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I. SUMMARY

This report covers the period 1 June 1975 through 30 June 1976 and describes the research carried out in two major areas: 1) Materials for Energy Storage and 2) Heterogeneous Catalysis.

A. Research Program Plan

1. Materials for Energy Storage:

The discovery of new types of solid electrolytes (such as beta alumina, RbAg_4I_5 , copper and silver halides and stabilized zirconia) with large values of ionic conductivity at relatively low temperatures has enhanced the prospect of developing battery systems possessing a high energy storage-to-weight ratio, high power output capability, long life in service, efficiency in charge-discharge characteristics and the capability of being constructed from inexpensive, readily obtainable materials. Three complementary areas of research are being pursued. The first involves a search for new materials to be used as solid state electrolytes and electrodes; the second involves detailed studies on electrolytes already known to be predominantly ionic conductors, and the third involves a fundamental investigation of sintering and hot pressing of materials of interest. Toward these ends, the studies begun the previous year on the cuprous halides as model systems are being completed. The search for electrolyte materials is being concentrated on the hollandites, which are capable of operating at ambient temperatures. Mössbauer and NMR techniques are being used to characterize these materials. Solid electrode materials under investigation include the tungsten and vanadium bronzes. The sintering studies are being pursued in order to develop methods of preparing dense, polycrystalline electrolytes and electrode materials.

2. Heterogeneous Catalysis:

A number of the most important heterogeneous catalysts consist of tiny crystallites of metal supported upon a carrier such as silica or alumina. The support leads to a greater metallic surface area per gram of metal and permits use of the catalyst at temperatures up to 500°C without rapid sintering. However, relatively little is known of the exact nature of the

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crystallites (including the nature of their attachment to the support), the effect of the support upon the catalyst behavior, the effect of metallic particle size on catalytic characteristics and the effect of the method of catalyst preparation upon catalytic activity. It is the purpose of this project to provide some resolution of these problems.

Standard batches of catalysts are being prepared by different methods, of varying particle sizes and on different supports. These catalysts will be characterized as completely as possible using x-ray diffraction and scanning and transmission electron microscope studies (to determine crystallite size, orientation, strain, dislocation density and radial density function), EPR studies (to yield information about the migration of reactants and products on the support and, possibly, the nature of the catalytic sites on the metal), kinetic studies (to determine the kinetic form and rate constants for reactions chosen to give optimum information about catalytic characteristics) and selectivity studies (to determine relative yields of several concurrent reactions). Analytical studies will be undertaken to correlate the data on the two sets of catalysts to be studies (on silica and alumina supports) in this project and to develop a theoretical understanding of the underlying phenomena.

B. Technical Results

1. Materials for Energy Storage

An organic precursor method had been previously employed to obtain lithium titanate ($\text{Li}_2\text{Ti}_3\text{O}_7$) with densities of 75-80% of theoretical x-ray density. By using cold pressing and sintering techniques, no increase in density was achieved. Therefore, a hot pressing technique was developed. This has resulted in samples which are fine grained and which possess a density of better than 95% of theoretical densities. Pellets of the single phase lithium ferrosphinel, LiFe_5O_8 , of 94-96% of theoretical density were also synthesized. The LiFe_5O_8 samples exhibited a room temperature conductivity of $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ with an appreciable ionic contribution.

Initial attempts were made to prepare porous Y_2O_3 by the sintering of suitable precursors. This ceramic would then be used as a porous separator to retain the molten electrolyte in the desired configuration.

The effect of a dispersed second phase on the ionic transport properties of electrolytes has been investigated. At low temperatures, an order of magnitude increase in ionic conductivity was effected by the appropriate dispersion of alumina particles in a CuCl matrix.

Studies have been completed on the copper halides without a dispersed phase in which it was shown that the mobilities of copper interstitials and copper vacancies were exceedingly high.

2. Heterogeneous Catalysis

The rates of formation and the isotopic distribution patterns of the cyclopentanes which result from isotopic exchange between cyclopentane and deuterium were investigated for the Pt/SiO₂ catalysts previously prepared. The results indicate that hydrogen reacts very rapidly with oxygen adsorbed on Pt. Furthermore, the oxide formed upon protracted storage is much less reactive than that resulting from brief exposure, and the oxygen content on stored catalysts is greater than that of catalysts exposed to oxygen for 15 minutes at 25°C. This is believed to be due to the slow filling of open surface sites upon prolonged storage.

The catalytic activity declines during runs involving isotopic exchange between deuterium and cyclopentane, with activity and selectivity being fully restored by repeating the standard pretreatment conditions. (Heating in oxygen at 300°C for 1/2 hour, then 300°C in hydrogen for one hour, followed by heating in helium for 1/2 hours at 450°C and then cooling in helium to the desired experimental temperature.) The deactivation results from the deposition of carbon on the catalysts.

The effect on the rate and selectivity of a variety of pretreatment conditions was also investigated.

The activity and selectivity of the Pt/SiO₂ catalysts have been determined for hydrogenation of propylene and methylcyclopentane. Once again, the pretreatment conditions affect the activity and selectivity levels. These catalysts were also examined by means of x-ray diffraction techniques. Surface areas, dispersion, strains present and root mean square amplitudes of vibration were among the properties investigated.

For future studies, small batches of the Pt/Al₂O₃ catalysts have been prepared and their dispersions determined.

II. RESEARCH REPORTS

A. Materials for Energy Storage

Faculty:

- D. H. Whitmore, Professor, Materials Science and Engineering
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- D. L. Johnson, Professor, Materials Science and Engineering
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Graduate Students:

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The purpose of this proposed research is to identify promising fast ion conductors for use as electrolytes and to develop separators utilizing these electrolytes for relatively low temperature battery applications.

Several of the advanced battery systems presently being considered for load leveling or vehicular propulsion are operative at temperatures considerably above ambient. Two of the most widely investigated systems are the sodium-sulfur and lithium-sulfur batteries.

The sodium-sulfur battery operates at temperatures of 350°C so as to keep the polysulfide cathode material molten, thus reducing polarization effects. The high temperature of operation also gives the sodium beta- or beta"-alumina solid electrolyte a favorable conductivity.

The battery utilizing the lithium-sulfur system is operative at 425°C, this temperature being dictated by the melting point of the molten salt electrolyte used. With early cells this temperature of operation not only presented corrosion problems but also caused instabilities in the electroactive materials at this temperature of operation. In particular, sulfur volatilization at the cathode and corrosion by lithium of the anode components dictated that the chemical activities of these materials be reduced, leading to the system LiAl/FeS_2 . This has had, however, the effect of reducing the cell voltage from 2.3 to 1.6 and the theoretical energy density from 1200 to 364 Wh/lb. It would be highly desirable, therefore, to lower the temperature of operation of the lithium-sulfur system so that the use of lithium and sulfur each of unit activity could be used.

One approach to the solution of this problem would be the identification and fabrication of a lithium ion conductive ceramic of high conductivity at a temperature lower than that of the present lithium-sulfur battery. Considerable research has been directed toward finding a lithium ion conducting analog of sodium β or β'' -alumina at Northwestern.

Our initial efforts have been directed to the properties of a lithium-titanium-oxygen compound of nominal composition, $\text{Li}_2\text{Ti}_3\text{O}_7$, and MgO-stabilized β'' -alumina of nominal composition $\text{Na}_2\text{MgAl}_{10}\text{O}_{17}$. The $\text{Li}_2\text{Ti}_3\text{O}_7$ phase exhibits the ramsdellite structure in which channels (two TiO_6 octahedra wide) exist parallel to the c-axis, these channels offering the possibility for rapid migration of lithium ions. Accordingly, ramsdellite phases with the general formula $\text{Li}_x\text{Ti}_{4-x/4}\text{O}_8$ ($2 \leq x \leq 4$) have been synthesized as polycrystalline sintered compacts using a variety of techniques, and preliminary data, obtained by NMR and dielectric loss measurements, indicate the possibility of fast Li^+ motion in these materials.

During the first year of the ARPA project, research was focused on materials which possess the hollandite structure (a distorted rutile structure with linear tunnels). In the second year, polycrystalline samples of some alkali titanates possessing the ramsdellite structure and MgO-stabilized β'' -alumina were prepared. Several methods of preparation of the titanates were carried out. These techniques include mixing high-purity, alkali carbonates and TiO_2 powders in acetone, drying and then compacting and

sintering them. In the initial phases of this program, the ramsdellite samples prepared exhibited densities which were approximately 70% of the theoretical x-ray value and also showed considerable open porosity. In order to improve this situation, an organic precursor method was employed to obtain powders of Li_2O and TiO_2 mixed on an atomic scale; this method was originally developed for barium titanate by N. Pechini. In this technique lithium carbonate and tetraisopropyltitanate were dissolved in separate solutions of citric acid in ethylene glycol. These solutions were assayed and then mixed together to obtain the desired lithium-to-titanium ratio. The resulting solution was heated to evaporate the excess solvent, which resulted in an organic glass with the metal ions in solution. This organic glass was then calcined at about 650°C in air, giving a sinterable oxide powder. The best samples obtained by recalcining a second time at 650°C and sintering such powders (1150°C for 40 hours) exhibited densities on the order of 80% of the theoretical value and very little open porosity. The porosity present in these samples seemed to arise from the volatilization of some constituent during processing.

NMR line-narrowing measurements on the Li titanates between 70° and 400°K suggest that lithium ions are mobile in these compounds with an apparent activation energy of 0.17 eV. A number of other Li stannates, silicates, germanates and titanates were also prepared by sintering and examined with the aid of the NMR line-narrowing technique. On the basis of the screening work to date, the Li titanate, $\text{Li}_2\text{Ti}_3\text{O}_7$, was singled out for further evaluation as a solid electrolyte candidate.

A great deal of our recent efforts have been directed toward improving the density of the polycrystalline titanate ($\text{Li}_2\text{Ti}_3\text{O}_7$) sample from the 75-80% of theoretical x-ray density which had been achieved using the organic precursor method of Pechini. Using different starting materials and cold pressing and sintering techniques, we made no major strides towards achieving an increase in the density, primarily because of our inability to prevent grain coarsening from occurring during sintering; this coarsening results in pores being entrapped within the grains themselves, rather than remaining at the grain boundaries where their elimination might be achieved during continued heating of the sample.

Our latest experiments to improve the density of the $\text{Li}_2\text{Ti}_3\text{O}_7$ samples have involved hot pressing in air at about 1050°C and pressures of about 5,000 psi. The starting materials for this process are lithium carbonate and titanium dioxide powders which are mixed and fired at 1000°C for 20 hours. The resulting pellet is then crushed and ground, cold-pressed at 10,000 psi without a binder and introduced into a ceramic (dense Al_2O_3) die and piston hot-press assembly, along with a covering of some coarse-grained alumina powder to facilitate hot ejection of the sample after hot pressing has been accomplished. The temperature of the piston, die and sample is gradually raised (at a heating rate of $10^\circ/\text{min.}$) until 700°C is reached, at which temperature an initial pressure of 2,500 psi is applied to the sample. Heating is continued, with the pressure being raised to about 5,000 psi at a temperature of 950°C ; this pressure is continuously applied to the sample as its temperature is raised to about 1040°C and is maintained on the sample for 1 hour at that temperature. The pressure is then removed, and the sample is hot ejected from the press and allowed to cool down in the furnace to room temperature. The resulting sample is fine-grained and possesses a density which is better than 95% of theoretical density. There are some indications of the presence of a second phase at the grain boundaries, but this appears to amount to only about one percent of the total volume of the sample. There is no x-ray evidence that a second phase is present in the hot-pressed sample.

Professor D. L. Johnson has suggested an innovative and technically feasible approach to solving the problem of a fast lithium ion conductor which operates at reasonable temperatures. The idea is to sinter a thin ceramic body (the separator) to a given porosity and then to infiltrate the body with a low-melting eutectic which will wet the ceramic.* In this way, the separator will offer mechanical support, retaining the molten electrolyte in the desired configuration. Candidates for the ceramic are Y_2O_3 , ThO_2 and BeO .

*U.S. Patent 3,404,041 issued to Y. H. Inami and assigned to Philco-Ford filed March 31, 1966 describes a similar technique applied to Fibrafrax. Of course this material lacks the mechanical strength of Professor Johnson's proposed porous ceramic.

The most direct method of producing a porous material is to partially sinter a powder. However, this often provides a low strength material, particularly with the usual oxide materials which have particle sizes in the one micron range, since the interparticle bonds which form between adjacent particles tend to be points of weakness. The structure that is desired is a more cellular configuration, such as is found in bone, coral and other natural skeletal structures. Analogs of these can be fabricated by various techniques, such as preparing the oxides from suitable organic or inorganic precursors, or by direct replication of existing materials, such as bone and coral. In the latter technique, the structure to be replicated is vacuum impregnated with a suitable wax, after which the solid coral or bone is leached out with acid. The resulting porous wax form is then impregnated with a slip of the ceramic and fired, after melting out the wax [White, et al., *Science* 176, 922 (1972)].

Initial attempts at preparing porous Y_2O_3 involve the former of these techniques, that is, sintering of suitable precursors. A citric acid-water solution of $Y(NO_3)_3$ is boiled down and calcined to give a fine grained ($\sim 200 \text{ \AA}$) oxide powder, which is then pressed and sintered. The very fine-grained starting powders undergo local sintering and tend to form a higher-strength porous material than results from partial sintering of larger particles.

In a parallel study, Professor Wagner's group has studied the effect of a dispersed second phase on the ionic transport properties of electrolytes. Liang [*J. Electrochemical Society* 120, 1289 (1973)] reported that a second phase dispersion of alumina particles in lithium iodide increased the room temperature conductivity by two orders of magnitude. It was reported that the alumina was not soluble in the LiI so the increase in ionic conduction could not be explained by classical doping concepts. No mechanism was suggested. It was of great interest to determine if this was a general phenomenon applicable to other systems and, if possible to determine the mechanism--particularly since Liang had made batteries based on Al_2O_3 -LiI which exhibited a shelf life of greater than two years! Accordingly, a study was initiated to disperse fine particles of Al_2O_3 in a well-characterized electrolyte, CuCl. Mole fraction of dispersoid, particle

size and operating temperature were the variables studied. From these studies, it was concluded that the phenomenon is indeed a general one, that is, additions of a finely divided "inert" second phase affect the transport properties of the matrix. It appears that the dispersoid acts in a manner similar to a colloid in liquid systems, the dispersoid acquiring a charge which affects the local defect concentration in the matrix materials. Hence, the effect is dependent on the volume fraction of the dispersoid and on the particle size (surface area of the dispersoid). If, as is believed, the dispersoid does acquire a charge, then the local defect equilibria is shifted to accommodate this charge, and the effect will be greater at lower temperatures where the usual concentrations of defects in the matrix material is low. This is exactly what has been found using CuCl as a model system. At low temperatures, an order of magnitude increase in ionic conductivity can be effected by the appropriate dispersion of alumina particles. The difference between the conductivities of the single phase matrix (CuCl) and the two phase system (CuCl + Al₂O₃) decreases with increasing temperature.

Studies have also been completed on the copper halides in which it was shown that the mobilities of copper interstitials and copper vacancies were exceedingly high--sufficiently large to categorize them as so-called "super-ionic conductors." A paper, "Ionic Conductivity in Pure and Cadmium-doped Cuprous Iodide" has been submitted to the Journal of The Electrochemical Society. During the last six months this research has been redirected to lithium ion conductors. A compound, LiFe₅O₈, was synthesized from ferrous oxalate and lithium carbonate. X-ray diffraction patterns indicated the single phase lithium ferrosphenel, LiFe₅O₈. Pellets of 94 - 96% theoretical density were prepared and assembled between gold foils as electrodes. The ac conductivity was measured between 1 and ~ 10 kHz with no frequency dependence. Above about 10 kHz there was a frequency dependence. Furthermore, the conductivities varied with oxygen pressure over the sample, increasing with increasing oxygen pressure. Most significant are the preliminary results which show that LiFe₅O₈ exhibits a room temperature conductivity of about $5 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at 300°C. In order to obtain an estimate of the ionic fraction of the conductivity, a dc constant

current source was applied to the sample at 100°C. The resistivity increased by two orders of magnitude, indicating an appreciable ionic contribution to the total conductivity.

B. Heterogeneous Catalysis

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Metallic catalysts of Group VIII such as platinum, palladium and nickel are of major importance both scientifically and technologically. A number of the most important catalysts consist of tiny particles of metal supported upon a carrier such as silica or alumina. The use of a support leads to a greater metallic surface area per gram of metal since on the support crystallite sizes can be as small as 15 to 150 Å. Furthermore, the presence of the support permits the catalyst to be used at temperatures up to 500° without rapid sintering and consequent loss of metallic area.

Supported catalysts are essential to the production of products in the petroleum and chemical industries. Moreover, improvements in heterogeneous catalysis offer prospects of substantial reductions in the consumption of fuel. Although much is known about supported catalysts, relatively little is known concerning: 1) the exact nature of the

crystallites, i.e., size, shape and nature of the attachment to the support; 2) the effect of the support upon the detailed catalytic characteristics of the metal; 3) the effect of metallic particle size and shape upon the catalytic characteristics; and 4) the effect of the method of catalyst preparation upon the details of catalytic activity.

Platinum catalysts were chosen for the initial studies, because there is more background information available for them than for other metals, they are less easily poisoned, and the procedure for the measurement of dispersion (percentage of surface atoms of the metal crystallites) appears to be better defined. Silica was chosen as the first support material to be studied, primarily because it is the most inert of the materials commonly used as catalyst supports.

In what follows, the reaction of hydrogen with various catalysts, treated first with oxygen or untreated are described. Then the kinetics for hydrogenation of propylene and of methylcyclopentane are discussed, followed by a discussion of the x-ray studies of Pt/SiO₂ catalysts.

1. The Reaction of Hydrogen and Oxygen with Pt/SiO₂ Catalysts and the Effect of Conditions of Pretreatment upon the Character of these Catalysts in Isotopic Exchange between Cyclopentane and Deuterium

In previous reports, the preparation of a set of platinum on silica gel catalysts was described, and measurements of the dispersion (the fraction of total hydrogen atoms which are on the surface) of these catalysts were presented (see Table I). An investigation of the rates of formation and of the isotopic distribution patterns of the cyclopentanes which result from isotopic exchange between cyclopentane and deuterium was also begun using these catalysts. In these studies, the catalysts were always given the pretreatment, O₂, 300, 0.5; H₂, 300, 1; He, 450, 1, where the first number is the temperature in °C to which the catalysts were heated in the given atmosphere, and the second is the time in hours.

This work had confirmed that hydrogen reacts very rapidly with oxygen adsorbed on Pt. The oxygen was absorbed first by treatment of clean platinum with oxygen for 15 min. at 25°C. Other effects also merit

investigation, e.g., the reactivity with hydrogen of the surface oxide on platinum which results from storage of a reduced catalyst in air for a substantial period of time. Platinum catalysts which have been initially reduced and then exposed to air for long periods are often used as catalysts for hydrogenation reactions without re-exposure to hydrogen above room temperatures. Moreover, conditions of pretreatment other than that given above can also affect the isotopic distribution patterns of exchanged cyclopentane and the rate of the exchange.

In the apparatus for measuring percentage exchange, a continuous flow of ultrahigh purity argon was substituted for the previously used helium, followed by neon. An argon-purged switching valve was inserted which either directs the carrier gas through the catalyst or by-passes the catalyst. Thus, a pulse of hydrogen may be trapped in the catalytic reactor for a desired time period and then released and measured, thereby permitting a direct measurement of the amount of hydrogen reacting with surface oxide for various times and temperatures to be made.

We have established that the oxide formed upon protracted storage is much less reactive than that resulting from exposure to oxygen for only 15 min. at 25°C. Furthermore, this effect is structure sensitive. A few pulses of hydrogen at 25°C removes almost all of the oxygen from 6-SiO₂-PtCl but only about half of that from 40-SiO₂-PtCl and only 16% of that from 81-SiO₂-IonX. The trapping experiments showed that the oxide on the stored catalyst is almost fully removed by exposure to hydrogen for 0.5 - 1 hour at 25°C. These experiments also established that the oxygen content on stored catalysts is greater than that which results from exposure to oxygen for only 15 min. at 25°C. We believe that open surface sites are necessary for the adsorption of hydrogen if reduction of surface oxide is to be rapid and that the open sites still present after only fifteen minutes at 25°C are slowly filled by oxygen atoms upon prolonged storage. We have established that the unreactivity of stored catalysts is not due to adsorbed water or organic contaminants.

2. Deactivation

The catalytic activity declines during runs involving isotropic exchange between deuterium and cyclopentane. The activity and selectivity are fully restored by repeating the standard pretreatment. It appeared likely that this deactivation resulted from deposition on the catalyst of carbon residues which were burned off during exposure to oxygen at 300°C. In this research we have trapped pulses of oxygen on the deactivated catalyst for about 80 min. and then released them for measurement of evolved carbon dioxide. The degree of deactivation is proportional to the amount of carbon dioxide formed. We have also treated the deactivated catalyst with hydrogen at steadily rising temperatures. Between 81° and 100°C, substantial amounts of cyclopentane are evolved. Above 200°C, smaller amounts of methane are formed. Treatment with hydrogen to 450°C gives a catalyst with the same character as that of a fresh catalyst heated to 450°C in hydrogen. The standard pretreatment is heating in oxygen at 300°C for 1/2 hour, then 300°C in hydrogen for 1 hour, followed by heating in helium for 1/2 hour at 450°C and then cooling in helium to the desired experimental temperature.

3. Selectivity

In the previous report, the results of the investigation of the selectivity and rate of exchange between cyclopentane and deuterium on all of the catalysts of Table I were presented. The selectivities varied systematically with dispersion. The catalysts deactivated during use. Further experiments have been performed which establish that one can extrapolate the rates back to zero time and that there is almost no change in selectivity during deactivation.

All of the previous work on rate and selectivity had involved catalysts pretreated by the same regime used in measuring dispersion. We have now investigated a rather large variety of other conditions of pretreatment. Among the more important were flushing with inert gas after H₂300 at 300°C rather than at 450°C, omitting the inert gas flush after H₂300, heating in hydrogen to 450°C after H₂300 and cooling in hydrogen, mere reduction of the stored catalyst at 100°C in hydrogen, standard

Table I
Pt/SiO₂ Catalysts

Preparation	Mesh	Pt%	Dispersion, %	Cryst. Size, nm
Impregnated	70-80	1.10	40	2.3
	120-140	1.17	40	2.3
	70-80	1.97	6	15
	120-140	1.91	7	13
Ion Exchange	70-80	0.49	63.5	1.4
	120-140	0.85	81	1.1
	120-140	0.48	63	1.4
	70-80	1.48	21.5	4.2
	120-140	1.48	27	3.3

treatment plus O₂25, H₂25, the effect of regeneration after deactivation upon selectivity and rate and the effect of regeneration by H₂450 upon selectivity and rate.

Regeneration by O₂300 yields a catalyst of the initial rate and selectivity. Regeneration by N₂450 yields a catalyst of the same rate and selectivity as that resulting from O₂300, H₂450 on a fresh catalyst. The various pretreatment conditions yield catalysts whose rates vary from 33 to 100% of that of the standard pretreatment. The pretreatments also affect the selectivities. For example, reduction of stored catalyst at 100°C or the treatment O₂25, H₂25 yield catalysts which show substantial increases in cyclopentane-d₅ and reductions in cyclopentane d₁₀ vs those of a catalyst given the standard pretreatment.

4. Hydrogenation of Propylene and Methylcyclopentane

During the past year, the activity and selectivity of the series of Pt/SiO₂ catalysts have been determined for hydrogenation of propylene (P) and methylcyclopentane (MCP). These experimental results complement those previously obtained with cyclopropane (CP).

At 0°C and a hydrogen/hydrocarbon ratio of 15/1, turnover numbers for CP and MCP are the same, i.e., $0.15 \pm 0.02 \text{ sec}^{-1}$, and constant for dispersions from 6 to 40%. Turnover numbers increase with dispersions above 40% to $0.21 \pm 0.02 \text{ sec}^{-1}$ for CP and $0.32 \pm 0.03 \text{ sec}^{-1}$ for MCP. At -57°C and a hydrogen/P ratio of 18/1, turnover numbers increase monotonically from $0.04 \pm 0.003 \text{ sec}^{-1}$ to $0.10 \pm 0.005 \text{ sec}^{-1}$ as dispersion varies from 6 to 81% in the propylene hydrogenation.

The activation energies are remarkably invariant and similar in magnitude for all three reactions. For catalysts of 6, 40 and 81% dispersion, a value of $10.0 \pm 0.5 \text{ kcal/mole}$ was measured for CP; for MCP, the value was $9.8 \pm 0.4 \text{ kcal/mole}$, while for propylene, it was $10.3 \pm 0.5 \text{ kcal/mole}$.

For MCP hydrogenation at 0°C, the selectivity ratio, i-butane/n-butane, is nearly constant in the range 17-20 for dispersions greater than 20%; however, this ratio is noticeably smaller, 11-12, for the 6% dispersion catalysts.

Pretreatment conditions have an important effect on measured activity and selectivity levels; such effects differ between CP and MCP on the one hand and P on the other. The basic experimental findings to date are that stable and reproducible levels of catalytic activity for the CP and MCP hydrogenations require pretreatment in hydrogen at temperatures of 300+°C, while the same can be accomplished for P hydrogenation by hydrogen pretreatment at 25°C. The reasons for this are not clear and are currently under investigation.

5. X-Ray Studies of Pt/SiO₂ Catalysts

The Pt/SiO₂ catalysts have also been examined by means of x-ray diffraction. Surface areas measured by small-angle scattering can be compared to those determined by gas adsorption and Fourier analysis of Bragg peaks.

This Fourier analysis for percentage Pt exposed ranging from 7% (131 Å) to 40% (26 Å) revealed that there were strains only when the Pt particles were of the same size as the pores in the silica gel. At small

sizes, there are no strains. By examining the particle sizes in different crystallographic directions and the particle size distributions in these directions, it was found that (except for the smallest fraction exposed) the Pt particles are nearly spherical in shape.

The root mean square amplitudes of vibration have also been determined. These increase dramatically as the size decreases. This marks the first time these amplitudes have been measured in such small particles. These changes in vibration may be involved in the variations in selectivity with fraction exposed. Table II provides a summary of the data which has been obtained on catalysts with dispersions of 40% and below.

Table II

Summary of X-Ray Measurements on Pt/SiO₂ Catalysts

Dispersion % ^a	$\langle D_{\text{eff}} \rangle_{111}$ nm	$\langle D_{\text{eff}} \rangle$ nm	$\langle D_{\text{eff}} \rangle_{220}$ nm	$\langle D_{\text{eff}} \rangle_{311}$ nm	Disp. % Calc.
7	13.1	8.15	10.8	8.1	8
	11.1	7.5			10
21.5	4.85	4.3	4.45	4.45	24
	4.75	4.25	4.5	4.7	25
27	4.3	3.9	4.2	3.05	27.2
	4.0	3.85	8.85	3.9	28.7
40.7	2.95	2.6	2.2	19.5	43.7
	2.5	2.3			46.9

^aBy hydrogen chemisorption

The lattice parameters and the Debye temperatures of the various dispersions were: 7%, 3.9240 Å, 224°K; 21%, 3.9217, 196; 27% 3.9201, 176; 40%, 3.9197, 160. For bulk platinum, the lattice parameter is 3.9239.

In addition the distribution of the diameters of the crystallites in the various crystallographic directions have been measured.

6. Pt/Al₂O₃ Catalysts

A sample of Aerocat alumina was obtained from the American Cyanamid Company and has been crushed to the desired sieve sizes. Small batches of Pt/Al₂O₃ have been prepared and their dispersions determined preparatory to preparing large amounts of Pt/Al₂O₃. Aerocat alumina appears to be the best alumina for our purpose. It is very pure and, in particular, free from sulfate.

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