Robertson envisages aggregates of point defects as the active sites. Uhara *et al.*[943-946] showed that a marked decrease in catalytic activity of cold-worked nickel wires occurs when the metal is annealed at temperatures between 200°C and 400°C, a temperature range at which lattice vacancies can be annealed out.

Another important problem is whether or not the specific catalytic activity of metal catalysts varies with the particle size. The development of supported catalysts having extremely finely divided metal particles consisting in some cases of only a few atoms led to increased interest in this fundamental question, particularly after Schuit and Van Reijen[947] showed that supported metal catalysts, under specified conditions, can give as reliable results as evaporated films. The first systematic investigations of this subject were those of Boreskov *et al.*[948, 949] who showed that the specific activity of platinum catalysts for the oxidation of sulfur dioxide and of hydrogen varied by

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[939] J. Eckell, Z. Electrochem., 46, 369 (1940).

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[941] A. J. B. Robertson and D. Crocker, Trans. Faraday Soc., 54, 931 (1954).

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[946] I. Uhara, S. Yamagimoto, K. Tani, G. Adachi, and S. Terantani, J. Phys. Chem., 66, 2691 (1962).

[947] G. C. A. Schuit and L. L. Van Reijen, Advances in Catalysis, 10, 243 (1958).

[948] G. K. Boreskov and V. X. Chesalova, Zh. Fiz. Khim., 30, 2560 (1956).

[949] G. K. Boreskov, M. G. Slin'ko, and V. S. Chesalova, Zh. Fiz. Khim., 30, 2787 (1956).

less than one order of magnitude for catalysts differing in their specific surface by four orders of magnitude. Related observations were made in electrocatalysis. For instance, J. Bett *et al.*[950] found that the specific activity of platinum electrocatalysts for oxygen reduction remained the same when the mean particle size of the platinum was varied between 400A and 30Å. The results clearly indicated that special sites such as edge and corner platinum atoms are not required for this reaction. The most complete investigation was carried out by Boudart *et al.*[951] who found only a twofold difference in specific activity for cyclopropane hydrogenation between platinum highly dispersed on γ-alumina or less dispersed platinum catalysts or platinum foils, while the specific surfaces of these catalysts differed by four orders of magnitude. In contrast, a very marked susceptibility for oxygen poisoning was found for the highly dispersed catalysts that was not observed for the other samples. These results prompted Boudart[952] to divide catalytic reactions into two categories termed facile and demanding (structure insensitive and sensitive). For facile reactions, the majority of sites possess ample activity under the conditions of operation. These facile reactions are those which fail to sense the nonuniformity of solid surfaces which becomes important under more demanding circumstances when the reaction is difficult from the viewpoint of reactivity (demanding reaction). The concept of facile and demanding reactions was used recently by Dalla Betta *et al.*[953] in the discussion of their work on cyclopropane hydrogenation on group VIII metals. These authors speculated that reactions which involve intermediates π-bonded to the surface are facile, while those involving multiple-bonded chemisorbed species are more likely to be demanding. Poltorak *et al.*[954] also studied the specific catalytic activity of platinum catalysts as a function of particle size and came to the conclusion that, for hydrogenation, dehydrogenation, isotope exchange, and isomerization of hydrocarbons, only contact between platinum and the reactants is important. For other reactions, such as the oxidation of alcohols, proper surface morphology or particle size of the platinum is essential. This pattern mentioned by Poltorak is not always true. Boudart *et al.*[955] searched for and found a demanding platinum catalyzed hydrocarbon reaction which is the previously discussed neopentane hydrogenolysis and isomerization. Boudart *et al.* found that the selectivity, defined as the ratio of the isomerization rate to the hydrogenolysis rate, varied by a factor of one hundred for the platinum catalysts studied and also observed that the selectivity for isomerization increased with the temperature of heat treatment of the catalysts. These changes in the

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[950] J. Bett, J. Lundquist, E. Washington and P. Stonehart, Electrochimica Acta, 18, 343 (1973).

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[953] R. A. Dalla Betta, J. A. Cusumano, and J. H. Sinfelt, J. Catalysis, 19, 343 (1970).

[954] O. M. Poltorak, V. S. Boronin, and A. N. Mitrofanova, 4th International Congress on Catalysis, Moscow, 1968, Reprints of Papers compiled for The Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas 77001, Vol. 3, p. 1235.

[955] M. Boudart, A. W. Aldag, L. D. Ptak, and J. E. Benson, J. Catalysis, 11, 35 (1968).

rates of the two parallel reactions could be explained, following Anderson and Avery,[956] by assuming 1,3-diadsorption as well as triadsorption of the neopentane on the platinum surface (1,2-diadsorption is not possible for this molecule). In the triadsorbed state which, by geometrical arguments, seems permitted only on (111) faces of the crystal or at triplet sites exhibiting the arrangement of the (111) face, neopentane does not become hydrogenolyzed as rapidly as in the diadsorbed state. Recent LEED work showed that platinum surfaces tend to develop (111) facets when heated in vacuum to 900°C.[957] [958] Hence, the increased selectivity of heat-treated platinum catalysts can be attributed to more abundant triadsorption. In conclusion, Boudart *et al.*[959] work shows that the specific activity of platinum for neopentane hydrogenolysis depends on the mode of catalyst pretreatment. This reaction demands a special geometric configuration on the platinum surface representing an active center in the sense used by Balandin[960] [961] and Taylor.[962]

Nitrogen is a very stable molecule and the adsorption of N_2 may be expected to be a demanding reaction. Many authors tried to study nitrogen adsorption on nickel at room temperature but inconsistent results were obtained. Finally, Eischens[963] was able to show with infrared techniques that molecular nitrogen does adsorb, at room temperature, on supported nickel. Van Hardeveld[964] found that this infrared active adsorption of nitrogen occurs not only on nickel but also on platinum and palladium and presumably on other metals as well. However, this adsorption occurred only on metal particles of 15-70Å diameter. It was concluded that crystals in this size range possess a large number of special sites which are absent or much scarcer on larger or smaller crystals. The interesting theoretical and experimental work of Van Hardeveld led to a quite detailed picture of these special sites. His considerations were based on the axiom that small crystals must be shaped so that their free energy is a minimum. This means that they will crystallize in such a way that the number of bonds between all atoms, including surface atoms, is a maximum. This condition can be met if the particle is as nearly spherical as possible, yet at the same time the surface has to be built up preferentially of the highly coordinated (111) and (100) planes. Using marble models, it was shown

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[956] J. R. Anderson and N. R. Avery, J. Catalysis, 5, 446 (1966).

[957] H. B. Lyon and G. A. Samorjai, J. Chem. Phys., 46, 2539 (1967).

[958] M. McLean and H. Mykura, Surface Science, 5, 466 (1966).

[959] M. Boudart, A. W. Aldag, L. D. Ptak, and J. E. Benson, J. Catalysis, 11, 35 (1968).

[960] A. A. Balandin, Z. phys. Chem., 132, 289 (1929); Advances in Catalysis, 19, 1 (1969).

[961] A. A. Balandin, Advances in Catalysis, 10, 96 (1958); "Catalysis and Chemical Kinetics," Acad. Press. Inc., New York (1964); Advances in Catalysis, 19, 1 (1969).

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[963] R. P. Eischens and J. Jacknow, Proc. 3rd International Congress on Catalysis, Vol. 1, page 627, North-Holland Publishing Co., Amsterdam (1965).

[964] R. Van Hardeveld and A. Van Montfoort, Surface Science, 4, 396 (1966).

that in crystals larger than 70Å the surface will mainly consist of (111) and (100) planes which have B_3 and B_4 sites. The subscripts under the B mean the number of possible contact points, i.e., coordination number at the particular site for an adatom. Crystals smaller than 70Å cannot be constructed with only (111) and (100) planes as boundary planes. Other planes, such as (110) and (113), must be present. These planes have B_5 sites. The marble models also indicated that on very small crystals (10Å) hardly any B_5 sites occur. Since infrared active nitrogen adsorption takes place only on crystals which are in the size range where B_5 sites occur, it was concluded that B_5 sites facilitate the adsorption of this very stable molecule. The initial heat of nitrogen adsorption was found to be 12 Kcal/mole. Although this heat of adsorption might suggest chemisorption, Van Hardeveld gives convincing arguments in favor of physical adsorption.

Bond[965] published a theoretical paper on the effect of very small particle size on the catalytic activity of metals. For cubo-octahedral geometry, the fractions of atoms present in surface, edge, and corner locations and of atoms in extended crystallographic planes were calculated as a function particle size. The significance of small coordination numbers of surface atoms was discussed. Bond also shed light on the B_5 site from the point of view of molecular orbital theory.

V. CONCLUDING REMARKS

Catalysis is a subject so vast that it may well be comparable in diversity to general chemistry. It would be a vain attempt to formulate definite conclusions concerning this rapidly developing field. Throughout the years, the approach to catalytic problems was influenced by the evolution of thought in general chemistry and physics. Each of the various research trends revealed some facts of lasting value which resulted in considerable overall progress in the understanding of catalysis. It is now fully appreciated that catalysis is a chemical problem and that the concepts of chemistry are most promising for the interpretation of the observations in this field. This leads to a more unified view of catalysis as compared to about 15 to 20 years ago when catalysis on metals, semiconductors, and insulators appeared to be more separated fields than is true today. Also, the differences between heterogeneous catalysis and homogeneous catalysis do not seem fundamental any more. To discuss the trends in these ideas on catalysis was one purpose of this review. The other was to integrate the new field of electrocatalysis and particularly the area of electrocatalytic hydrocarbon oxidation with the general field of catalysis. It is interesting to see that similar results were obtained by the electrochemists working in electrocatalysis and by the workers in the field of heterogeneous gas phase catalysis. It is hoped that correlating these results will further the understanding of the processes involved.

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[965] G. C. Bond, 4th International Congress on Catalysis, Moscow, 1968, Reprints of Papers compiled for the Catalysis Society by Joe W. Hightower, Chemical Engineering Department, Rice University, Houston, Texas, 77001, Vol 3, p. 1217.

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