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APR 76 G A SOMORJAI, E E PETERSEN DA-ARO-D-31-124-73-G152

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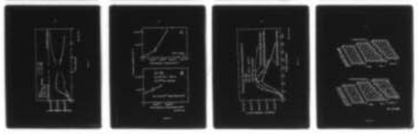

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The dehydrogenation and hydrogenolysis of cyclohexane and cyclohexene, and the dehydrocyclization of n-heptane were studied on platinum single crystal surfaces of varying atomic surface structure. The reactions were studied at low pressures (10^{-6} torr) in a UHV chamber, and at atmospheric pressures in a UHV apparatus equipped with a moveable cup to isolate the crystal catalyst from the vacuum chamber and expose it to high pressure reaction mixtures. (over)

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The surface structure and surface composition of the crystals were determined by low-energy electron diffraction and Auger electron spectroscopy.

At low pressures, atomic steps have been identified as the active sites for C-H and H-H bond breaking processes. The dependence of the dehydrogenation and hydrogenolysis rates on the platinum surface structure revealed kinks in the steps as active sites for C-C bond scission in addition to their ability for breaking C-H and H-H bonds. The catalyst surface was covered with a carbonaceous overlayer, which was ordered or disordered. The properties of this overlayer influence significantly both the rate and the product distribution of the catalytic reactions.

High pressure studies confirmed the C-H bond breaking ability of atomic steps. A flat (111) crystal surface is active for dehydrogenation at these conditions but shows a strong sensitivity to deactivation by competitive adsorption of the product benzene. Atoms at steps are not only more active for bond breaking, but also are less susceptible to deactivation.

The dehydrocyclization rate of n-heptane to toluene showed a maximum at an intermediate atomic step density. A flat terrace of a minimum width is necessary, in addition to steps, for maximum activity.

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EFFECT OF MORPHOLOGY ON CATALYTIC ACTIVITY:
HYDROCARBON REFORMING REACTIONS ON PLATINUM CRYSTAL SURFACES

Final Report

by

G. A. Somorjai and E. E. Petersen

30 April 1976

U. S. ARMY RESEARCH OFFICE

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University of California, Berkeley, California 94720

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INTRODUCTION

In the late 1910's and 1920's, Irying Langmuir, Hugh Taylor, and others integrated the existing experimental data taken with heterogeneous catalysts and realized that catalysis occurs when a strong association of a reactant molecule with surface atoms alters the internal structure of the reactant molecule, allowing a chemical change to occur more easily. Experimental evidence demonstrated that catalytic surfaces have atomic-sized areas that are more active than other areas on the same surface. These active areas, or "active sites", were thought to be particular surface atoms, or groups of atoms, whose relationship with surrounding catalyst atoms allowed them to associate with reactant molecules in a favorable way.

During the last 50 years, one of the objectives of heterogeneous catalysis research has been to identify the surface atoms, the active sites, which catalyze each step in a reaction of interest. In general, the technique used is to vary the surface structure of the catalyst in a systematic way, and to observe the changes in activity and selectivity that may result. Three forms of metal catalysts have been used in these studies: Metal particles dispersed on porous supports, metal films and metal crystals. Crystals are used because their surface morphology can be determined with electron diffraction methods, and various structural features can be introduced in a controlled manner.

In this work, five different faces of platinum single crystals were used to investigate the catalytic activity of three surface features; Flat, close-packed planes of metal atoms, edge atoms present at the termination of a flat plane (~~see Fig. 1~~) and corner atoms present at kinks, or zig-zags, in → over atomic steps. These may be thought of as models of atom groupings which may be present on metal particles in industrial catalysts. Several hydrocarbon-hydrogen reactions, representative of those that occur in commercial petroleum reforming processes, were studied. The catalyst samples were cleaned and characterized using ultra-high vacuum techniques. Reactions were studied at both low (10^{-6} Torr) and atomspheric pressures. Results on the dehydrocyclization of n-heptane and the dehydrogenation of cyclohexane are reported here.

EXPERIMENTAL SYSTEM

A sketch and schematic of one of the two apparatus used is shown in Fig. 2. The main reactor is a 34 liter stainless steel ultra-high vacuum chamber pumped by a 200 ℓ/s ion pump and titanium sublimation pumps. Base pressure of the system is about 5×10^{-10} Torr. The crystal catalyst was supported on nonreactive tantalum electrodes, enabling the catalyst to be resistively heated to over 1 100°C. Crystal temperature was measured with a Pt-Pt/Rh thermocouple spotwelded to the crystal. A quadrupole mass spectrometer and an Auger electron spectrometer are mounted on the chamber.

The crystal surface was cleaned before each experiment by heating it to about 900°C in 10^{-6} Torr O_2, then pumping out the O_2 with the crystal remaining hot. The cleaned crystal was cooled and its surface composition determined with the Auger electron spectrometer. Low pressure (10^{-7}-10^{-4} Torr) reaction products were analyzed using the mass spectrometer.

For high pressure (ca 1 atm) reaction experiments, the crystal was isolated from the main UHV chamber with the reactor cup, as shown in Fig. 2. Reactant gas mixtures were circulated past the catalyst in the 0.76 liter batch reactor flow loop. A gas chromatograph was used to monitor the accumulation of products by taking 1 ml samples with a valve included in the flow loop. Conversions were sufficiently low (< 10%) so the reactant concentrations remained approximately constant, and the reaction rates for the systems studied were slow enough so there were no mass transfer limitations. Reaction rates determined in this apparatus on platinum crystals agree with reported data from supported platinum catalysts to within a factor of two.(1)

One millimeter thick crystal samples were cut from a one-quarter inch diameter platinum single crystal rod. The crystal rod was oriented with a Laue X-ray diffractometer, and the samples were cut with a spark cutter. Both faces of a crystal sample, each of the same orientation, were polished to a mirror finish. The structures of the crystal surfaces were characterized by Low-Energy Electron Diffraction in the second apparatus used, a UHV chamber where the low pressure reaction studies were performed.(2)

REACTION SYSTEMS STUDIED

Crystal faces studied in this work are designated as the (111), (755) and (211) planes in Miller index notation (see Fig. 1). The (111) plane of platinum is a flat, close-packed hexagonal array. The (755) surface has terraces of (111) planes with a monatomic step up to another (111) plane every six atoms (on the average). A more descriptive notation for the surface is Pt(S)-[6(111)×(100)], where (S) denotes a stepped surface. Similarly, the (211) surface can be designated Pt(S)-[3(111)×(100)]. It has narrower terraces and a higher step density (by a factor of two) than the [6(111)×(100)] surface.

Studies of two reactions will be reported here; The dehydrocyclization of n-heptane to toluene, and the dehydrogenation of cyclohexane to benzene. Hydrocarbon pressures were varied between 5 and 80 Torr, hydrogen pressures between 0 and 760 Torr, and crystal temperatures between 220 and 325°C.

DEHYDROCYCLIZATION OF n-HEPTANE

Figure 3 shows the results of four experiments on the three catalyst surfaces. Accumulation of the product toluene is plotted as a function of time. The slope of each curve at a given time is the rate of reaction at that time. Initially, the flat (111) surface formed toluene rapidly, but deactivated rather quickly. Deactivation was less apparent on the stepped surfaces at 300°C, and the rate on the [6(111)×(100)] surface was twice the rate on the [3(111)×(100)] surface.

As the temperature was increased to 325°C on the [6(111)×(100)], both the initial rate and the rate of deactivation increased. This deactivation was due to deposition of a carbonaceous overlayer on the catalyst during the reaction. By stopping the reaction and opening the reactor cup, the amount of carbon could be measured with the Auger Spectrometer. The carbon accumulation and the deactivation increased with decreasing hydrogen pressure, increasing n-heptane pressure and increasing temperature.

These results are similar to those obtained on the (111) and [6(111)×(100)] surfaces at low (10^{-4} Torr) pressures in a study in Professor Somorjai's laboratories.(3) In that study, the rate was found to decrease rapidly on the (111) surface, where a disordered carbonaceous overlayer was observed. In contrast, an ordered carbonaceous overlayer was observed with LEED on the [6(111)×(100)] surface, whose dehydrocyclization rate remained constant for at least one hour and was an order of magnitude greater.

Apparently the (111) surface is active for dehydrocyclization, but is rapidly deactivated by coverage of its flat surface by a disordered carbonaceous overlayer. Step atoms of the [6(111)×(100)] may retain their activity by "sticking out" and not being blocked by the overlayer. The lower activity of the [3(111)×(100)] suggests that the presence of a flat terrace large enough to accomodate a forming toluene molecule next to the step atoms is important. Although the [3(111)×(100)] surface has twice the step density of the [6(111)×(100)], its terraces are one-half the width, too narrow for a toluene molecule lying down to fit easily. Low pressure studies indicate that the structure and ordering of the carbonaceous overlayer is important for this reaction.

DEHYDROGENATION OF CYCLOHEXANE

Carbonaceous overlayer deactivation was also apparent for this reaction, but to a lesser extent. In this reaction, product inhibition due to the accumulation of benzene in the high pressure batch reactor was important. Irreversible deactivation was less than one-third of the reversible benzene inhibition, so data was fit with a first-order product inhibition function.

Table I lists the specific rates and inhibition parameters for the three surfaces at reaction conditions of 15 Torr cyclohexane, 100 Torr hydrogen and 300°C. The (111) surface was active for dehydrogenation, but was very susceptible to product inhibition. At these conditions, the inhibition parameter, K, for the flat surface was about 40 times those of the stepped surfaces, and was very sensitive to hydrogen pressure; $K \propto [H_2]^{-3}$. A negative order dependence was also observed for the dehydrogenation rate on this surface.

The [3(111)×(100)] crystal was approximately twice as active as the [6(111)×(100)]. Inhibition parameters on the stepped surfaces were relatively insensitive to hydrogen, and dehydrogenation rates increased with hydrogen. At 300 Torr hydrogen, the rate on the (111) decreased so that it was less active than the [3(111)×(100)], and the K's were approximately the same. No large differences in the activation energies or the amounts of carbon deposited were noted.

Adsorption of the product benzene will cover platinum atoms and inhibit the rate of dehydrogenation. Benzene adsorption on the (111) surface was very sensitive to hydrogen pressure. The large negative order dependence of K on hydrogen is expected when an adsorbate covering one site (H) blocks the adsorption of a molecule covering a larger number of sites (C_6H_6).

Rapid partial coverage of the (111) terraces of the stepped surfaces by a carbonaceous overlayer may explain the lower activity of these surfaces at 100 Torr hydrogen. Uncovered edge atoms might retain their activity and might not be as sensitive to benzene inhibition as (111) planes. Accordingly, the observed dehydrogenation rate doubled as step density doubled. Increasing the hydrogen pressure increased the rate on the stepped surfaces, possibly by decreasing the carbon coverage.

At low pressures we have found that the dehydrogenation of cyclohexane and cyclohexene to benzene occurs at an appreciable rate only on stepped platinum surfaces. The rate of cyclohexane dehydrogenation to benzene is constant as long as there are steps (tested as low as 7% steps) on the catalyst surface, but is almost an order of magnitude lower on the Pt(111) surface, as seen in Fig. 4. Thus atomic steps seem to be the preferred surface sites for beaking H-H and C-H bonds.

The relative rates of dehydrogenation and hydrogenolysis for cyclohexane can best be monitored by the ratio of benzene to n-hexane in the reaction products. As shown in Fig. 4, the rate of benzene production is independent of step and kink density, while n-hexane production increases slowly with step density and rapidly with kink density. The rate of n-hexane production per kink site is determined by the slope of the line in Fig. 4b, which gives 4 10^{-23} mol s^{-1} per kink atom. This is almost an order of magnitude higher than the slope in Fig 4a, which corresponds to 5 10^{-29} mol s^{-1} per step atom. The observed low hydrogenolysis activity on the stepped surfaces may be caused by thermally generated kinks in the steps. Since the formation of n-hexane and other hydrogenolysis products must be the result of C-C bond scissions, it seems that kinks are very effective in breaking C-C bonds as well as C-H and H-H bonds. Thus we have been able to identify two active sites of lower coordination number on platinum surfaces, steps with C-H and H-H and kinks in steps with C-C, C-H and H-H bond breaking activities.

During the low pressure experiments, the catalyst surfaces were always covered with a carbonaceous overlayer. The coverage was almost independent of pressure ranging from 10^{-7}-10^{2} Torr, but varied markedly with temperature and the molecular weight of the saturated hydrocarbon reactant molecules. The higher the temperature and the reactant molecular weight, the higher the coverage, reaching monolayer amounts for cyclohexane at 725 K or n-heptane at 575 K. Unsaturated hydrocarbons, such as ethylene or benzene, form complete monolayers at all temperatures and pressures, and double layers in certain conditions, with the reactant adsorbed on the overlayer. The overlayer consits of partially dehydrogenated hydrocarbon species formed from the dissociation of the reactants. This carbonaceous overlayer may be ordered or disordered depending on the platinum surface structure, the nature of the reactant and the hydrogen-hydrocarbon ratio used in the experiment. Several reactions are very sensitive to the presence of ordering on the overlayer. Cyclohexene conversion to benzene is poisoned unless the overlayer is ordered, and n-heptane to toluene conversion occurs only in the presence of an ordered overlayer. Other reactions like the hydrogenolysis of cyclohexane occur readily even in the presence of a disordered overlayer.

CONCLUSION

The feasibility of studying industrially important and chemically interesting reactions on UHV prepared single crystal catalysts at reaction pressures of one atmosphere has been demonstrated by this work. Catalytic effects of two structural features of platinum catalysts on several complex hydrocarbon reactions were investigated. The capability to vary systematically the surface morphology of well-characterized catalyst surfaces may lead to the identification of surface structures responsible for high activity and selectivity, and to the development of models for use in the design of improved industrial catalysts.

REFERENCES

*(1) D. R. Kahn, E. E. Petersen and G. A. Somorjai, Journal of Catalysis 34, 294-306 (1974).

*(2) D. W. Blakely and G. A. Somorjai, Journal of Catalysis 42, 181-196 (1976).

(3) R. W. Joyner, B. Lang and G. A. Somorjai, Journal of Catalysis 27, 405 (1972).

(4) A. Clark, The Chemisorptive Bond, p. 26, Academic Press, London (1974).

(5) J. L. Garnett, Catalysis Review 5, 229 (1972).

*References 1 and 2 form the appendix of this report.

Fig. 1

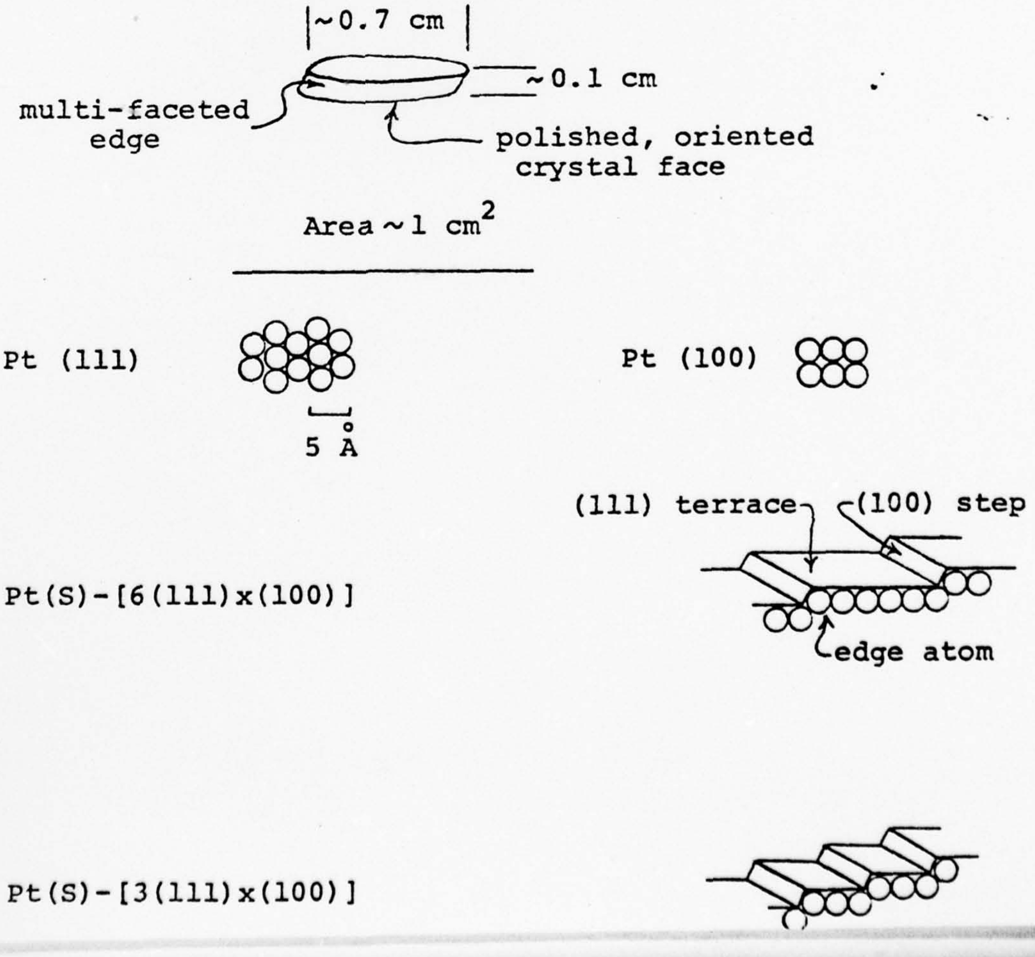
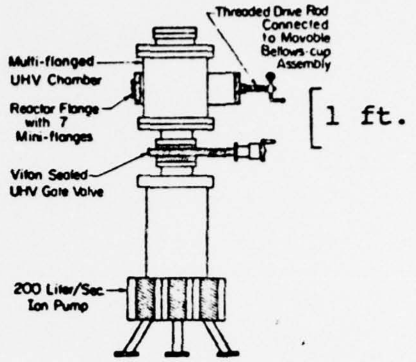
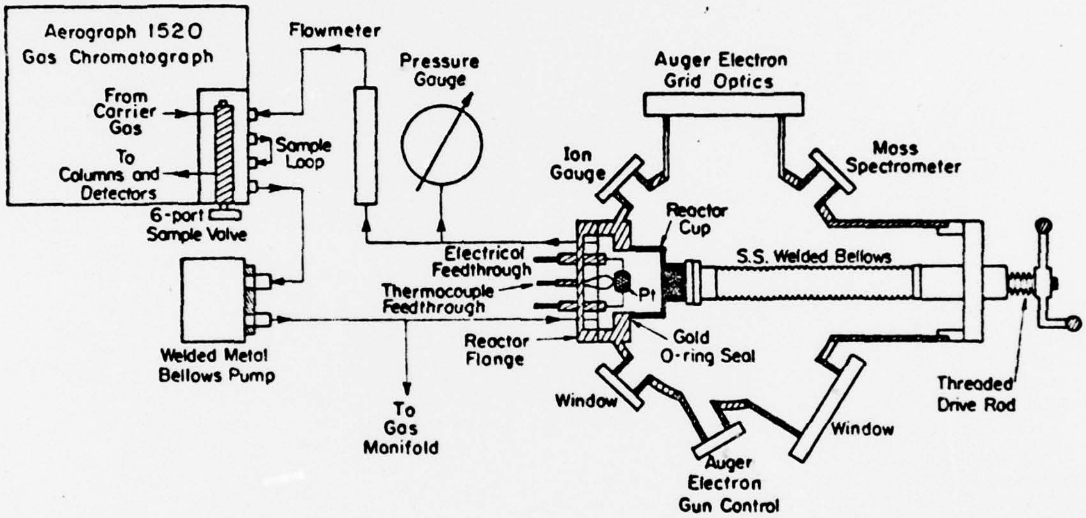


FIGURE 2.





SCHEMATIC OF FLOW LOOP FOR HIGH PRESSURE (1 ATM.) CATALYSIS ON SINGLE CRYSTAL PLATINUM SURFACES

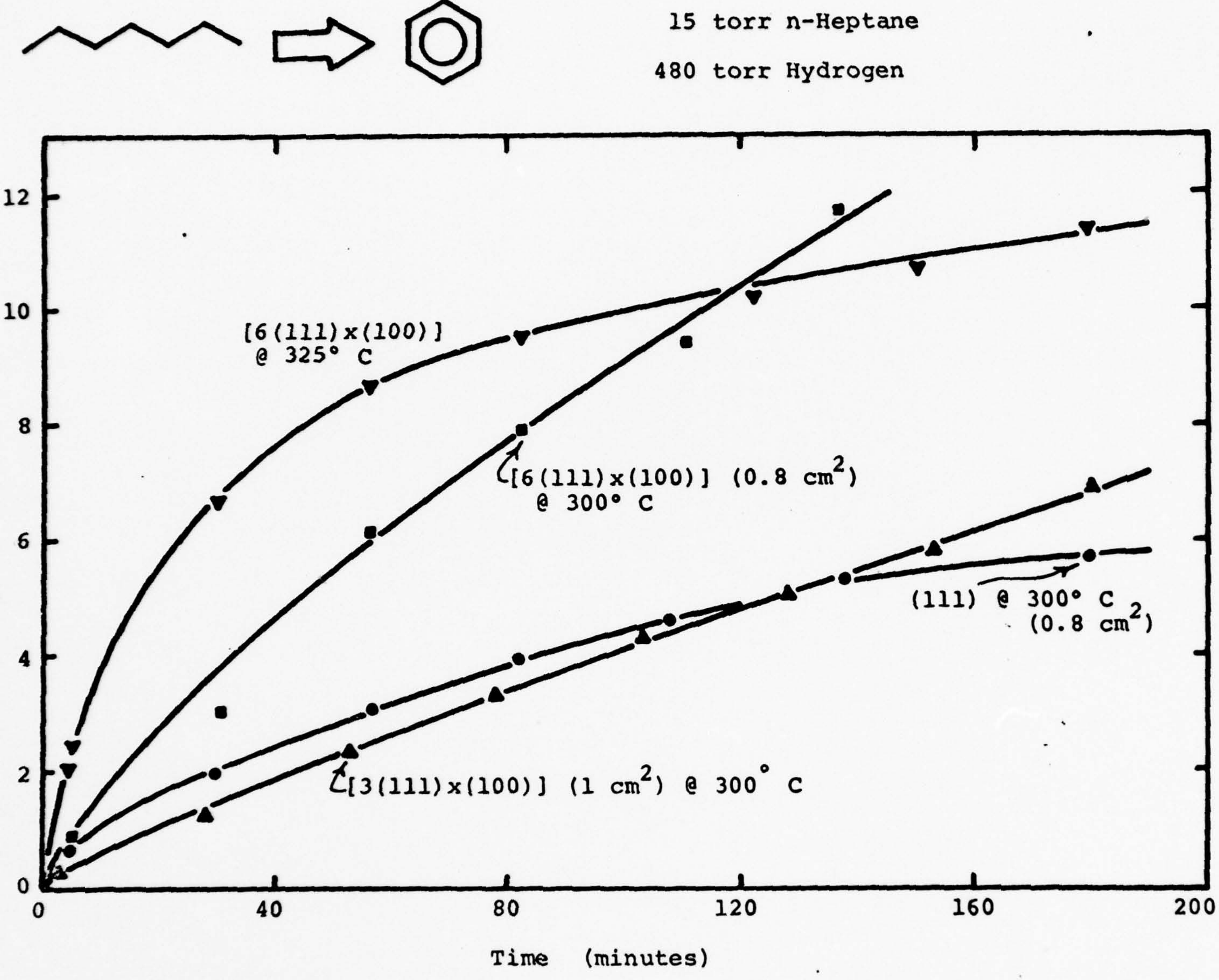
TABLE 1. CYCLOHEXANE → BENZENE

-15 torr Cyclohexane.
-300° C.

$$R = \frac{R_s}{1 + K[\mathrm{Benz}]}$$

100 torr H_2	(111)	[6(111)x(100)]	[3(111)x(100)]
R_s (μmole/min·cm^2)	7.8	0.85-1.1	2.3
K (torr^{-1})	190	4.5 -5.0	4.1
300 torr H_2	**(111)**		**[3(111)x(100)]**
R_s (μmole/min·cm^2)	2.2-2.4		5.9
K (torr^{-1})	3.3-5.2		3.9

FIGURE 3.



15 torr n-Heptane

480 torr Hydrogen

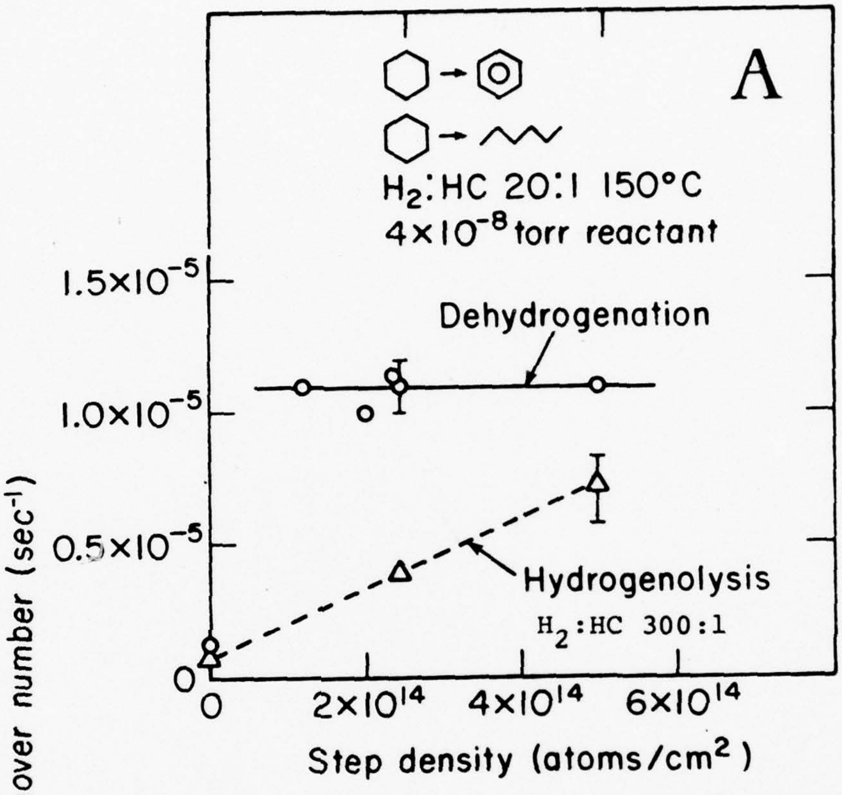

A
H₂:HC 20:1 150°C
4×10⁻⁸ torr reactant
1.5×10⁻⁵
1.0×10⁻⁵
0.5×10⁻⁵
0
Dehydrogenation
Hydrogenolysis
H₂:HC 300:1
0
2×10¹⁴
4×10¹⁴
6×10¹⁴
Step density (atoms/cm²)
Tunrnover number (sec⁻¹)

Fig. 4a

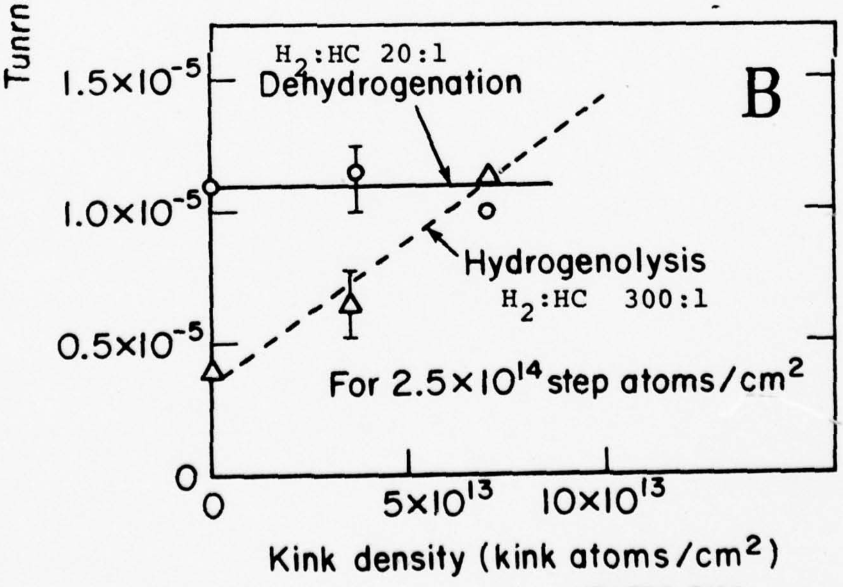

B
H₂:HC 20:1
Dehydrogenation
1.5×10⁻⁵
1.0×10⁻⁵
0.5×10⁻⁵
0
Hydrogenolysis
H₂:HC 300:1
For 2.5×10¹⁴ step atoms/cm²
0
5×10¹³
10×10¹³
Kink density (kink atoms/cm²)
XBL 756-3163

Fig. 4b

JOURNAL OF CATALYSIS 34, 294–306 (1974)

The Hydrogenolysis of Cyclopropane on a Platinum Stepped Single Crystal at Atmospheric Pressure

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Received March 13, 1974

An apparatus was constructed to study catalytic reactions on one or more platinum single crystals *in situ* both at 1 atm total pressure and in high vacuum (10^{-4}–10^{-9} Torr). The main feature of the design is a novel movable bellows-cup mechanism by which the catalyst can be encased in a small volume for the high pressure experiments. Using this apparatus, the cyclopropane hydrogenolysis was investigated at 1 atm on a platinum stepped single crystal (Pt(s)-[6(111) × (100)]) having a total surface area of 0.76 cm^2. Initial specific reaction rates were reproducible to about 10%, and *to within a factor of 2 were identical to published values for this reaction on highly dispersed supported platinum catalysts.*

INTRODUCTION

During the last 7–8 yr a number of new tools have become commercially available for studying the surface of a solid on an atomic scale. One technique is low energy electron diffraction (LEED), whereby one can determine the structure of well-defined clean surfaces, the possible rearrangement of these surfaces in the presence of adsorbed gases, and the structure of adsorbed gases relative to the metal substrate. Another method is Auger electron spectroscopy (AES), from which it is possible to obtain a quantitative estimate of the composition of surface species down to 1% of a monolayer, thereby gaining valuable information about impurities at the surface. It should be noted here that these techniques are usually done in high vacuum (10^{-4}–10^{-11} Torr) due to the nature of the methods and the equipment used in the analyses. LEED and AES are of particular importance to catalytic chemists because of the obvious value that such information has in the interpretation of chemical reactions on catalytic surfaces. The reader is referred to recent reviews (*1–4*) for detailed descriptions of these techniques and their various applications.

The use of LEED and AES has led to an increasing interest in studying well-defined catalyst surfaces, notably oriented single crystals of known initial chemical purity. Lang, Joyner and Somorjai (*5, 6*), Joyner, Lang and Somorjai (*7*) and Baron, Blakely and Somorjai (*8*) have measured surface structure, composition, and some rates of reaction on platinum single crystals at low pressure. Both low Miller index and high Miller index crystal faces of platinum have been examined. The latter have been shown to consist of low index (111) and (100) terraces of constant width, linked by steps of monatomic height, and to exhibit remarkable thermal stability (*5*). One particular reaction which has been studied extensively is the dehydrocyclization of *n*-heptane to form toluene (*7*). This was investigated between 100 and 400°C at pressures in the 10^{-4} Torr range on single crystals having surface areas of less than 1 cm^2. A mass spectrometric technique was used to monitor the formation of product. The ini-

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tial rate of toluene formation on the high index or stepped surface was found to be approximately an order of magnitude greater than initial rates on low index surfaces.

The chemisorption properties of stepped platinum surfaces have been shown to be very different from those of low index platinum surfaces (*6*). Two striking examples which are of particular importance to catalysis are those involving hydrogen and oxygen. Both chemisorb readily at relatively low temperatures on stepped surfaces but do not chemisorb easily on low index faces (*6*). Furthermore, it has been shown that the dissociation of these diatomic molecules takes place at the atomic steps on the high index surfaces.

In a molecular beam study of H_2/D_2 exchange on low and high Miller index platinum single crystal surfaces, Bernasek, Siekhaus and Somorjai (*9*) reported that the exchange reaction took place readily on a high index (997) platinum single crystal surface, whereas no detectable HD could be measured using a low index (111) platinum surface. The difference in reactivity was ascribed to the unique properties of the stepped surface.

A direct correspondence between the above chemisorption and surface reaction studies and those carried out in more conventional catalytic systems is obscured by a number of factors. Of particular significance is the enormously reduced pressure under which LEED, AES, or mass spectrometric experiments are conducted. Typically, catalytic reaction rates are measured at reactant partial pressures on the order of 1 atm; whereas LEED measurements, for example, are made at 10^{-6}–10^{-10} Torr—a pressure some 10^{9}–10^{13} smaller than ordinarily used in catalytic studies. It is possible that at higher pressures larger surface coverages may give rise to "on top" structure that does not form at low partial pressures (*10*). Hence, chemisorption and surface reaction studies carried out at 1 atm may not be directly correlated with UHV studies. It would seem logical therefore to study catalytic reactions at high pressures (1 atm or higher) on well-oriented single crystal surfaces. In this manner the results of ultrahigh vacuum (UHV) and high pressure reaction studies could be compared on the same catalyst and under similar reaction conditions, the only difference being the total system pressure.

Further justification for studies of this type comes from the analysis of more traditional catalytic research performed on highly dispersed supported metal catalysts. During the last 6–7 yr additional emphasis has been placed on characterizing catalysts more fully, as to details of preparation, surface area of metal exposed (dispersion), average metal particle size, and the distribution of particle size, in order to make a rational interpretation of catalytic activity. Several excellent reviews of techniques for characterizing highly dispersed catalysts have appeared in the current literature (*11–13*).

Renewed interest in the geometrical factor in catalysis has prompted studies of the effect of metal crystallite size on specific activity and selectivity in heterogeneous catalysts. A number of investigators have found relationships of this type which has led to classifying reactions into two main groups (*14*). The terms "facile" and "structure-insensitive" have been used to describe types of reactions where specific activity is independent of the mode of preparation of the catalyst or the catalyst metal particle size. Hence each surface site is about as effective catalytically as its neighbor. On the other hand, those reactions in which the specific activity or selectivity is a function of metal particle size or mode of catalyst preparation have been termed "demanding" or "structure-sensitive." Table 1 lists a number of reactions which belong to each particular classification.

One of the interesting aspects of the structure-sensitive studies has been that the effect is only prevalent in the 15–50 Å diam particle size range. The question arises as to the unique properties that metal crystallites of this size range possess. To gain a more fundamental understanding of this phenomenon, a number of models of small crystallites have been developed (*16, 25–27*). In brief, small crystallites have been

TABLE 1

Survey of Structure-Sensitivity Studies

a. Benzene [illegible]drogenation [Dorling [illegible]oss (*15*)] Pt/SiO_2	a. Ethane hydrogenolysis [Sinfelt *et al.* (*19, 20*)] Ni/SiO_2–Al_2O_3, Rh/SiO_2
b. Dehydrogenation of cyclohexane Hydrogenation of cyclopentane H_2/D_2 exchange [Poltorak and Boronin (*16*)] Pt/SiO_2	b. Neopentane hydrogenolysis and isomerization [Boudart *et al.* (*21*)] Pt/Al_2O_3, Pt/SiO_2, Pt
c. Cyclopropane hydrogenolysis [Boudart *et al.* (*17*)] Pt/Al_2O_3, Pt/SiO_2, Pt	c. Hydrogenolysis of methylcyclopentane [Corroleur *et al.* (*22*)] Pt/Al_2O_3, Pt/SiO_2
d. Ethylene hydrogenation [Dorling, Eastlake, and Moss (*18*)] Pt/SiO_2	d. Hydrogenation of 1,2- and 1,3-butadiene [Oliver and Wells (*23*)] Ni/Al_2O_3, Ni/SiO_2, Ni
	e. Hydrogenation of benzene [Coenen, Van Meerten and Rijnten (*24*)] Ni/SiO_2

modeled as imperfect cubo-octahedra (fcc metals). It has been assumed that even in the smallest crystallites, metal atoms occupy crystallographic positions. Furthermore, crystallites are shaped so that their free energy is a minimum. This means maximizing the number of bonds between atoms, including surface atoms, and results in particles of roughly spherical shape. The models have shown that in the 15–50 Å diam particle range, there is a high fraction of surface atoms in edge, step, and corner positions. In particular, for step sites, the fraction of surface atoms in steps is approximately 0.3 for 15 Å diam particles, and decreases an order of magnitude for 50 Å diam particles.

Based on these studies of small metal crystallites it would appear that single crystal surfaces would be ideal models for highly dispersed supported metal catalysts. Single crystals containing low index surfaces as well as those exhibiting ordered atomic steps could be independently studied, thereby making it possible to investigate directly the influence of surface morphology on heterogeneous catalytic activity and selectivity.

In summary, a survey of the current literature has revealed that there is a gap between chemisorption and surface reaction studies performed in UHV on single crystal surfaces and those carried out at 1 atm on highly dispersed supported catalysts. The work embodied in this and succeeding papers arose out of the need to bridge the gap between these two fundamental areas of catalytic research. The overall objective was to measure reaction rates on well-defined single crystal surfaces both at high pressure (1 atm) and in UHV (10^{-4}–10^{-8} Torr) within the same apparatus. The higher pressure measurements would involve the use of gas chromatographic detection while a mass spectrometric technique could be employed in the low pressure measurements. Studying various types of reactions on both low index and high index single crystal surfaces would enable a relationship between surface morphology and catalytic activity to be developed.

The present work describes the apparatus which was constructed to achieve these extensive goals and reports initial rate data for the hydrogenolysis of cyclopropane at 1 atm total pressure on a platinum stepped single crystal. Platinum was selected as the catalyst to be investigated because of its obvious importance in many industrial processes. The hydrogenolysis of cyclopropane was chosen as the first test reaction because of the considerable amount of data and experience which has been amassed in our laboratory for this reaction (*28–32*). The rate is known to be relatively high at room temperature on bulk and supported platinum catalysts. In addition, only one product (propane), is formed on platinum catalysts below 150°C, thereby simplifying chromatographic detection.

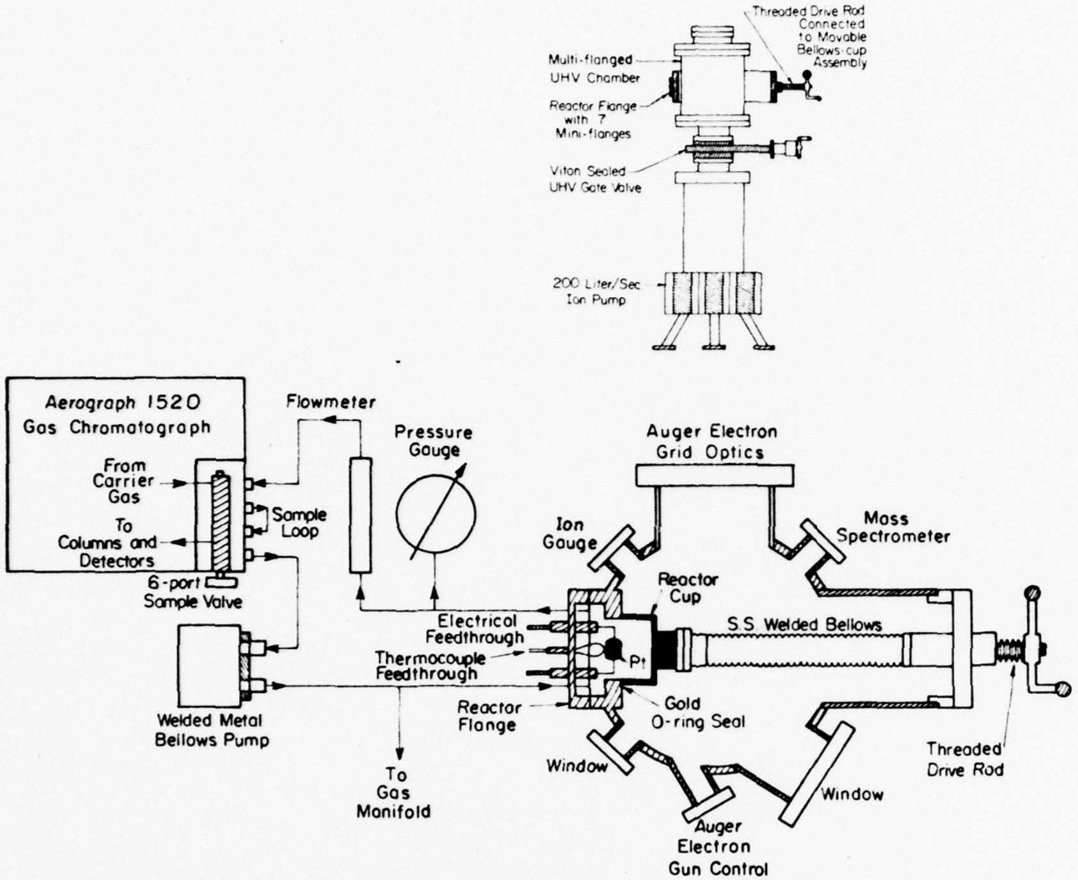

FIG. 1. Schematic of UHV assembly and flow loop for high pressure (1 atm) catalysis on single crystal platinum surfaces.

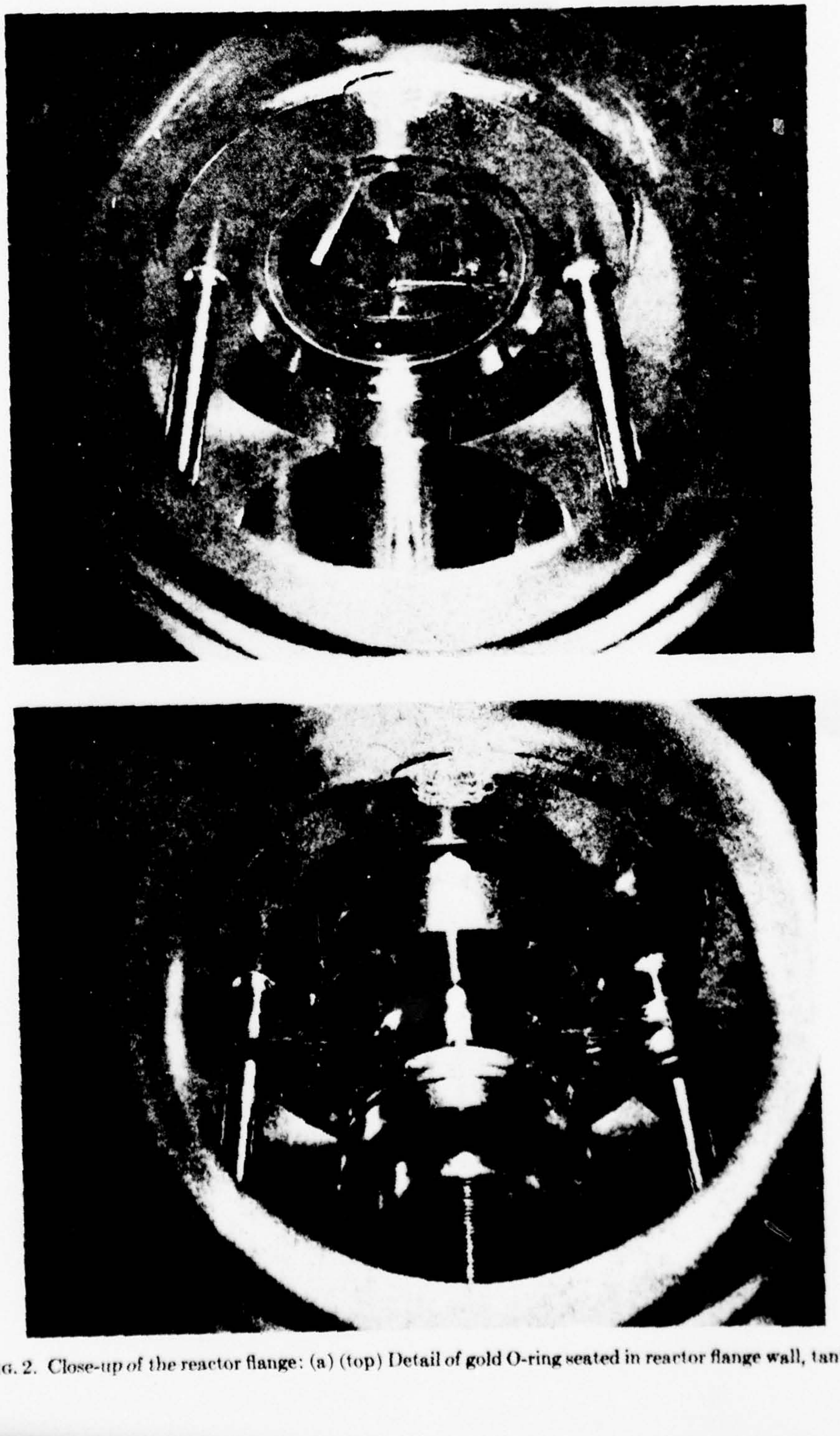

FIG. 2. Close-up of the reactor flange: (a) (top) Detail of gold O-ring seated in reactor flange wall, tantalum

EXPERIMENTAL APPARATUS

The apparatus was constructed to perform catalytic experiments on one or more platinum single crystals both in ultra high vacuum (UHV) and at 1 atm total pressure without physically altering the position of or severing connections made to a catalyst crystal. A schematic of the UHV assembly and the flow loop for the high pressure catalytic measurements is shown in Fig. 1.

The UHV system consists of two 12-in. i.d. multiflanged stainless-steel chambers separated by a Viton-sealed gate valve. The lower UHV chamber contains a 200 liter/sec ion pump and titanium sublimation pump capable of reducing the pressure in the total assembly to 5×10^{-10} Torr. The upper chamber consists of a high pressure reactor within the UHV reactor. The main feature of the design is a movable bellows-cup mechanism by which the stationary catalyst can be encased in a small volume for the high pressure experiments. The reactor cup attached to the bellows drive mechanism is capable of traversing the total internal diameter of the reactor, and is shown in the fully extended position in the schematic. Flanges in the upper chamber are provided for:

a. Monitoring the pressure in the UHV reactor by means of a nude ion gauge;

b. Measuring the UHV gas phase composition by a quadrupole mass spectrometer (Granville-Phillips Spectra Scan 750 Residual Gas Analyzer);

c. Determining the composition of the catalyst crystal surface down to 1% of a monolayer via the technique of Auger electron spectroscopy;

d. Housing the movable stainless steel welded bellows-reactor cup assembly;

e. Supporting and heating the catalyst via suitable electrical feedthroughs and serving as one half of the high pressure reactor volume.

The high pressure reactor volume is isolated from the UHV system by gold O-ring between two knife edges, one on the reactor cup and the other in the reactor flange. As many as 20 cup closures have been obtained using a single gold O-ring. With a pressure of 1000 Torr inside the reactor cup the pressure in the UHV chamber can be maintained at 1×10^{-8} Torr, resulting in a negligible loss of reactants or products from the high pressure reactor during the course of a typical catalytic experiment.

The platinum crystal shown in the schematic is supported by means of two 0.070-in. diam tantalum electrodes, which in turn are connected via electrical feedthroughs to a dc regulated power supply capable of heating the platinum crystal to 1000°C. A Pt/Pt–10%Rh thermocouple is spot-welded to the edge of the platinum crystal, enabling the crystal temperature to be monitored to within ±0.1°C.

A close-up of the reactor flange as seen through the 6-in. viewing port flange is provided in Fig. 2a and 2b. In Fig. 2a the reactor cup has been partially withdrawn to expose the catalyst crystal to the UHV environment. Clearly visible is the 0.0625-in. diam gold O-ring which has been uniformly pressed into a 3.375-in. diam groove in the reactor flange wall. The two case-hardened 0.5-in. diam stainless steel rods welded to the 6-in. reactor flange above and below the reactor cup serve not only to guide the reactor cup in its transverse path, but also to prevent deformation of the upper chamber when applying the necessary force to seal the high pressure reactor. Figure 2b is a view of the reactor cup seated on the gold O-ring, thereby encapsulating the catalyst crystal in a small volume suitable for the high pressure experiments.

The high pressure flow loop (GC loop) is fabricated from 0.25-in. o.d. stainless steel tubing and consists of a 0–1500 Torr Heise gauge measuring absolute pressure to ±0.25 Torr, a 0–5000 sec/min Fischer-Porter flow meter, and an MB-10 stainless steel welded bellows pump (Metal Bellows Corp.) providing a maximum flow rate of

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electrodes, and Pt/Pt–10% Rh thermocouple wires. (b) (bottom) Reactor cup seated on the gold O-ring to form the high pressure reactor.

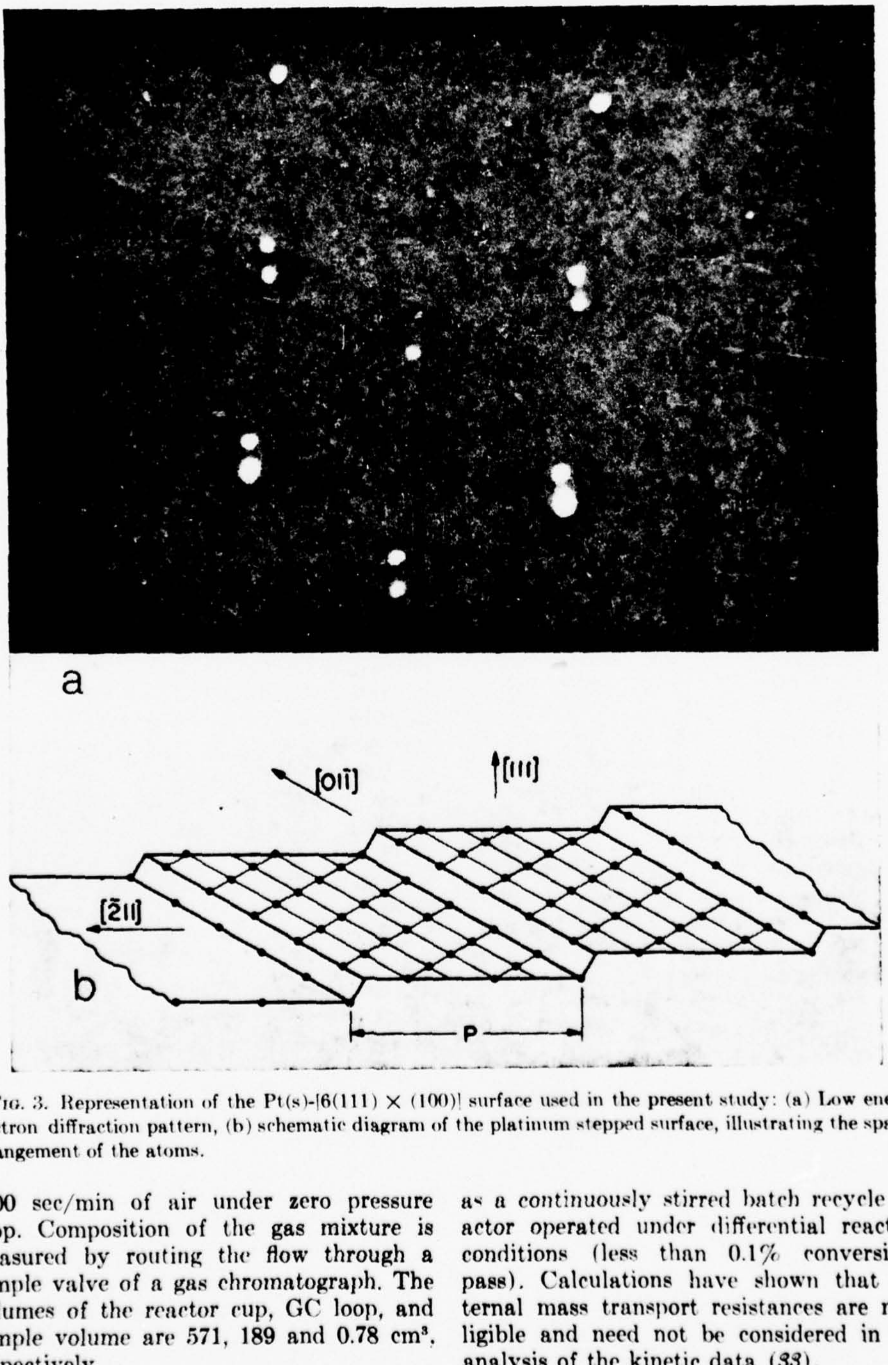

FIG. 3. Representation of the Pt(s)-[6(111) × (100)] surface used in the present study: (a) Low energy electron diffraction pattern, (b) schematic diagram of the platinum stepped surface, illustrating the spatial arrangement of the atoms.

2800 sec/min of air under zero pressure drop. Composition of the gas mixture is measured by routing the flow through a sample valve of a gas chromatograph. The volumes of the reactor cup, GC loop, and sample volume are 571, 189 and 0.78 cm^3, respectively.

The high pressure system can be modeled as a continuously stirred batch recycle reactor operated under differential reaction conditions (less than 0.1% conversion/pass). Calculations have shown that external mass transport resistances are negligible and need not be considered in the analysis of the kinetic data (*33*).

The platinum used in this study was purchased in the form of 0.25-in. diam single crystal rods grown by electron-beam zone refining (99.99% minimum purity) (*34*). Platinum stepped surfaces are generated by cutting the platinum crystal at small angles from low index planes. The resulting high Miller index surfaces have been shown to consist of terraces of constant width linked by steps of monatomic height (*5*, *35*). A low energy electron diffraction pattern and a schematic representation of the stepped surface used in this study are given in Fig. 3a and b. The surface is denoted as Pt(s)-[6(111) × (100)], indicating that the terrace is of (111) orientation, 6 atomic rows in width, while the step is of (100) orientation and one atom in height. To obtain this geometry the surface was first X-ray oriented by a back reflection Laue technique to within ±0.5°, and then spark-machined at 9.5° from the (111) face toward the (100) plane. A LEED analysis was conducted later to confirm the orientation. After cutting, the crystal was mechanically polished by a series of abrasives, the final polish being 0.25 μm Al_2O_3 powder, and finally etched in hot 50% aqua regia for 10 min prior to use. The resulting stepped crystal was 0.5 mm thick and had a total surface area of 0.76 cm^2. The circumferential area represented approximately 13% of the total surface area and was presumed to be polycrystalline in orientation.

The 0.070-in. diam tantalum electrodes used to support the catalyst crystal were triply zone refined (99.999% minimum purity) and etched in an 80% solution of nitric and hydrofluoric acids for 10 min.

The cyclopropane was obtained from Matheson and contained less than 0.4% impurities. Propylene accounted for approximately 70% of this impurity. The gas was passed through a bed of activated $MgClO_4$ to remove traces of water.

Hydrogen was obtained from the Lawrence Berkeley Laboratory and had a minimum purity of 99.99%, the major impurity being oxygen. This was also passed through activated $MgClO_4$ prior to introduction into the gas chromatograph or reactor flow loop.

In what will be termed a "standard run," the platinum single crystal is first pretreated in 1×10^{-6} Torr oxygen at 900–925°C for 2 hr with the reactor cup open. This is sufficient to remove carbonaceous residues from the crystal surface based upon previous LEED–AES measurements (*36*, *37*). The oxygen is then pumped out of the UHV system for additional 1 hr, while maintaining the crystal temperature above 900°C, to remove adsorbed oxygen especially at the platinum step sites. The crystal is then cooled rapidly to 300°C, at which time the reactor cup is closed and hydrogen is admitted to a total pressure of 780 Torr. The platinum crystal is maintained in 1 atm of stagnant hydrogen at 75°C for a period of 2 hr. These conditions are more than sufficient to fully saturate the platinum bulk with hydrogen atoms based upon the solubility and diffusivity data of Ebusuzaki, Kass and O'Keefe (*38*). During the reduction period a cyclopropane–hydrogen mixture is prepared in the GC loop, such that when expanded into the total reactor volume ($V_R + V_{GC} = 760$ cm^3), the initial partial pressures of cyclopropane and hydrogen are 135 and 675 Torr, respectively. Pre-reaction chromatograms of the mixture in the GC loop are taken to determine the initial composition of the reactant mixture. At the conclusion of the reduction period with the bellows circulation pump on, the valves separating the reactor and GC loop volumes are opened, thereby routing the flow directly past the catalyst crystal and commencing the catalytic run.

The reaction gases were monitored periodically by means of a 6-port sample valve housed in a Varian Aerograph 1520 gas chromatograph containing dual thermal conductivity detectors. Hydrogen was chosen as a carrier gas to maximize the sensitivity of the thermal conductivity detector and to avoid the anomalous behavior of He/H_2 mixtures reported by Purcell and Ettre (*39*). The components (propane, propylene, and cyclopropane) were separated at 35°C using a carrier gas flow of 30 ml/min in a 20 ft × ⅛-in. SS column packed with 30% bis-2-methoxy ethyl adipate on 60/80 mesh *A*/*W* Chromosorb P.

The output from the detectors was recorded on a Honeywell Electronik 15 strip chart recorder. The chromatographic peaks were integrated by the triangulation method. Calibration curves for each hydrocarbon component developed in a range of typical operating conditions were used to convert peak areas to hydrocarbon concentrations (*33*).

RESULTS AND DISCUSSION

Initial experiments showed that the apparatus described in the previous section was easily capable of monitoring the rate of formation of propane at 1 atm total pressure on the Pt(s)-[6(111) × (100)] single crystal having a surface area of only 1 cm^2.

Following the standard procedure for a run, blank experiments without the platinum crystal in the reactor were made to determine the activity of the stainless steel walls, the tantalum electrodes, and the platinum thermocouple wires. At 75°C there was no detectable propane formed during the first 55 min of elapsed reaction time. Thereafter a very small propane peak was observed in the gas chromatograms which increased slightly by the end of the 200-min run. However, the propane peak formed never exceeded the size of the diminishing propylene impurity peak. In summary, at 75°C there was no detectable reaction of cyclopropane to propane in the reactor system without the platinum crystal. The propane which was formed could be attributed completely by mass balance to the reaction of the propylene impurity contained in the cyclopropane. Approximately 45% of the initial 0.22 vol % propylene impurity in the cyclopropane reacted to form propane, corresponding to 4.4 × 10^{-6} moles of propane.

The results of two typical experimental runs (10A and 12A) carried out under identical conditions to determine the reproducibility of the data are shown in Fig. 4. The procedure used in these runs was exactly the same as in the blank runs, with the exception that now the Pt(s)-[6(111) × (100)] single crystal had been inserted into the system. The data have been corrected for the propylene impurity which reacted completely to propane in less than 15 min of elapsed reaction time. The only important difference between the two runs was that in Run 10A the initial crystal temperature was 73.6°C, while that in Run 12A was 74.4°C. It should be noted that the data points generally follow a smooth curve, indicating that the experimental techniques employed were good and that the calculation of chromatographic peak areas by the triangulation method was consistent. The curves are remarkably similar in shape. The initial rates for Runs 10A and 12A (1.96 × 10^{-6} and 1.76 × 10^{-6} moles C_3H_8/min·cm^2 Pt, respectively) differ by approximately 10% while the conversion at 200 min of elapsed reaction time is identical in both cases at 1.7%. Considering the possible sources of error in these experiments, the agreement is quite good. These and other data have led us to conclude that the reaction rates reported are probably reproducible to about 10%.

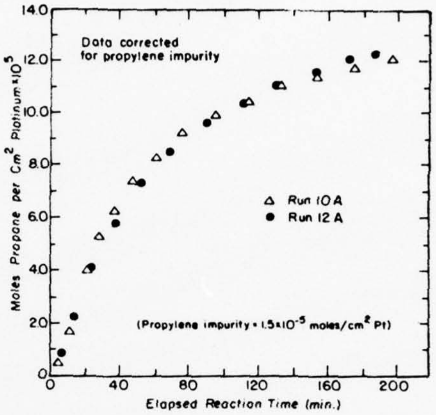

FIG. 4. Cyclopropane hydrogenolysis on the Pt(s)-[6(111) × (100)] single crystal surface (As = 0.76 cm^2). P_{CP}^0 = 135 Torr. $P_{H_2}^0$ = 675 Torr. Average crystal temperature = 74°C.

Additional rate measurements at two higher temperatures (100 and 132°C) provided a basis for calculating a value of the activation energy for the cyclopropane–hydrogen reaction. The initial rate and temperature data for Runs 10A, 12A, 15 and

TABLE 2

SUMMARY OF THE INITIAL RATE DATA FOR THE DETERMINATION OF E^* FOR THE CYCLOPROPANE HYDROGENOLYSIS ON THE Pt(s)-[6(111) × (100)] SINGLE CRYSTAL

Run no.	Initial partial pressure of cyclopropane P_{CP}^0 (Torr)	Crystal temp averaged over initial rate measurement T_c (°C)	$1/T_c$ (°K^{-1} × 10^3)	Initial reaction rate R_0 (moles C_3H_8/min·cm^2 Pt)
10A	135.0	73.5	2.88	1.96×10^{-6}
12A	135.0	74.4	2.88	1.76×10^{-6}
15	135.0	100.2	2.68	5.98×10^{-6}
16	135.0	132.5	2.46	2.55×10^{-5}

16 are summarized in Table 2. An Arrhenius plot of these points was constructed in Fig. 5 and the best straight line was drawn through the data. The activation energy of the cyclopropane hydrogenolysis reaction calculated from this plot was $E^* = 12.2 \pm 1.0$ kcal/mole. Values of the activation energy reported in the literature for this reaction on platinum catalysts range from 8.0 to 12.2 kcal/mole (*28–30, 40–48*).

Having obtained a value of E^*, it was possible to compare the initial specific rates of reaction on the stepped single crystal surface with specific rates reported on polycrystalline supported platinum catalysts. The rates obtained in this study have been corrected to 75°C using the above activation energy and presented in Table 3 in units of moles C_3H_8/(min·cm^2 Pt). The average value given in units of molecules C_3H_8/min·Pt site) was calculated by using a combined site density for the total exposed platinum surface area.

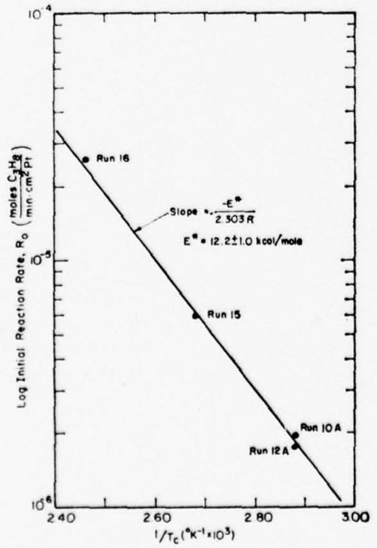

FIG. 5. Activation energy for the hydrogenolysis of cyclopropane based upon initial reaction rates on the Pt(s)-[6(111) × (100)] single crystal (A_s = 0.76 cm^2). P_{CP}^0 = 135 Torr; $P_{H_2}^0$ = 675 Torr.

Hegedus (*30, 49*) carried out a series of cyclopropane hydrogenolysis experiments on single pellets of Pt/Al_2O_3. The physical characteristics of one typical pellet and kinetic reaction rate data obtained on this catalyst are given in Table 4A and B. Using this information and assuming 100% dispersion of the platinum, the rate of the cyclopropane hydrogenolysis at 75°C and 135 Torr CP was calculated and is presented in Table 3. A more realistic value for the platinum dispersion, say 50%, would result in a specific rate (820 molecules C_3H_8/min·Pt site) which is nearly the same as the average of the four rates in Runs 10A, 12A, 15, and 16 (812 molecules C_3H_8/min·Pt site).

Boudart and co-workers (*17*) have studied the cyclopropane–hydrogen reaction on a number of highly dispersed η-Al_2O_3 and γ-Al_2O_3 supported platinum catalysts. A turnover number (molecules converted/min·catalyst site) of $N = 9.8$ was reported for a series of these highly dispersed catalysts at 0°C and 10 Torr initial cyclopropane partial pressure. The specific rates calculated from this data are also given in Table 3, based upon the kinetic parameters reported by Dougharty (*28*) and assuming a platinum site density of 1.12×10^{15} atoms/cm^2. To within a factor of 2, the

TABLE 3

Comparison of Initial Specific Rate Data for the Cyclopropane Hydrogenolysis on Platinum Catalysts

Data source	Type of catalyst	Calcd spec reaction rate @ $P_{CP}^0 = 135$ Torr and $T = 75°C$		Comments
		(moles C_3H_8/min·cm² Pt)	(molecules C_3H_8/min·Pt site)	
Present study	Run 10A	2.1×10^{-6}		Rate on Pt(s)-[6(111) × (100)] single crystal based on $E^* = 12.2$ kcal/mole.
	Run 12A	1.8×10^{-6}		
	Run 15	1.8×10^{-6}		
	Run 16	2.1×10^{-6}		
	Av	1.95×10^{-6}	812[a]	
Hegedus (*30*, *49*) (see Table III-5)	0.04 Wt% Pt on η-Al_2O_3	7.7×10^{-7} based on 100% Pt dispersion	410[b]	
Boudart *et al.* (*17*) and Dougharty (*28*)	0.3% and 2.0% Pt on η-Al_2O_3;	8.9×10^{-7}	480	$\eta_{CP} = 0.2$, $E^* = 8.5$ kcal/mole.
	0.3% and 0.6% Pt on γ-Al_2O_3	2.5×10^{-6}	1340	$\eta_{CP} = 0.6$, $E^* = 8.5$ kcal/mole. (Dougharty reports $E^* = 8$-9 kcal/mole and $n = 0.2$-0.6)

[a] Value based upon 87% (111) orientation and 13% polycrystalline orientation.

[b] Based upon av Pt site density of 1.12×10^{15} atoms/cm². This value would be nearly equal to average of above values if dispersion was approximately 50%.

TABLE 4

A. Physical Characteristics of the Platinum Catalyst Pellet Used by Hegedus (*30*, *49*)

0.25 wt% Pt on η-Al_2O_3 diluted with η-Al_2O_3 to 0.04 wt% Pt
η-Al_2O_3 surface area, 230 m²/g
Wt of pellet, 0.295 g
Pellet density, 1.14 g/cm³

B. Initial Rate Data for the Cyclopropane Hydrogenolysis Using the Catalyst Pellet of Hegedus (*30*, *49*)

Catalyst calcined in 3% O_2 in N_2 @ 400–410°C for 2 hr
Catalyst reduced in H_2 @ 300°C for 10 hr
$C_{H_2}^0 = 41.4 \times 10^{-6}$ (moles/cm³) ($P_{H_2} = 900$ Torr)
$C_{CP}^0 = 3.45 \times 10^{-6}$ (moles/cm³) ($P_{CP}^0 = 75.0$ Torr)
$T_{rxn} = 75°C$
$(ka_0)_i = 2.61$ sec^{-1}
Reaction found to be first order in cyclopropane concentration.

initial rate data of Boudart *et al.* and that of the present study are identical.

The fact that at 1 atm total pressure a platinum stepped single crystal behaves very much like a highly dispersed supported platinum catalyst for the cyclopropane hydrogenolysis is a very significant result. It supports the contention that well-defined single crystal surfaces are excellent models for polycrystalline supported metal catalysts. It also tends to verify Boudart's hypothesis that the cyclopropane hydrogenolysis is an example of a structure-insensitive reaction. However, additional experiments on other stepped and low index platinum single crystals under conditions identical to that reported here are needed for more complete verification of the structure insensitivity of this reaction.

In conclusion, this work has shown that it is possible to measure rates of reaction on a single platinum crystal having a surface area of 1 cm^2 at atmospheric pressure using a thermal conductivity detector of a gas chromatograph. It has begun the task of bridging the gap between traditional heterogeneous catalytic studies and those using new analytical tools to probe the surface of a catalyst on an atomic scale. Using single crystals as models for polycrystalline supported catalysts these studies appear to be well suited to uncover the relationship between the morphology of the catalyst surface and its catalytic activity.

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REFERENCES

1. Somorjai, G. A., and Farrell, H. H., *Advan. Chem. Phys.* **20,** 215 (1971).
2. May, J. W., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 21, p. 151. Academic Press, New York, 1970.
3. Chang, C. C., *Surface Sci.* **25,** 53 (1971).
4. Somorjai, G. A., and Szalkowski, F. J., *in* "Advances in High Temperature Chemistry" (L. Eyring, Ed.), Vol. 4, p. 137. Academic Press, New York, 1972.
5. Lang, B., Joyner, R. W., and Somorjai, G. A., *Surface Sci.* **30,** 440 (1972).
6. Lang, B., Joyner, R. W., and Somorjai, G. A., *Surface Sci.* **30,** 454 (1972).
7. Joyner, R. W., Lang, B., and Somorjai, G. A., *J. Catal.* **27,** 405 (1972).
8. Baron, K., Blakely, D. W., and Somorjai, G. A., *Surface Sci.* **41,** 45 (1974).
9. Bernasek, S. L., Siekhaus, W. J., and Somorjai, G. A., *Phys. Rev. Lett.* **30,** 1202 (1973).
10. Somorjai, G. A., "Principles of Surface Chemistry." Prentice-Hall, Englewood Cliffs, NJ, 1972.
11. Sinfelt, J. H., *Catal. Rev.* **3,** 175 (1969).
12. Cinneide, A. D. O., and Clarke, J. K. A., *Catal. Rev.* **7,** 213 (1972).
13. Whyte, T. E., Jr., *Catal. Rev.* **8,** 117 (1973).
14. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
15. Dorling, T. A., and Moss, R. L., *J. Catal.* **5,** 111 (1966).
16. Poltorak, O. M., and Boronin, V. S., *Russ. J. Phys. Chem.* **40,** 1436 (1966).
17. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6,** 92 (1966).
18. Dorling, T. A., and Eastlake, M. J., and Moss, R. L., *J. Catal.* **14,** 23 (1969).
19. Carter, J. C., Cusumano, J. A., and Sinfelt, J. H., *J. Phys. Chem.* **70,** 2257 (1966).
20. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8,** 348 (1967).
21. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11,** 35 (1968).
22. Corolleur, C., Gault, F. G., Juttard, D., Maire, G., and Muller, J. M., *J. Catal.* **27,** 466 (1972).
23. Oliver, R. G., and Wells, P. B., *Int. Congr. Catal., 5th,* Amsterdam, *1972,* Prepr. 45.
24. Coenen, J. W. E., Van Meerten, R. Z. C., and Rijnten, H. T., *Int. Congr. Catal., 5th,* Amsterdam, *1972,* Prepr. 46.
25. Van Hardeveld, R., and Van Montfoort, A., *Surf. Sci.* **4,** 396 (1966).
26. Poltorak, O. M., Boronin, V. S., and Mitrofanovia, A. N., *Int. Congr. Catal., 4th,* Moscow, *1968,* Prepr. 68.
27. Bond, G. C., *Int. Congr. Catal., 4th,* Moscow, *1968,* Prepr. 67.
28. Dougharty, N. A., PhD thesis, Dep. Chem. Eng., Univ. of California, Berkeley, 1964.
29. Balder, J. R., PhD thesis, Dep. Chem. Eng., Univ. of California, Berkeley, 1967.
30. Hegedus, L. L., PhD thesis, Dep. Chem. Eng., Univ. of California, Berkeley, 1972.
31. Clay, R. D., PhD thesis, Dep. Chem. Eng., Univ. of California, Berkeley, 1967.
32. Hahn, J. L., Master's thesis, Dep. Chem. Eng., Univ. of California, Berkeley, 1968.
33. Kahn, D. R., PhD thesis, Dep. Chem. Eng., Univ. of California, Berkeley, 1973.
34. Materials Research Corp., Orangeburg, NY.
35. Perdereau, J., and Rhead, G. E., *Surface Sci.* **24,** 555 (1971).
36. Joyner, R. W., Gland, J. L., and Somorjai, G. A., *U. S. At. Energy Comm. Rep.* **LBL-414** (1971).
37. Somorjai, G. A., *Catal. Rev.* **7,** 87 (1972).
38. Ebusuzaki, Y., Kass, W. J., and O'Keefe, M., *J. Chem. Phys.* **49,** 3329 (1968).
39. Purcell, J. E., and Ettre, L. S., *J. Gas Chromatogr.* **3,** 69 (1965).
40. Bond, G. C., and Sheridan, J., *Trans. Faraday Soc.* **48,** 713 (1952).

41. Bond, G. C., and Turkevich, J., *Trans. Faraday Soc.* **50,** 1335 (1954).
42. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53,** 368, 377, 383, 388 (1957).
43. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56,** 1501 (1960).
44. Newham, J., *Chem. Rev.* **63,** 123 (1963).
45. McKee, D. W., *J. Phys. Chem.* **67,** 1336 (1963).
46. Sinfelt, J. H., Yates, D. J. C., and Taylor, W. F., *J. Phys. Chem.* **69,** 1877 (1965).
47. Anderson, J. R., and Avery, N. R., *J. Catal.* **8,** 48 (1967).
48. Dalla Betta, R. A., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **19,** 343 (1970).
49. Hegedus, L. L., and Petersen, E. E., *J. Catal.* **28,** 150 (1973).

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The Dehydrogenation and Hydrogenolysis of Cyclohexane and Cyclohexene on Stepped (High Miller Index) Platinum Surfaces

by

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ABSTRACT

The dehydrogenation and hydrogenolysis of cyclohexane and cyclohexene were studied on platinum single crystal surfaces of varying atomic surface structure at low pressures (10^{-6} torr) in the temperature range of 300-723 K. The quantitative reaction rates were monitored by a mass spectrometer, the surface structure and surface composition were determined by low-energy electron diffraction and Auger electron spectroscopy. Atomic steps have been identified as the active sites for C-H and H-H bond breaking processes. The dependence of the dehydrogenation and hydrogenolysis rates on the platinum surface structure revealed kinks in the steps as active sites for C-C bond scission in addition to their ability for breaking C-H and H-H bonds. The active catalyst surface was covered with a carbonaceous overlayer, which was ordered or disordered. The properties of this overlayer influence significantly both, the rate and the product distribution of the catalytic reactions. An expanded classification of structure-sensitive reactions is suggested.

Introduction

One of the important aims of studies of hydrocarbon catalysis is to uncover the sites where C-H, C-C, and H-H bonds are broken followed by suitable rearrangements of the hydrocarbon fragments. Identification of these active centers might permit the architecture of catalyst surfaces with optimum concentrations of surface sites with a variety of bond breaking activities.

The dehydrogenation and hydrogenolysis of cyclohexane and cyclohexene were studied on platinum single crystal surfaces at low pressures (about 10^{-6} torr (1 torr = 133.3 N/m^2)) to find the correlation between the reactivity and the atomic surface structure. We would like to report the discovery and identification of two such surface sites on platinum crystal surfaces that differ in the number of nearest neighbor platinum atoms surrounding them. H-H and C-H bond breaking processes predominate at one of the sites while C-C bond breaking occurs in addition to breaking H-H and C-H bonds at the other. We shall also present evidence that during the catalytic reactions the platinum surface is partially or completely covered with a layer of carbonaceous deposit, ordered or disordered, whose properties play a significant role in determining both the resistance to poisoning and product distribution during the catalytic reactions.

The reactions of cyclohexane and cyclohexene are well suited for identifying active surface sites with various bond breaking activities for several reasons. The dehydrogenation occurs rapidly at relatively low temperatures and at low partial pressures of hydrogen, since it is thermodynamically favored at these conditions. Since dehydrogenation requires only C-H bond breaking activity, the effectiveness of the platinum crystal surfaces to breaking C-H bonds could be investigated in a systematic manner. The appearance of hydrogenolysis products such as n-hexane would signal the presence of sites with C-C bond breaking activity. Since the mass spectra of benzene and n-hexane are readily distinguishable from cyclohexane both the dehydrogenation and hydrogenolysis activity of a given crystal face were readily monitored using a quadrupole mass spectrometer.

The dehydrogenation of cyclohexane, cyclohexene, and cyclohexadiene on the Pt(111) crystal face has recently been studied in this laboratory.[1] The (111) crystal face of platinum is catalytically quite inactive; it apparently lacks the active sites that must be present in large enough concentration for efficient dehydrogenation and hydrogenolysis. Both cyclohexane and cyclohexene were maintained on the surface without much dehydrogenation at 300 K and their ordered surface structures were identified. Cyclohexadiene, however, instaneously dehydrogenated to benzene even on this inactive platinum surface. The rate-limiting steps in dehydrogenating cyclohexane to benzene was the dehydrogenation of the cyclohexene intermediate. The Pt(111) crystal face will not dehydrogenate cyclohexane beyond cyclohexene even at higher temperatures (>425 K).

In this paper it is shown that the reactivity of cyclohexane and cyclohexene is entirely different on platinum surfaces with a high concentration of atomic steps than it is on the (111) crystal face; in this case these molecules dehydrogenate readily. Atomic steps, which were found responsible for breaking H-H bonds in studies of hydrogen-deuterium exchange,[2] were also effective in breaking the C-H bonds. It appears that atomic steps are the active sites on platinum surfaces for performing these important bond scissions. The atomic surface structures where C-C bond scissions occur efficiently, in addition to C-H and H-H bond scissions, have been identified as kinks in steps. The quantitative reaction rates (as turnover numbers) for dehydrogenation and hydrogenolysis were determined and correlated with the various atomic surface structures. Thus, the structure insensitivity of the cyclohexane to cyclohexene dehydrogenation reaction, and the structure-sensitivity of the dehydrogenation of cyclohexene and hydrogenolysis of cyclohexane have been established.

Experimental

The measurements of the dehydrogenation and hydrogenolysis rates of cyclohexane and cyclohexene were carried out at low pressures (10^{-7}-10^{-6} torr total pressure) in the presence of excess hydrogen. The hydrogen to hydrocarbon ratio was varied to investigate the hydrogen pressure dependence of the reaction rate. The temperature range of our studies was 300-725 K. The schematic of the low pressure reaction chamber is shown in Fig. 1. It is equipped with UTI 100C quadrapole mass spectrometer that is placed about 5 cm from the single crystal catalyst surface. The two catalyst samples mounted in the center of the chamber may be independently heated resistively to 1900 K, if desired. The presence of the second carbon-contaminated catalyst sample at ambient temperature does not affect the reaction rate measured for the sample under study. Each single crystal catalyst sample has approximately 1.0 cm^2 of surface area. Hydrogen and the hydrocarbon reactant may be introduced into the reaction chamber independently by the use of two variable leak valves. The gases in the 15 liter reaction chamber are well-mixed since the mean free path (approximately 20 m at 8×10^{-7} torr) of the reactant is much larger than the dimensions of the chamber. The reaction chamber is equipped with low-energy electron diffraction optics for studying the structures of the catalyst surface and adsorbates, with a retarding potential Auger electron spectrometer to monitor the surface composition, and an ion bombardment gun for ion sputter removal of unwanted surface impurities.

The ultra-high vacuum pumping system consisted of a 140 liter per second Vac-Ion pump and a titanium getter pump which could be independently isolated by gate valves. Ultra-high vacuum of 5×10^{-10} torr could readily be achieved after baking the chamber walls to 250°C.

The platinum single crystal catalyst samples used in this study were prepared from three different single crystal rods obtained from different manufacturers, Materials Research Corporation and Research Organic/Inorganic Chemical Corporation. The rods contained different impurities (carbon and calcium; carbon and phosphorus; and carbon, phosphorus and sulfur) which when removed gave a reproducible catalyst surface both by low-energy electron diffraction and the catalytic reaction rates.

The catalyst samples were prepared by orienting with a Laue back-reflection X-ray technique, spark cutting an approximately 1 mm thick slice with the proper crystallographic orientation exposed, polishing both sides and etching. The carbon, phosphorous and sulfur impurities could be removed by oxidation in 5×10^{-8} torr of oxygen at 1075 K. The adsorbed oxygen was removed by heating the samples to 1375 K in vacuum. A high concentration of calcium impurity, which possibly remained in the sample from the reduction of the platinum ore, could only be removed by extensive oxidative heat treatments. The sample was oxidized at 1500 K in 10^{-5} torr of oxygen for 24-48 hours. This treatment fixes the calcium on the surface in the form of a stable oxide which will decompose with calcium vaporization from the surface with brief heating to 1900 K. A small calcium impurity may be removed also by argon ion bombardment and 1100 K anneal cycles. The clean platinum surface structure can be identified by both the low-energy electron diffraction pattern and the Laue X-ray diffraction pattern. Table I lists the orientations of various crystal faces that are used in these studies with the notation that is described, in detail, elsewhere.[3] In brief, (S) indicates a stepped surface, $[6(111)\times(100)]$, for example, identifies a surface with atomic terraces of (111) orientation six atoms wide, on the average, separated by steps of monatomic height of (100) orientation (deduced from the direction of the cut). The orientation of the samples on the unit stereographic triangle is shown in Fig. 2.

The first five samples differ only in the step density and the number of kinks in the steps, all catalysts having (111) orientation terraces and monatomic height steps. The fourth and fifth catalyst samples were obtained by cutting the crystal rod off the [110] zone toward the $[0\bar{1}1]$ zone. The sixth sample was cut to expose (100) orientation terraces. The (100) orientation surface of platinum reconstructs to form a buckled hexagonal layer of platinum atoms atop of the square bulk lattice characterized by a (5×20) low-energy electron diffraction pattern.[4] This surface was not stable in monatomic height step configuration, but faceted to give greater than 50 Å wide steps of (100) and (311) orientation.

The relative structural stabilities of the various high Miller Index surfaces will be discussed further in a subsequent paper.[5]

Figure 3 shows schematic diagrams and the observed diffraction patterns of two catalytically representative stepped catalyst surfaces. In Fig. 3a a catalyst surface with straight steps of monatomic height and a 6 atom wide terrace giving a step atom density of 2.5×10^{14} atoms/cm^2, 18% of the total number of surface atoms, Pt(S)-[6(111)×(100)], is shown. While the catalyst in Fig. 3b has the same terrace width and step density, there are kinks in the steps with a density of 7×10^{13} atoms/cm^2 (or 30% of the total number of step atoms, 5% of the total surface). The step height is obtained from the variation of the intensity maxima of the doublet diffraction beam features with electron energy which has been discussed elsewhere.[6] After catalytic reactions of hydrocarbons, the catalyst surface could be readily regenerated. The carbon deposits were removed by oxygen heat treatment and subsequent removal of oxygen by vacuum reduction. The purity of the catalyst surface was checked by Auger electron spectroscopy before each run.

After the catalyst sample is cleaned, the temperature is lowered to reaction temperature and hydrogen is introduced to the reaction chamber at the desired flow rate, 3×10^{14} molecules/second. The valve to the ion pump is then partially closed to reduce the pumping speed to approximately 2 liters/second and increase the hydrogen pressure to 8×10^{-7} torr. Background mass spectra are taken and the hydrocarbon, cyclohexane or cyclohexene, is introduced through a separate valve to a pressure of 4×10^{-8} torr. The standard conditions for the measurements taken in this study are 4×10^{-8} torr of hydrocarbon reactant, 8×10^{-7} torr of hydrogen and 2 liter/sec pumping speed. Under these flow conditions, a reactant hydrocarbon molecule strikes the catalyst surface, on the average, approximately fives times before it is pumped and conversions are 1-2% for cyclohexane and 1-50% for cyclohexene. With the valve to the ion pump partially closed to give a conductance of approximately 2 liter/sec, there is very little backstreaming of decomposition products from the ion pump.[7] The rates for backstreaming and reaction with the chamber walls have been monitored in blank control reactions and is less than 10% of the rate of production of any reaction product except methane where it is approximately 80%. The mass spectrometer was used to monitor the partial pressures of reactant and product gases and was calibrated using the nude ionization gauge as a standard for all of the hydrocarbons. The temperature of the catalyst was measured with a platinum/platinum-10% rhodium thermocouple spot welded to the top edge of the crystal. After the run was finished the conductance of the valve to the ion pump for hydrogen was measured so the reaction rate could be quantified. The reactions rates were calculated using the measured pumping speed and partial pressures in the equation for a back mixed reactor,[8]

$$R_i = 3.2 \times 10^{16} S P_i \quad , \qquad (1)$$

where R_i is rate of production of product i in molecules/sec, S is the pumping speed in cm^3/sec and P_i is the partial pressure of i-th product in torr. Auger electron spectra were taken only after the reaction mixture was pumped from the chamber. Low-energy electron diffraction observations could be made during a reaction without affecting the reaction rate or observed diffraction pattern. Dehydrogenation reactions were studied, since at the low hydrogen pressures used, equilibrium greatly favors the dehydrogenated products cyclohexene and benzene over cyclohexane.

RESULTS

A. The Dehydrogenation and Hydrogenolysis of Cyclohexane.

In a series of studies, we have determined the variation of the turnover number, the number of product molecules per platinum surface atoms per second, with the hydrogen to hydrocarbon ratio at a constant hydrocarbon pressure of 4×10^{-8} torr. The results are shown in Fig. 4 for the several stepped surfaces studied. The variation is very similar for all catalyst surfaces. The reaction rates increase with increasing hydrogen to hydrocarbon ratio. If no hydrogen is introduced into the reaction chamber the catalyst behaves very differently. No benzene is produced and cyclohexene production is reduced greatly. There is also a higher than normal amount of carbon residue on the surface, approximately one monolayer. Pretreating the catalyst in hydrogen and then removing it prior to hydrocarbon introduction does not increase the activity for dehydrogenation of hydrogenolysis.

We shall present the results of the reaction rate studies for dehydrogenation and hydrogenolysis that were obtained on stepped platinum surfaces first. Then we shall present the same rate data obtained for stepped surfaces which have a large concentration of kinks in the step. In Fig. 5a the turnover number for dehydrogenation to benzene and hydrogenolysis to n-hexane are shown as a function of step density at 423 K. The dehydrogenation rate is independent of step density, while the hydrogenolysis rate increases with increased step density. The hydrogenolysis rate that was measured via the rate of formation of n-hexane, one of the hydrogenolysis products was lower than the rate of dehydrogenation to benzene. The molar hydrogenolysis product distribution, (saturated aliphatic hydrocarbons only), appears to be $C_6:C_3:C_1$ = 1:1:4. Even though n-hexane is a minority hydrogenolysis product, it is a reliable measure of the degree of hydrogenolysis because of its ease of mass spectrometric detection and it is not formed in a background reaction with the walls of the reaction chamber. Besides the saturated hydrogenolysis products and benzene, we find the olefinic products cyclohexene, ethylene, and propylene. Cyclohexene is an intermediate in the dehydrogenation to benzene and its various reactions will be discussed separately in the next section. The olefinic product distribution of ethylene:propylene:cyclohexene:benzene is 10:1:0.5:1.

The turnover numbers for dehydrogenation and hydrogenolysis on kinked surfaces are shown in Fig. 5b. The kink density is defined as the number of kink sites per square centimeter (the total number of atoms on the surface is approximately $1.5 \times 10^{15}/\text{cm}^2$). For example, on the Pt(S)-[7(111)×(310)] surface every third atom along the step should, on the average, be in a kink position. Therefore, for this surface the step density is $2.0 \times 10^{14}/\text{cm}^2$ and the kink density is approximately $7 \times 10^{13}/\text{cm}^2$. By comparing the turnover numbers with those obtained from stepped surfaces that were shown in Fig. 5a, it appears that the rate of hydrogenolysis is markedly higher in the presence of kinks. The dehydrogenation rate is approximately constant and remains unaffected by variation of kink density while the hydrogenolysis rate increases by an order of magnitude from a surface free of steps, Pt(111). The kinks in the stepped surface appear to be very effective in breaking C-C bonds leading to much enhanced hydrogenolysis rates. The hydrogenolysis product distributions do not change appreciably with step or kink density, only the rate increases. The independence of the dehydrogenation rate from the step and kink density shows that this reaction is indeed structure-insensitive. The hydrogenolysis rate increases with kink density just as with increasing step density, thus, hydrogenolysis appears to be structure-sensitive.

There was always an induction period of 10 to 20 min before the benzene product reached its steady state rate of production as detected by the mass spectrometer after the introduction of cyclohexane onto the crystal surface. This is shown in Fig. 6 for several catalyst temperatures. The catalyst was initially at 300 K. When steady state reaction rates were obtained, the catalyst temperature was rapidly increased (in approximately 30 seconds) to 423 K and the reaction rate monitored. This was repeated with heating to 573 K and 723 K. The benzene desorbed during rapid heating of the catalyst surface is approximately 1×10^{13} molecules or less and represents only a small fraction of the carbon on the surface. The steady state reaction rates at a given temperature are the same whether the catalyst was initially at that temperature or another. This induction period coincides with a higher than steady state uptake of cyclohexane. A mass balance calculation on carbon, utilizing the known adsorption and desorption rates of reactants and products during the induction period indicated carbon was deposited on the surface. The amount calculated agreed reasonably well with that determined by the Auger electron spectra taken after the reaction mixture was pumped from the chamber, since the electron beam may induce polymerization of hydrocarbons and further carbon deposition. The formation of the adsorbed carbon layer always precedes the desorption of benzene and olefinic products.

However, the amount of adsorbate changes as a function of temperature. This is shown in Fig. 7. A 4:1 ratio of the carbon 274 eV Auger peak to the platinum 238 eV Auger peak corresponds to a complete monolayer of carbon by calibration with acetylene. The carbon coverage ranges from 0.1 monolayer at 300 K to almost 1.0 monolayer at 723 K. The line has a slope of 2±0.2 kcal/mole. During and after the reaction this carbon deposit was always present on the surface not only at our low pressure reaction conditions, but also after reactions that were carried out in another apparatus at higher pressures[9] (approximately 200 torr total pressure).

The temperature dependence of the dehydrogenation and hydrogenolysis rates for the various crystal faces at a fixed hydrogen to hydrocarbon ratio of 20:1 is shown in Fig. 8. The dehydrogenation rate to benzene decreases with increasing temperature, reaches a minimum of 573 K, then increases slightly at 723 K. The rate of formation of olefinic products have a similar temperature dependence as that of the rate of formation of benzene. The hydrogenolysis rate to saturated products increases with increasing temperature and an Arrhenius plot gives an activation energy of 3±0.3 kcal/mole that is the same for all of the crystal faces within our experimental accuracy.

We have found that the dehydrogenation reaction of cyclohexane to form benzene was sensitive to the ordering of the carbonaceous overlayer as shown in Fig. 9. Initially, the overlayer was ordered on all of the stepped surfaces that were studied and dehydrogenation yielded more benzene than cyclohexene. The low-energy electron diffraction pattern from the carbon deposit formed on stepped surfaces in 20:1 hydrogen to hydrocarbon reaction mixture at 423 K and above has a hexagonal unit cell approximately 5.1 Å on a side. This is about 5% larger than the next nearest neighbor distance of Pt and considerably smaller than the Van der Waal's radius of either benzene (7.3 Å) or cyclohexane (7.6 Å) indicating that the adsorbed layer is at least partially dehydrogenated and the diffraction pattern is certainly not due to the intact reactant or product molecules. Complete dehydrogenation that occurs on heating the adsorbed layer to above 1000 K yields graphitic deposits characterized by ring-like diffraction features of 2.46 Å unit cell size.[10] The platinum diffraction features after a reaction are readily visible and identical to those from the clean surface (except Pt(S)-[7(100)×(111)] where the surface reconstruction disappears).[4] The diffuseness of the extra diffraction features correlates with the terrace width, sharper spots on wider terraces.[11] This and the different diffraction pattern on the Pt(111) surface indicate the formation of the carbon overlayer is intimately associated with the steps. After several hours of reaction time, the carbonaceous overlayer slowly disorders. Simultaneously, the rate of production of cyclohexene increases while the rate of benzene formation decreases until the product becomes predominantly cyclohexene. As shown in Fig. 9 for the Pt(S)-[6(111)×(100)] surface at 423 K, the initial 2:1 benzene to cyclohexene product ratio typical for dehydrogenation on ordered carbonaceous overlayers becomes 1:3 on a disordered overlayer. Thus, for all practical purposes, the dehydrogenation on disordered overlayers produces cyclohexene as further dehydrogenation to benzene is poisoned.

A small amount of oxygen on a stepped surface is an effective poison for dehydrogenation. If the catalyst sample was not vacuum reduced at

1375 K after oxygen cleaning, approximately 0.1 of a monolayer of oxygen (by Auger electron spectroscopy) would be left on the catalyst. This was enough to completely stop the production of benzene and decrease the cyclohexene production by 50% at 423 K on the Pt(S)-[6(111)×(100)]. The low-energy electron diffraction features seen in Fig. 3a, but the background intensity was higher. The 0.1 monolayer coverage would be less than one oxygen atom per step atom if all the oxygen was adsorbed at the steps. (But, since the cyclohexene production is decreased as well as the benzene production, there may be some oxygen on the terraces as well as at the steps.) The oxygen was still present on the surface after 1 hr of reaction at 423 K and standard pressure conditions.

B. The Dehydrogenation and Hydrogenolysis of Cyclohexene.

The turnover number for the dehydrogenation of cyclohexene to benzene is about two orders of magnitude greater than for the dehydrogenation of cyclohexane. In Fig. 10a we plot the dehydrogenation rate as a function of step density. The turnover number increases rapidly with step density indicating that unlike the slower dehydrogenation reaction of cyclohexane, this reaction is structure-sensitive. In Fig. 10b the turnover number is plotted as a function of kink density. Although there is a small increase in the dehydrogenation rate, it may be considered insignificant compared to the marked change of rate with step density.

Unlike the dehydrogenation of cyclohexane, the cyclohexene dehydrogenation reaction poisons rapidly on many catalyst surfaces. Using a hydrogen to cyclohexene mixture of 20:1, the rate of dehydrogenation reaches a maximum, then it decreases rapidly as poisoning occurs, the catalysts losing approximately one-half of their activity in 10-12 mins. Figure 11 shows a representative plot of the turnover number as a function of time. On many catalyst surfaces, particularly on those with (111) orientation terraces, a disordered carbonaceous overlayer forms which poisons further dehydrogenation of cyclohexene. The poisoning is greatly decreased, however, if the carbonaceous overlayer is ordered.

The overlayer is disordered on (111) orientation terraced stepped surfaces while the overlayer orders on surfaces with (100) orientation terraces upon cyclohexene-hydrogen adsorption at 423 K. With an ordered overlayer, the rate of dehydrogenation remains high for hours and there is only slow deactivation of these catalysts. On both types of catalyst surfaces the coverage is approximately 1.0 monolayer of carbon after the induction period.

Discussion

A. Active Sites for C-H, H-H, and C-C Bond Breaking,

Dehydrogenation of cyclohexane and cyclohexene to benzene occurs readily at low pressures (less than 10^{-6} torr) on stepped platinum catalyst surfaces. This is in contrast with the very slow or negligible dehydrogenation rate of these molecules on the Pt(111) catalyst surface.[1] Thus, C-H bond breaking takes place at atomic steps, the same steps that are effective in breaking H-H bonds as revealed by studies in this laboratory of the hydrogen-deuterium exchange reaction at low pressures, using molecular beam scattering techniques.[2] Atomic steps on platinum surfaces appear to be the active sites for C-H and H-H bond scissions.

We have been able to identify another active site by studying the ratio of the dehydrogenation rate to hydrogenolysis rate of cyclohexane to benzene and n-hexane, respectively. While the benzene:n-hexane ratio is 3:1 on a stepped surface (with roughly 17% of the surface atoms in step positions), the ratio decreases rapidly with increasing kink density (Fig. 5b). Using a set of catalyst surfaces that were cut to maintain the same terrace width (step density equal to $2.5 \times 10^{14}/cm^{2}$), but with variable kink density in the steps, we have found that the hydrogenolysis rate increases linearly with kink density while the dehydrogenation rate remains unaffected. On a Pt(S)-[7(111)×(310)] catalyst surface approximately 30% of the atoms in the step are in kink positions, (in addition to the thermally generated kinks). For this surface the benzene to n-hexane ratio has reached unity. Thus, the microstructure of kinks in the steps is effective in breaking C-C bonds in addition to C-H and H-H bonds. The selectivity of these bond breaking processes at different atomic surface sites on platinum is certainly significant in that the atomic surface structure of platinum may be properly tailored to provide selectivity in chemical reactions where C-H and C-C bond breaking processes are to be separated.

B. The Carbonaceous Overlayer.

During dehydrogenation of cyclohexane and cyclohexene, the platinum crystal surfaces are always covered with a carbonaceous deposit of 0.1-1.0 monolayer judged by the carbon to platinum Auger peak intensity ratio. The coverage appears to increase with increasing reaction temperature, but is rather independent of pressure as indicated by recent high pressure studies on the Pt(S)-[6(111)×(100)] catalyst surfaces in this laboratory.[9] The overlayer coverage also depends on the particular surface reaction, higher molecular weight reactants and products (cyclohexene, benzene, n-heptane, toluene) yield greater coverage than low molecular weight reactants and products (cyclopropane, propane, etc.). Low molecular weight hydrocarbons (cyclopropane, ethane) which do not form carbonaeeous overlayers do not readily react on platinum surfaces at low pressures. The build-up of adsorbates during the induction period for cyclohexane and cyclohexene dehydrogenation to benzene indicates the need for the formation of a carbonaceous overlayer to obtain the products. This is not a build-up of the product benzene since it will desorb at a two orders of magnitude higher rate as evidenced by the rate of cyclohexene dehydrogenation.

During the dehydrogenation of cyclohexane the carbonaceous overlayer is ordered initially. After a few hours of reaction at 423 K, however, the overlayer becomes successively more disordered as judged by its low-energy electron diffraction pattern. The amount of carbon in the overlayer, however, remains constant at approximately 0.3 monolayers as determined by Auger electron spectroscopy. Simultaneously the product distribution in the dehydrogenation reaction changes as well. While benzene is the dominant product in the presence of the ordered overlayer, cyclohexene becomes the major product of the dehydrogenation reaction in the presence of the disordered overlayer. This is shown in Fig. 9. Thus, the disordering of the carbonaceous overlayer poisons the formation of benzene, i.e. the dehydrogenation of cyclohexene, and under the reaction conditions the cyclohexene intermediate becomes the final product. It should be noted that the turnover number for the cyclohexene-benzene reaction is two orders of magnitude higher (approximately 10^{-3}/second) than for the cyclohexane-benzene reaction (approximately 10^{-5}/second). Thus, the presence of the disordered overlayers poisons the fast second step, but not the first slow step in the dehydrogenation of cyclohexane to benzene.

The marked effect of the ordering characteristics of the carbonaceous deposit on the reaction rate is also clearly displayed during our studies of the dehydrogenation of cyclohexene. As shown in Fig. 11, there is rapid poisoning of the dehydrogenation rate within minutes as the disordered carbonaceous overlayer forms. However, when the overlayer is ordered (on (100) orientation terraced surfaces), the catalytic activity decreases much more slowly. Again, the poisoning of benzene production is prevented by the formation of an ordered overlayer. Since the platinum catalyst surface is covered with a carbonaceous layer at low as well as at high pressures, we must consider this layer an important part of the surface reaction.

Carbonaceous overlayers can have an important effect in both the catalytic activity and selectivity of a metal surface. Weinberg, Deans, and Merrill[12] postulated that the carbonaceous overlayer is the catalytic site for the hydrogenation of ethylene on the Pt(111) surface and similiarly, by Gardner and Hansen[13] for tungsten stepped surfaces. Yasumori et al.,[14] found preadsorbing acetylene prevents poisoning or restores the activity of a palladium film for the hydrogenation of ethylene. In all three cases, the structure of the carbonaceous overlayer has a marked effect on the catalytic activity in a manner which is not simple site blockage poisoning. Holbrook and Wise[15] found a specific pretreatment of their Pd catalyst which involved oxygen activation and hydrocarbon preadsorption could markedly affect the selectivity of an isomerization reaction. The rate of dehydrocyclization of n-heptane, as well as the selectivity to isomerization and hydrogenolysis, was observed in this laboratory[16] to be dependent on the ordering of the carbonaceous overlayer. These observations, in addition to the data presented in this paper indicate that the formation of the carbonaceous overlayer on the catalyst surface can affect the selectivity as well as activity of a catalytic reaction. The presence of these effects at both atmospheric and low pressure and on a variety of metals indicates the importance of the carbonaceous overlayers and the need for their further characterization. This leads to the conclusion that not all carbon on a catalyst surface is deleterious and only amorphous forms cause site blockage poisoning.

C. The Mechanism of the Dehydrogenation of Cyclohexane and Cyclohexene. Expanded Classification of Reactions According to Their Structure Sensitivity.

In dispersed metal catalysts, the metal is dispersed into small particles, the order of 5-500 Å in diameter, which are generally located in the micropores (20-1000 Å) of a high surface area support. This provides a large metal surface area per gram for high, easily measurable reaction rates, but hides much of the structural surface chemistry of the catalytic reaction. The surface structure of the small particles is unknown; only their mean diameter can be measured and the pore structure could hide reactive intermediates from characterization. Some of the same difficulties also hold for thin films. However, we can accurately characterize and vary the surface structure of our single crystal catalysts and in our reactor reactive intermediates can be readily measured; both are prerequisites for the mechanistic study of the catalysis on the atomic scale.

We have been able to identify two types of structural features of platinum surfaces that influence the catalytic surface reactions: (a) atomic steps and kinks, i.e. sites of low metal coordination number and (b) carbonaceous overlayers, ordered or disordered. The surface reaction may be sensitive to both or just one of these structural features or it may be totally insensitive to the surface structure. The dehydrogenation of cyclohexane to cyclohexene appears to be a structure-insensitive reaction. It takes place even on the Pt(111) crystal face that has a very low density of steps and proceeds even in the presence of a disordered overlayer. The dehydrogenation of cyclohexene to benzene is very structure-sensitive. It requires the presence of atomic steps (does not occur on the Pt(111) crystal face) and the presence of an ordered overlayer (it is poisoned by disorder). Others have found the dehydrogenation of cyclohexane to benzene to be a structure-insensitive[17-21] on dispersed metal catalysts. On our catalyst, surfaces which contain steps, this is also true, but on the Pt(111) catalyst surface, benzene formation is much slower. Dispersed particles of any size will always contain many step-like atoms of low coordination, and therefore, the reaction will display structure-insensitivity. Based on our findings, we may write a mechanism for these reactions by identifying the sequence of reaction steps:

$$\begin{tikzcd}
C_6H_{12}(\text{gas}) \arrow[d] & C_6H_{10}(\text{gas}) \arrow[d, shift left] & C_6H_6(\text{gas}) \\
C_6H_{12}(\text{ads}) \arrow[r, "\text{slow}"] & C_6H_{10}(\text{ads}) \arrow[u, shift left, "\text{ordered or disordered overlayer}"] \arrow[r, "\text{step}", "\text{ordered overlayer}"'] & C_6H_6(\text{ads}) \arrow[u]
\end{tikzcd}$$

The slow step in the dehydrogenation of cyclohexane to benzene is the production of the cyclohexene intermediate at these low pressures on stepped surfaces. Cyclohexene dehydrogenates very rapidly at a step to form benzene; approximately 1 in every 3 collisions of a cyclohexene molecule with an unpoisoned step results in the formation of a benzene molecule. However, on the Pt(111) surface, which is practically free of steps, the rate of dehydrogenation of cyclohexene had become slow enough to be rate-limiting.[1] Sinfelt, Hurwitz, and Shulman[22] concluded the dehydrogenation of methylcyclohexane to toluene, a very similar reaction to cyclohexane dehydrogenation to benzene, was rate limited by the desorption of toluene. Their arguments are equally valid if the slow step was the desorption of methylcyclohexene, followed by its very rapid dehydrogenation to toluene which would be hidden by the pore structure. Maatman, et al.,[19] postulated the slow step, in agreement with our results, as the formation of an intermediate species. Haensel, et al.,[23] have observed the intermediate cyclohexene species at very high (approximately 30,000 LHSV) space velocities. This indicates the intermediate is also found at atmospheric pressure reaction conditions and is very reactive at the step and edge atoms which must exist on the dispersed metal particles.

In addition to dehydrogenation reactions, hydrogenolysis is also taking place on the platinum surfaces. By monitoring the benzene to n-hexane ratio on the various catalysts as a function of surface structure, we have identified steps as primarily responsible for C-H and H-H bond breaking and kinks for C-C bond breaking in addition to C-H and H-H bond scissions. Thus, hydrogenolysis is initiated at kinks in the atomic steps. Since we need specific surface sites for hydrogenolysis to occur this is also a structure-sensitive reaction. However, hydrogenolysis is insensitive to the state of ordering of the carbonaceous overlayer. It proceeds whether the carbonaceous overlayer is ordered or disordered.

It appears that the classification of structure-sensitive reactions[24] should be expanded to separate those reactions that exhibit step (or kink) sensitivity into one group and those that are also sensitive to the structure of the overlayer, into another group. This expanded classification is shown in Table II. In addition to the dehydrogenation and hydrogenolysis reactions described in this paper we have included two other reactions that were studied recently.[16,25] It would be of great value to include in this classification several other hydrocarbon reactions (isomerization, hydrogenation, exchange). More reactions are presently being studied to expand these results on characterized surfaces. Monogue and Katzer[26] have proposed a subdivision of structure-sensitive (demanding) reactions along very similar lines. 'Primary structure-sensitivity' is the effect of changing particle size or step and kink density. Their 'secondary structure-sensitivity' includes effects of self-poisoning and oxygen impurity on reaction rate. The self-poisoning phenomena is, for hydrocarbon reactions on platinum, at least at low pressure, the sensitivity of a reaction to the order in the carbonaceous overlayer. However, caution must be exercised in studies of structure-sensitivity as the reaction mechanism or the surface structure may change markedly with pressure, temperature, and reactant ratio. Most of the surface structure-sensitivity of various catalytic reactions was derived from the particle size dependence of the reaction rate on polydispersed metal catalyst systems. Although there is excellent agreement between the classifications of the various reactions based on studies using supported metal catalysts with variable particle size and our studies using various single crystal surfaces, this may not be the case for all reactions. Perhaps the step density or the kink density is proportional to particle size while the ordering characteristics of the carbonaceous overlayer may or may not be affected by changes of particle size. In addition, studies similar to those reported on platinum must be carried out using crystal surfaces of other transition metals to ascertain that these arguments are more broadly applicable to describe the catalytic chemistry of transition elements. There is evidence that the heat of adsorption of hydrogen on palladium crystal surfaces varies markedly with step density[27] while gold crystal surfaces exhibit chemisorption behavior that is independent of step density.[28]

D. A Descriptive Model of Hydrocarbon Catalysis on Platinum Surfaces.

Studies to correlate the reactivity and the surface structure and composition of platinum surfaces indicate that the active platinum crystal surface must be heterogeneous. The heterogeneity involves the presence of various atomic sites that are distinguishable by their number of nearest neighbors (atoms in terraces, in steps and in kinks), and also variation in surface chemical composition. A model that depicts the active platinum surface is shown schematically in Fig. 12. Part of the surface is covered with a partially dehydrogenated carbonaceous overlayer, ordered or disordered, from which 'islands' of platinum clusters protrude. These are the platinum atoms in steps and at kinks that are active in various C-C, C-H, and H-H bond breaking activity. Perhaps because of the ease of dissociation and higher binding energy of hydrogen at the steps, these sites and their vicinity remain clean and represent areas of high turnover number. The species that form as a result of bond scission at these clusters may rearrange and then diffuse away onto the terrace that is covered with the overlayer, where desorption takes place. Alternately, rearrangement takes place on the ordered carbonaceous overlayer prior to desorption. The heat of desorption should be lower on the portion of the surface that is covered with the overlayer than at an exposed step.

The discovery that kink sites in steps are effective in breaking C-C bonds in addition to C-H and H-H bonds, thereby initiating hydrogenolysis reactions may also explain the effect of trace impurities or second component metals that introduce selectivity. Since these kink sites have fewer nearest neighbors than step or terrace sites, they are likely to bind impurities or other metal atoms with stronger chemical bonds. Thus, these sites are readily blocked by impurities. As a result selective "poisoning" of hydrogenolysis may be obtained by minute concentrations of well-chosen impurities or another metal component.

Acknowledgment

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References

1. J. L. Gland, K. Baron, and G. A. Somorjai, J. Cat. 36, 305 (1975).
2. S. L. Bernasek and G. A. Somorjai, J. Chem. Phys. 62, 3149 (1975).
3. B. Lang, R. W. Joyner, and G. A. Somorjai, Surf. Sci. 30, 440 (1972).
4. A. E. Morgan and G. A. Somorjai, Surf. Sci. 12, 405 (1968).
5. D. W. Blakely and G. A. Somorjai, to be published.
6. M. Henzler, Surf. Sci. 19, 159 (1970); 22, 12 (1970).
7. F. Williams and M. Boudart, J. Vac. Sci. Tech. 9, 362 (1972).
8. O. Levenspiel, Chemical Reaction Engineering, J. Wiley, New York, N. Y. (1962).
9. R. Herz, private communication.
10. J. W. May, Sur. Sci. 17, 267 (1969).
11. R. L. Park and J. E. Houston, Surf. Sci. 18, 213 (1969); R. L. Park, J. E. Houston, and D. G. Schreiner, Rev. Sci. Inst. 42, 60 (1971).
12. W. H. Weinberg, H. A. Deans, and R. P. Merrill, Surf. Sci. 41, 312 (1974).
13. N. C. Gardner and R. S. Hansen, J. Phys. Chem. 74, 3298 (1970).
14. I. Yasumori, H. Shinohara, and Y. Inoue, in "Catalysis," Ed. J. Hightower, North Holland Publishers, Amsterdam (1972).
15. C. M. Holbrook and H. Wise, to be published.
16. B. Lang, R. W. Joyner, and G. A. Somorjai, J. Cat. 27, 405 (1972); L.B.L. Report 2796, unpublished; D. W. Blakely, Ph.D. Thesis, University of California-Berkeley, 1975.
17. O. M. Poltorak and V. S. Boronin, Zh. Fiz. Khim. 40, 2671 (1966).
18. A. N. Mitrofanova, V. S. Boronin and O. M. Poltorak, Zh. Fiz. Khim. 46, 32 (1972).

Ref., contd.

19. R. W. Maatman, P. Mahaffy, P. Hoekstra, and C. Addink, J. Cat. 23, 105 (1971).

20. J. A. Cusamano, G. W. Dembinski, and J. H. Sinfelt, J. Cat. 5, 471 (1966).

21. M. Kraft and H. Spindler, in "Proceedings of Fourth International Congress on Catalysis," Vol. 2, p. 286, Akademiai Kiado, Budapest, 1971.

22. J. H. Sinfelt, H. Hurwitz, and R. A. Shulman, J. Phys. Chem. 64, 1559 (1960).

23. V. Haensel, G. R. Donaldson, and F. J. Riedl, in "Proc. Int. Congr. Catal., 3rd, 1964," Vol. 1, p. 294 (1965).

24. M. Boudart, A. Aldag, J. E. Benson, N. A. Dougarty, and C. Girvin Harkins, J. Cat. 6, 92 (1966).

25. D. Kahn, E. E. Petersen, and G. A. Somorjai, J. Cat. 34, 294 (1974).

26. W. H. Manogue and J. R. Katzer, J. Cat. 32, 166 (1974).

27. H. Conrad, G. Ertl, and E. E. Latta, Surf. Sci. 40, 435 (1974).

28. M. Chesters and G. A. Somorjai, Surf. Sci., to be published 1975.

Table I

Angle of Cut, Miller Indices and Designation of Stepped Platinum Surfaces

Angle of Cut	Miller Index	Designation
0° from $(\bar{1}11)$	$(\bar{1}11)$	Pt-(111)
9.5° from $(\bar{1}11)$	$(\bar{5}57)$	Pt(S)-[6(111)×(100)]
19.5° from $(\bar{1}11)$	$(\bar{1}12)$	Pt(S)-[3(111)×(100)]
9.5° from $(\bar{1}11)$ rotated 7°	$(\bar{1}\bar{1}, 12, 16)$	Pt(S)-[6(111)×(710)]
9.5° from $(\bar{1}11)$ rotated 20°	$(\bar{6}79)$	Pt(S)-[7(111)×(310)]
6.2° from (001)	$(\bar{1}, 1, 13)$	nominally, Pt(S)-[7(100)×(111)] facets to (100) and (311) planes.

Table II

Classification of reactions by step density and carbonaceous overlayer dependence.

Step Structure-Sensitive		Step Structure-Insensitive	
Overlayer structure sensitive	Overlayer structure insensitive	Overlayer structure sensitive	Overlayer structure insensitive
cyclohexene → benzene	cyclohexane → n-hexane		cyclohexane → cyclohexene
n-heptane → toluene			cyclopropane → propane

Figure Captions

Fig. 1. Schematic diagram of reaction chamber used for low pressure catalytic reaction studies.

Fig. 2. Crystallographic orientation and Miller Index of the platinum single crystal catalyst surfaces studied.

Fig. 3. Low-Energy electron diffraction patterns and schematic representation of:

(a) Pt(S)-[6(111)×(100)] which has a step density of 2.5×10^{14} step atoms/cm^2 and

(b) Pt(S)-[7(111)×(310)], step density of 2.3×10^{14} atoms/cm and kink density of 7×10^{13} atoms/cm^2.

Fig. 4. Initial steady state rate of production of benzene (——) and cyclohexene (---) from cyclohexane. The reaction conditions are 4×10^{-8} torr of cyclohexane and 423 K catalyst temperature (Δ - Pt(S)-[7(100)×(111)]; □ - Pt(S)-[3(111)×(100)]; 0 - Pt(S)-[6(111)×(100)]; ◐ - Pt(S)-[6(111)×(710)]; ● - Pt(S)-[7(111)×(310)].

Fig. 5. Cyclohexane dehydrogenation to benzene (-0-) and hydrogenolysis to n-hexane (-Δ-) as a function of (a) step density and (b) kink density.

Fig. 6. Induction period for production of benzene (——) and cyclohexene (---) from cyclohexane. Hydrogen:cyclohexane ratio 20:1; cyclohexane pressure 4×10^{-8} torr.

Fig. 7. The amount of carbon on the catalyst surface at steady state reaction under standard conditions. An Auger peak height ratio of 4.0 corresponds to approximately 1.0 monolayers of carbon. Line through points has a 2 kcal/mole slope.

<u>Caps.</u>, contd.

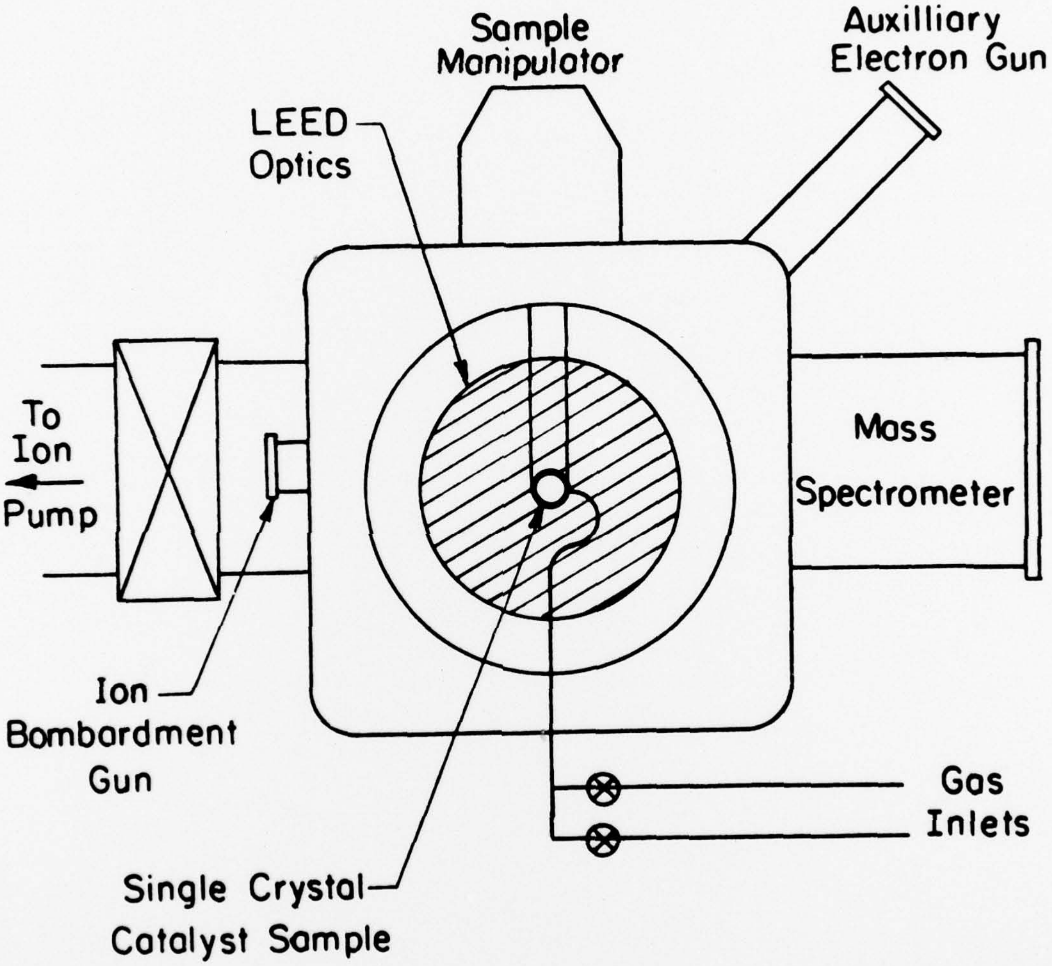
Fig. 8. Temperature dependence of dehydrogenation of cyclohexane to benzene (-0-) and hydrogenolysis (-Δ-). The overall activation energy for hydrogenolysis is 3±0.5 kcal/mole. Standard reaction conditions, data for Pt(S)-[6(111)×(100)].

Fig. 9. Inhibition of benzene (-0-) from cyclohexane and increase in cyclohexene formation (-□-) with time on Pt(S)-[6(111)×(100)] surface. All catalysts with (111) orientation terraces behave similarly.

Fig. 10. Cyclohexene dehydrogenation to benzene as a function of: (a) step density and (b) kink density. Standard reaction conditions.

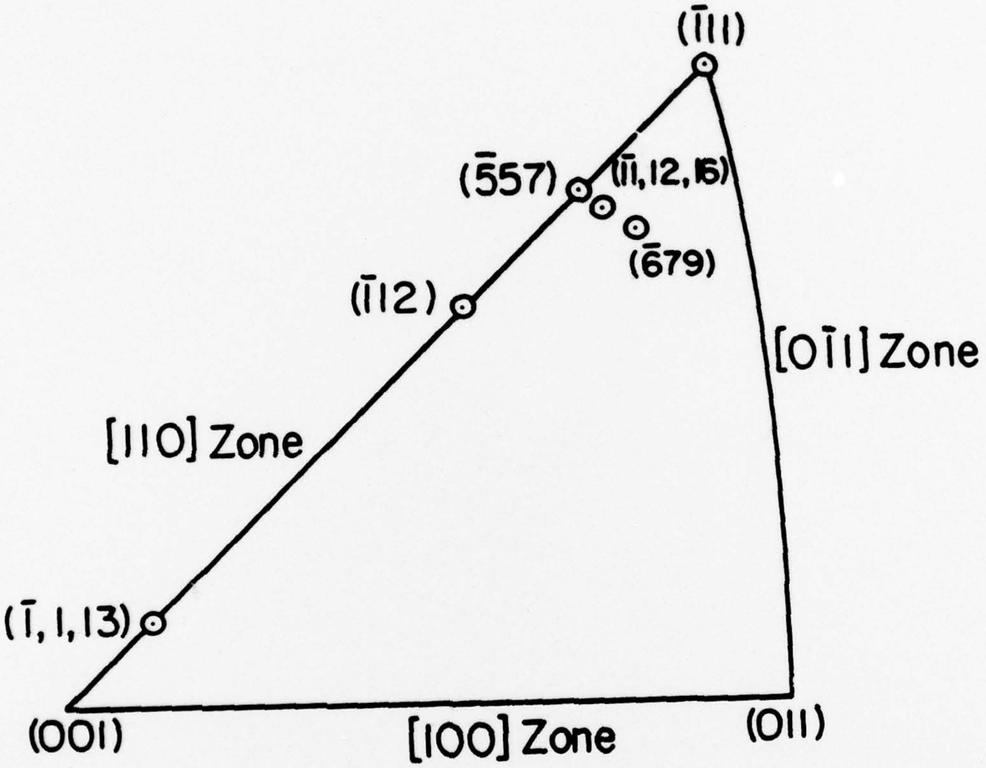
Fig. 11. Inhibition of benzene formation from cyclohexene on disordered carbonaceous overlayers (——), Pt(S)-[6(111)×(100)] and Pt(S)-[13(111)×(310)]; and lack of inhibition on ordered carbonaceous overlayer (---), Pt(S)-[7(100)×(111)].

Fig. 12. Schematic representation of a platinum catalyst with a monolayer of carbonaceous overlayer showing the exposed platinum clusters.



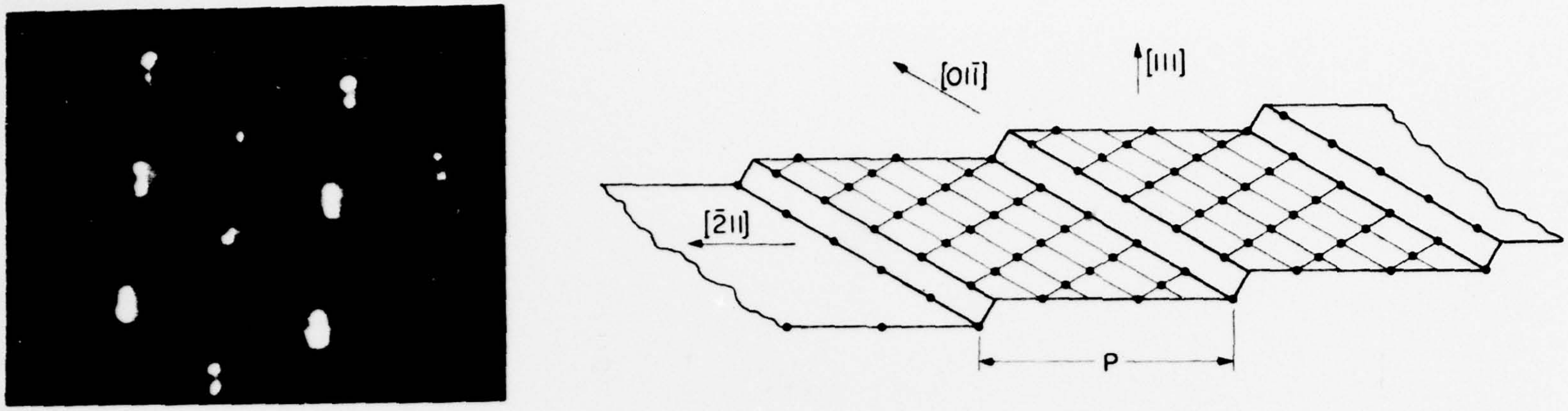
XBL 757-6714

Figure 1

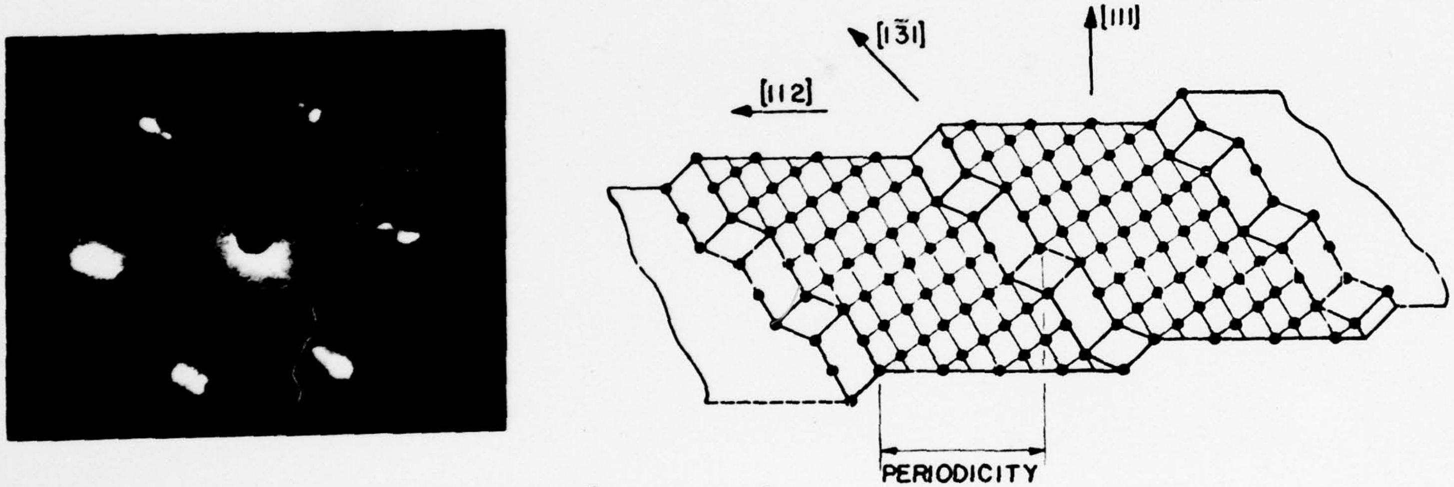


XBL 757-6713

Figure 2



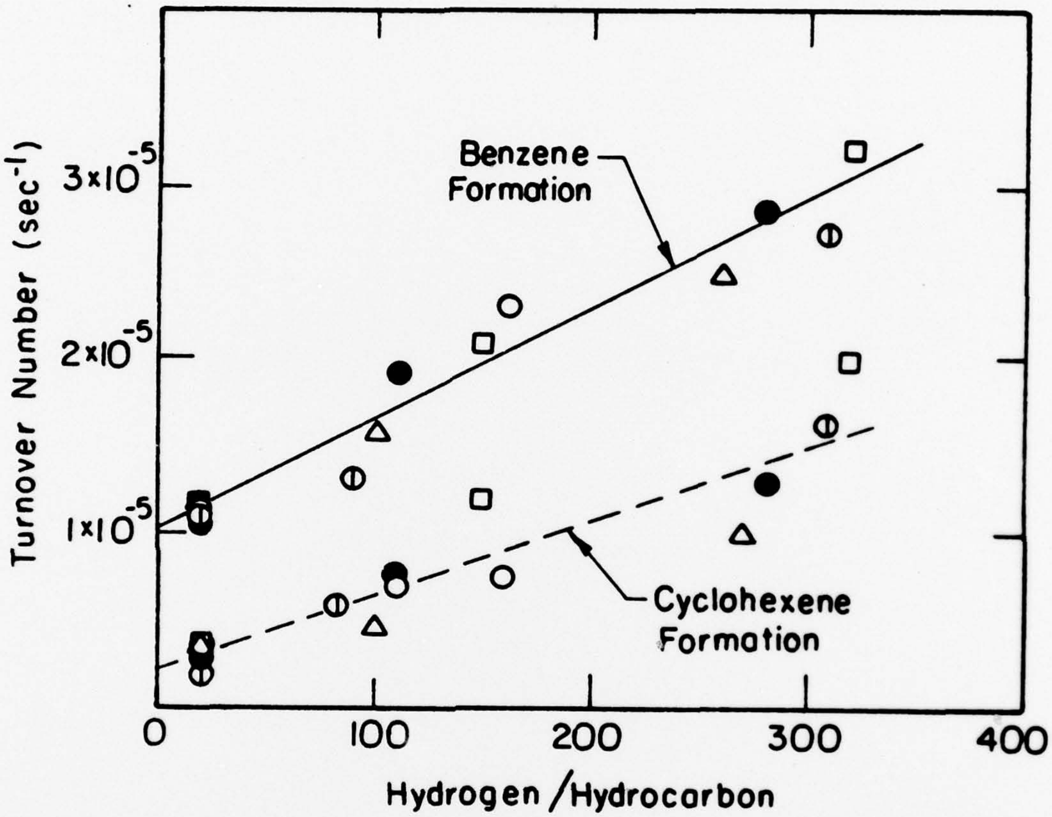
A. Pt(S)-[6(111)x(100)]



B. Pt(S)-[7(111)x(310)]

XBB 756-5011

Figure 3



XBL 758-6870

Figure 4

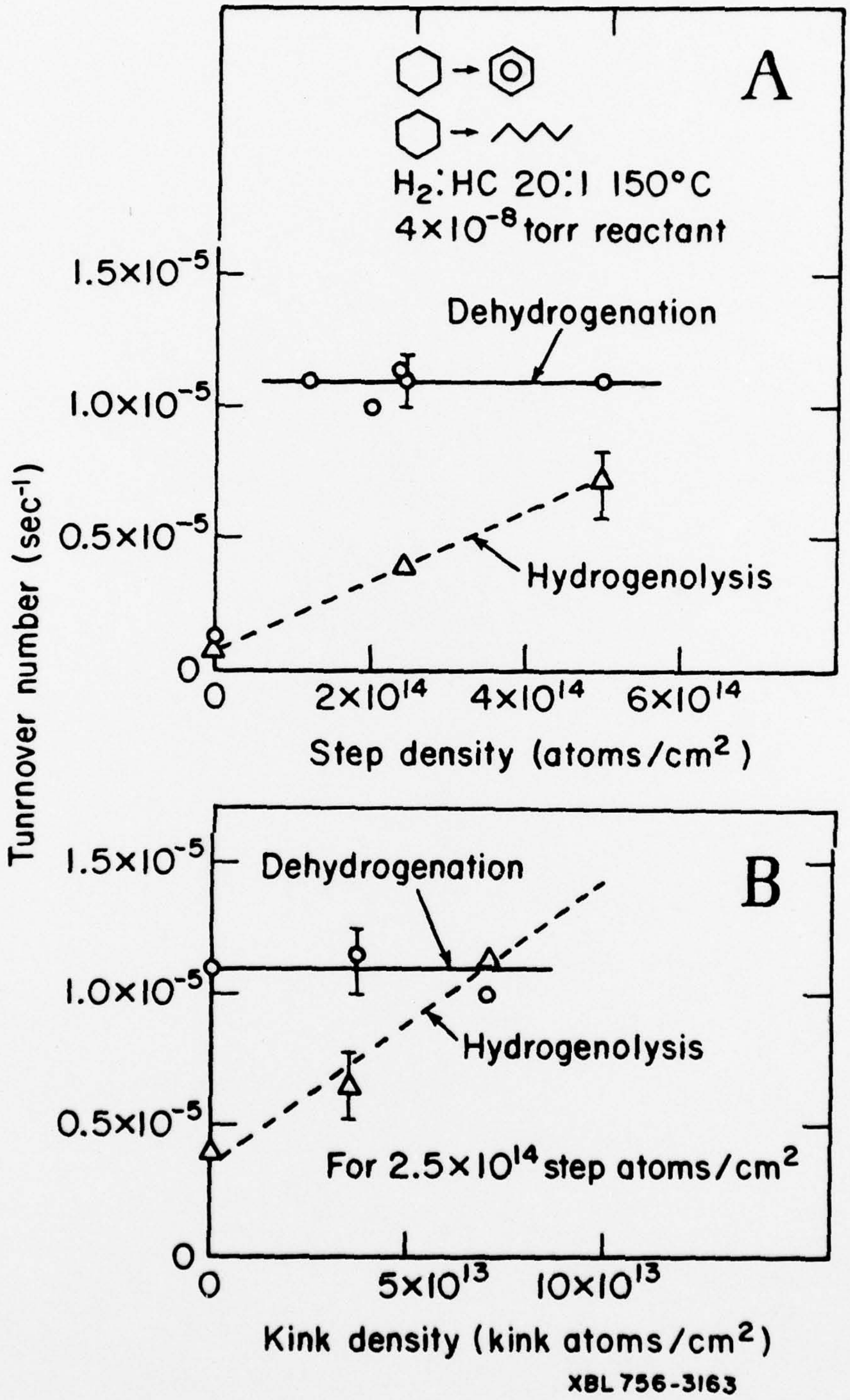
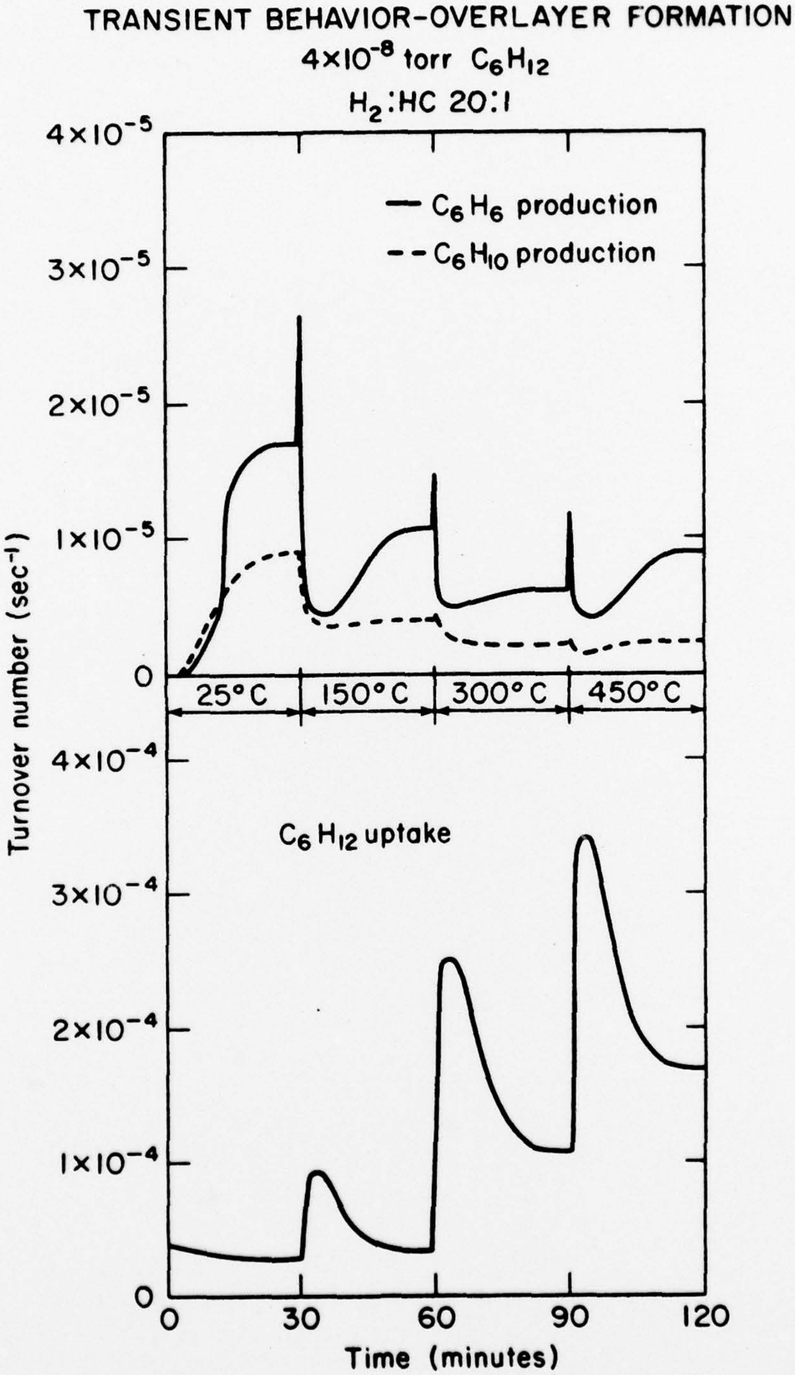
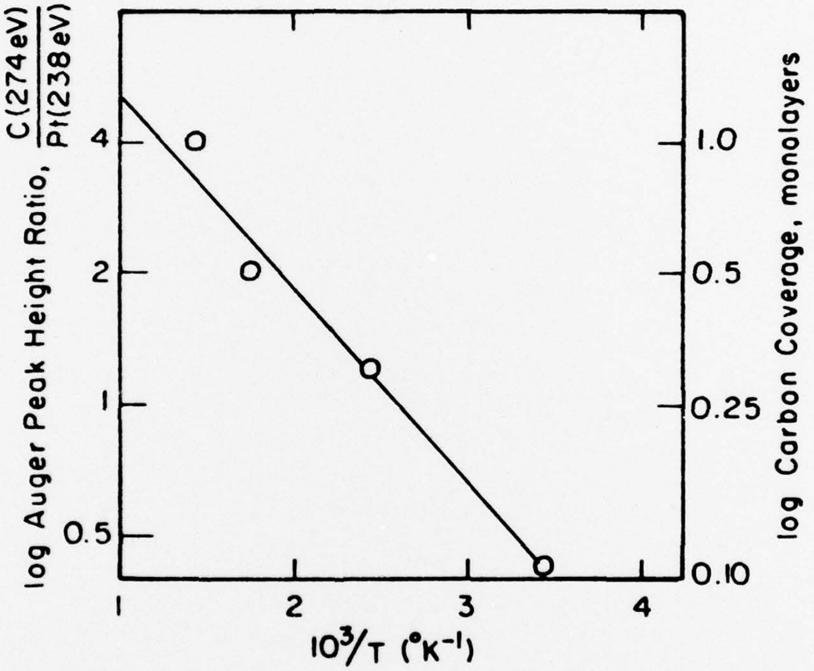

A
H₂:HC 20:1 150°C
4×10⁻⁸ torr reactant
Dehydrogenation
Hydrogenolysis
Tunrnover number (sec⁻¹)
1.5×10⁻⁵
1.0×10⁻⁵
0.5×10⁻⁵
0
0
2×10¹⁴
4×10¹⁴
6×10¹⁴
Step density (atoms/cm²)
B
Dehydrogenation
Hydrogenolysis
For 2.5×10¹⁴ step atoms/cm²
1.5×10⁻⁵
1.0×10⁻⁵
0.5×10⁻⁵
0
0
5×10¹³
10×10¹³
Kink density (kink atoms/cm²)
XBL 756-3163

Figure 5



XBL 756-3162

Figure 6



XBL 758-6869

Figure 7

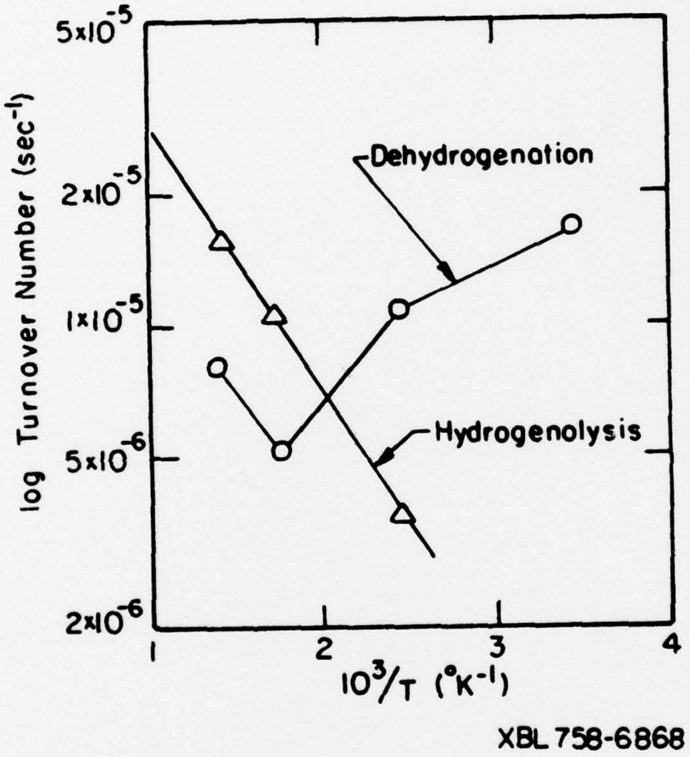
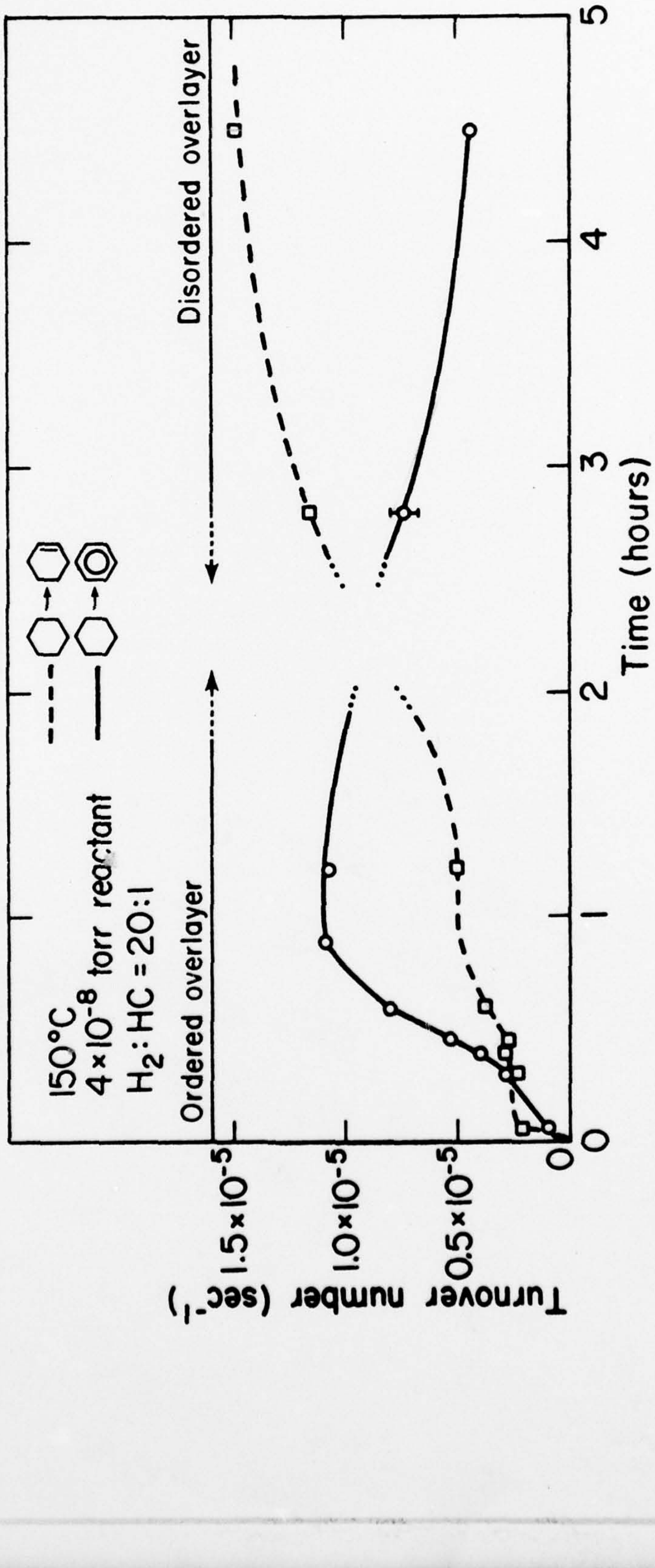
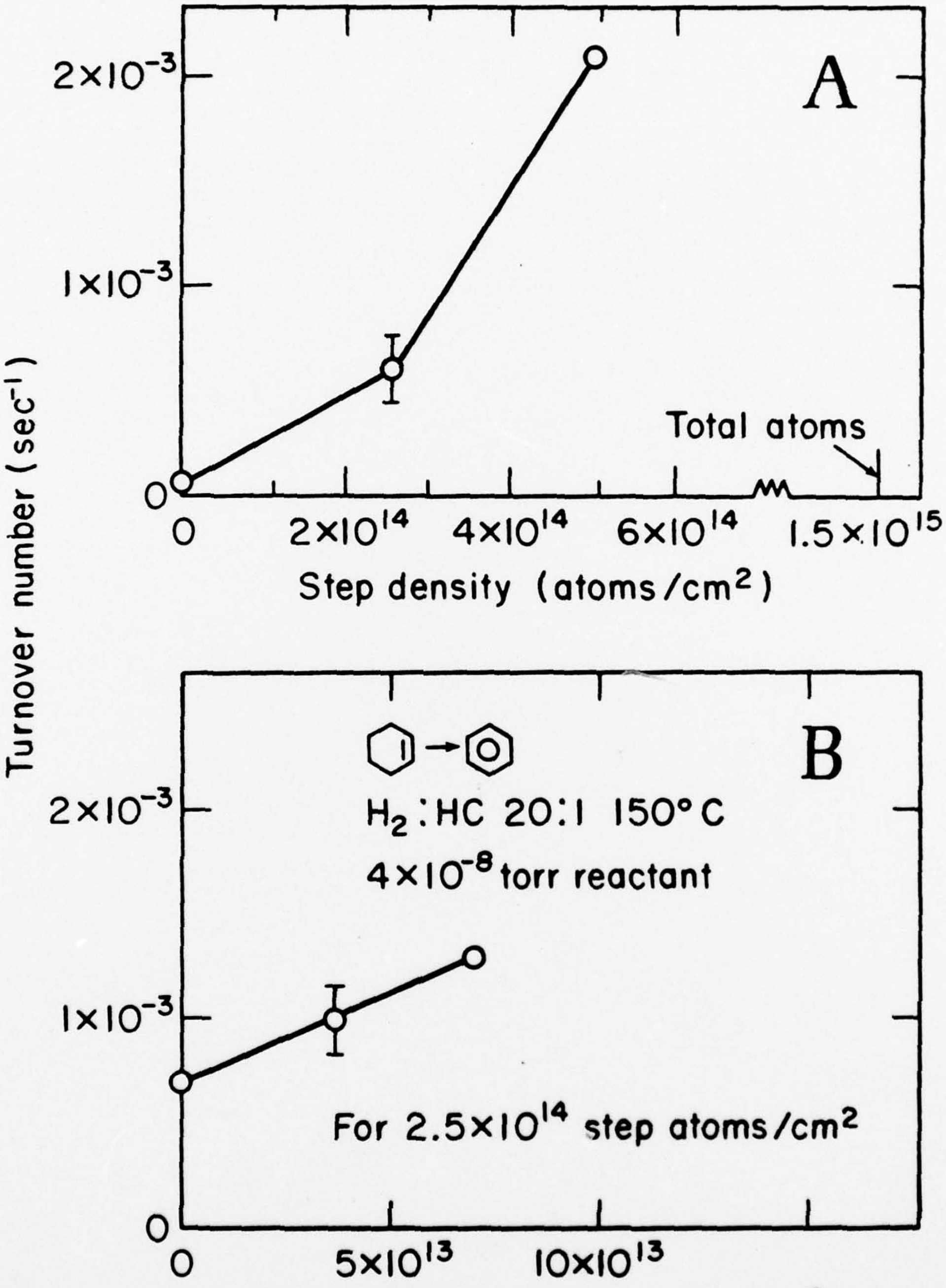

5x10^{-5}
2x10^{-5}
1x10^{-5}
5x10^{-6}
2x10^{-6}
log Turnover Number (sec^{-1})
Dehydrogenation
Hydrogenolysis
1
2
3
4
10^3/T (°K^{-1})
XBL 758-6868

Figure 8



XBL 756-3166

Figure 9



XBL756-3164

Figure 10

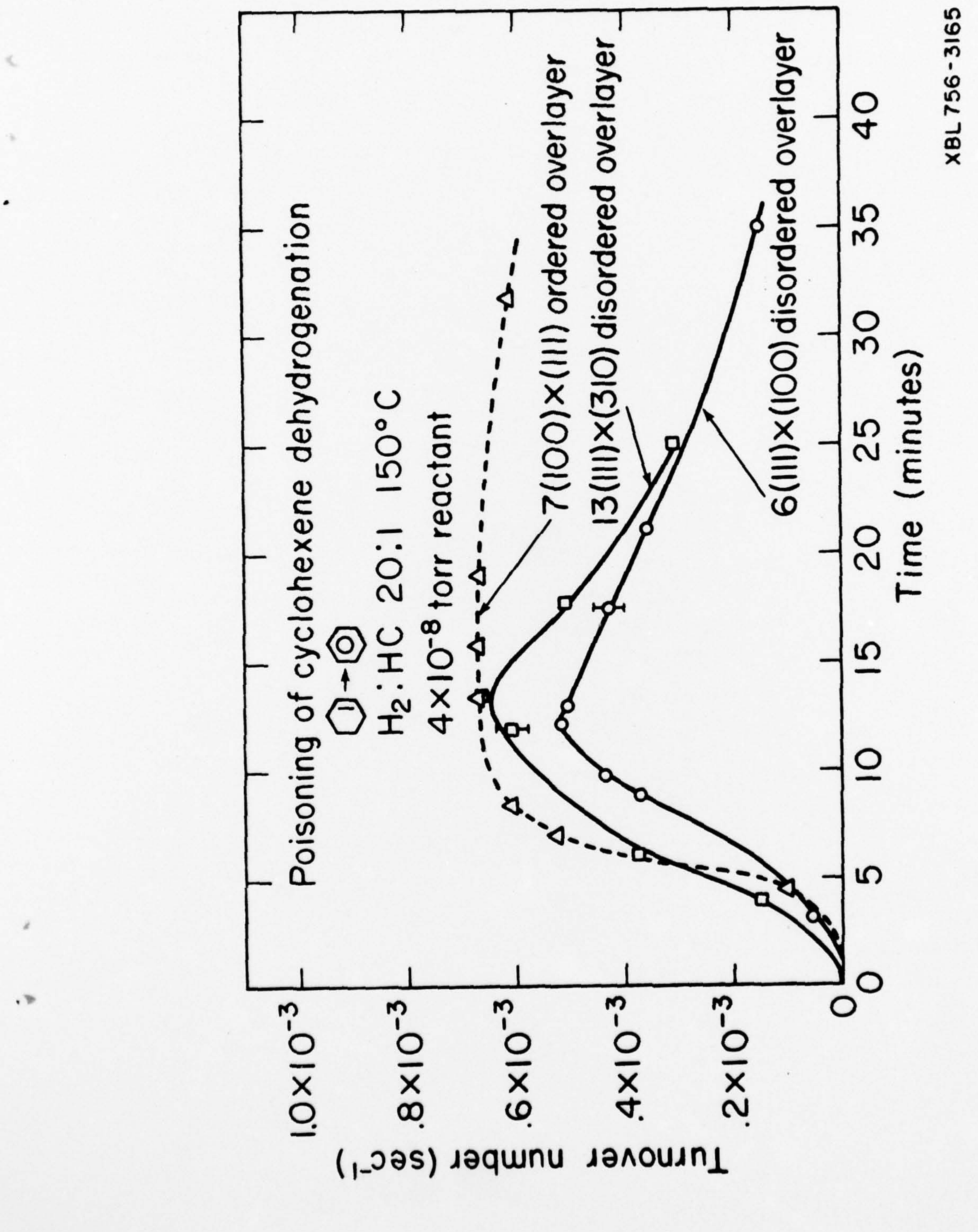
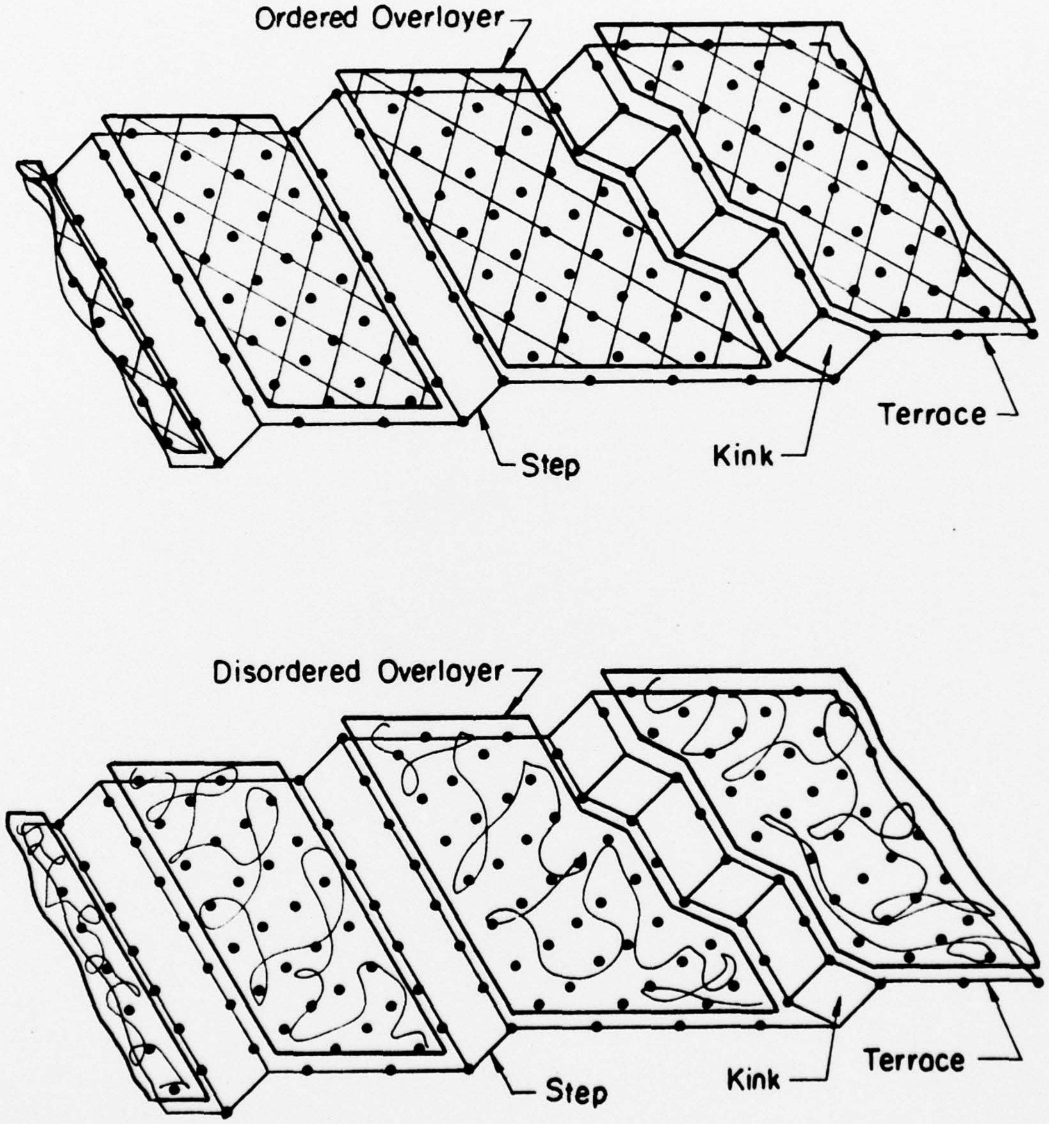

Poisoning of cyclohexene dehydrogenation
H_2:HC 20:1 150°C
4×10^{-8} torr reactant
7(100)×(111) ordered overlayer
13(111)×(310) disordered overlayer
6(111)×(100) disordered overlayer
Turnover number (sec^{-1})
1.0×10^{-3}
$.8\times10^{-3}$
$.6\times10^{-3}$
$.4\times10^{-3}$
$.2\times10^{-3}$
0
Time (minutes)
0
5
10
15
20
25
30
35
40
XBL 756-3165

Figure 11



XBL 733-5908

Figure 12