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THE HYDROGENOLYSIS OF CYCLOPROPANE ON A PLATINUM
STEPPED SINGLE CRYSTAL AT ATMOSPHERIC PRESSURE

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ABSTRACT

An apparatus was constructed to study catalytic reactions on one or more platinum single crystals in situ both at 1 atmosphere total pressure and in high vacuum ($10^{-4}$ to $10^{-8}$ 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)x(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 two were identical to published values for this reaction on highly dispersed supported platinum catalysts.
INTRODUCTION

During the last 7-8 years 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 employed high vacuum \((10^{-4} \text{ to } 10^{-11} \text{ torr})\) 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 \(^1\text{--}^4\) 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. Somorjai and coworkers have measured surface structure, composition, and some rates of reaction on platinum single crystals at low pressure. \(^5\text{--}^8\) 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. One particular reaction which has been studied extensively is the dehydrocyclization of n-heptane to form toluene. This was investigated between 100°C 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 initial 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. 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. 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 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 one atmosphere whereas LEED measurements, for example, are made at $10^{-6}$ to $10^{-10}$ torr--a pressure some $10^9$ to $10^{13}$ 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. 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 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 years 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.\textsuperscript{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.\textsuperscript{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 15-50Å dia. 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.\textsuperscript{16,25-27} In brief, small crystallites have been modeled as imperfect cubic-octahedra (fcc metals). It has been assumed that even in the smallest crystallites, metal atoms occupy crystallographic positions. Furthermore, crystallites are shaped
Table 1. Survey of structure-sensitivity studies

<table>
<thead>
<tr>
<th>(a)</th>
<th>Benzene hydrogenation</th>
<th>(a) Ethane hydrogenolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-Darling and Moss\textsuperscript{15}</td>
<td>-Sinfelt et al.\textsuperscript{19,20}</td>
</tr>
<tr>
<td></td>
<td>Pt/SiO\textsubscript{2}</td>
<td>Ni/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}, Rh/SiO\textsubscript{2}</td>
</tr>
<tr>
<td>(b)</td>
<td>Dehydrogenation of cyclohexane</td>
<td>(b) Neopentane hydrogenolysis and isomerization</td>
</tr>
<tr>
<td></td>
<td>Hydrogenation of cyclopentane</td>
<td>-Boudart et al.\textsuperscript{21}</td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}/D\textsubscript{2} exchange</td>
<td>Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/SiO\textsubscript{2}, Pt</td>
</tr>
<tr>
<td></td>
<td>-Pol'torak and Boronin\textsuperscript{16}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt/SiO\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>Cyclopropane hydrogenolysis</td>
<td>(c) Hydrogenolysis of methylcyclopentane</td>
</tr>
<tr>
<td></td>
<td>-Boudart et al.\textsuperscript{17}</td>
<td>-Corroleur et al.\textsuperscript{22}</td>
</tr>
<tr>
<td></td>
<td>Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/SiO\textsubscript{2}, Pt</td>
<td>Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/SiO\textsubscript{2}</td>
</tr>
<tr>
<td>(d)</td>
<td>Ethylene hydrogenation</td>
<td>(d) Hydrogenation of 1,2- and 1,3-butadiene</td>
</tr>
<tr>
<td></td>
<td>-Darling, Eastlake, and Moss\textsuperscript{18}</td>
<td>-Oliver and Wells\textsuperscript{23}</td>
</tr>
<tr>
<td></td>
<td>Pt/SiO\textsubscript{2}</td>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}, Ni/SiO\textsubscript{2}, Ni</td>
</tr>
<tr>
<td>(e)</td>
<td>Hydrogenation of benzene</td>
<td>(e) Hydrogenation of benzene</td>
</tr>
<tr>
<td></td>
<td>-Coenen et al.\textsuperscript{24}</td>
<td>-Coenen et al.\textsuperscript{24}</td>
</tr>
<tr>
<td></td>
<td>Ni/SiO\textsubscript{2}</td>
<td>Ni/SiO\textsubscript{2}</td>
</tr>
</tbody>
</table>
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 15–50Å dia. 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 15Å dia. particles, and decreases an order of magnitude for 50Å dia. 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} to 10^{-8} torr) within the same apparatus. The high 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.
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 atmosphere 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-inch i.d. multi-flanged 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 $5 \times 10^{-10}$ 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; and
(e) Supporting and heating the catalyst via suitable electrical feed-
throughs 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 $1 \times 10^{-8}$ 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-inch dia. tantalum electrodes, which in turn are connected
via electrical feedthroughs to a d.c. 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-inch
viewing port flange is provided in Figs. 2(a) and 2(b). In Fig. 2(a)
the reactor cup has been partially withdrawn to expose the catalyst
crystal to the UHV environment. Clearly visible is the 1/16-inch dia.
gold O-ring which has been uniformly pressed into a 3 3/8-inch dia.
groove in the reactor flange wall. The two case-hardened 1/2-inch dia.
stainless steel rods welded to the 6-inch 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 2(b) 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 (G.C. loop) is fabricated from 1/4-inch 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 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, G. C. loop, and sample volume are 571 cm³, 189 cm³, and 0.78 cm³, 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 per 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 1/4-inch dia. 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 terrances of constant width linked by steps of monatomic height.\textsuperscript{5,35} A low energy electron diffraction pattern and a schematic representation of the stepped surface used in this study are given in Figs. 3(a) and 3(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 sparkmachined 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 1/4 micron Al\textsubscript{2}O\textsubscript{3} powder, and finally etched in hot 50% aqua regia for 10 minutes prior to use. The resulting stepped crystal was 0.5 mm thick and had a total surface area of 0.76 cm\textsuperscript{2}. The circumferential area represented approximately 13% of the total surface area and was presumed to be polycrystalline in orientation.

The 0.070-inch dia. 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 minutes.

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 MgCl\textsubscript{2} 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 MgClO₄ 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 $1 \times 10^{-6}$ torr oxygen at 900-925°C for 2 hours 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 an additional hour, 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 admitted to a total pressure of 780 torr. The platinum crystal is maintained in atm of stagnant hydrogen at 75°C for a period of 2 hours. These conditions are more than sufficient to fully saturate the platinum bulk with hydrogen atoms based upon the solubility and diffusivity data of Ebisuzaki et al.³⁸ During the reduction period a cyclopropane-hydrogen mixture is prepared in the G. C. 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 torr and 675 torr, respectively. Pre-reaction chromatograms of the mixture in the G.C. 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 G.C. 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/H₂ 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 × 1/8-in. S.S. 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 minutes 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-minute 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 $4.4 \times 10^{-6}$ 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 minutes 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 minutes 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%.

Additional rate measurements at two higher temperatures (100°C 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 16 are summarized in Table 2. An Arrhenius plot of these points was constructed in Fig. 5 and the best straight line drawn through the data. The activation energy of the cyclopropane hydrogenolysis reaction calculated from this plot was \( E^* = 12.2 \pm 1.0 \text{ kcal/mole} \). 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
Table 2. Summary of the initial rate data for the determination of $E^*$ for the cyclopropane hydrogenolysis on the Pt(s)-[6(111)x(100)] single crystal.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Initial partial pressure of cyclopropane $P^0_{CP}$ (torr)</th>
<th>Initial crystal temperature averaged over initial rate measurement $T_c$ (°C)</th>
<th>$1/T_c$ ($°K^{-1} \times 10^3$)</th>
<th>Initial reaction rate $R_0$ (moles C$_3$H$_8$ min$^{-1}$ cm$^{-2}$ Pt$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10A/</td>
<td>135.0</td>
<td>73.5</td>
<td>2.88</td>
<td>1.96x10$^{-6}$</td>
</tr>
<tr>
<td>12A</td>
<td>135.0</td>
<td>74.4</td>
<td>2.88</td>
<td>1.76x10$^{-6}$</td>
</tr>
<tr>
<td>15</td>
<td>135.0</td>
<td>100.2</td>
<td>2.68</td>
<td>5.98x10$^{-6}$</td>
</tr>
<tr>
<td>16</td>
<td>135.0</td>
<td>132.5</td>
<td>2.46</td>
<td>2.55x10$^{-5}$</td>
</tr>
</tbody>
</table>
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 $C_3H_8/(\text{min} \cdot \text{cm}^2 \text{ Pt})$. The average value given in units of molecules $C_3H_8/(\text{min} \cdot \text{Pt site})$ was calculated by using a combined site density for the total exposed platinum surface area.

Hegedus\textsuperscript{30,49} carried out a series of cyclopropane hydrogenolysis experiments on single pellets of Pt/Al$_2$O$_3$. The physical characteristics of one typical pellet and kinetic reaction rate data obtained on this catalyst are given in Tables 4(a) and 4(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 $C_3H_8/\text{min} \cdot \text{Pt site}$) which is nearly the same as the average of the four rates in Runs 10A, 12A, 15, and 16 (812 molecules $C_3H_8/\text{min} \cdot \text{Pt site}$).

Boudart and coworkers\textsuperscript{17} have studied the cyclopropane-hydrogen reaction on a number of highly dispersed $\eta$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ supported platinum catalysts. A turnover number (molecules converted/minute・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\textsuperscript{28}.
Table 1. Comparison of initial specific rate data for the cyclopropane hydrogenolysis on platinum catalysts

<table>
<thead>
<tr>
<th>Data source</th>
<th>Type of catalyst</th>
<th>Calculated specific reaction rate ( r ) at ( P_{CP} = 135 \text{ torr} ) and ( T = 75^\circ \text{C} ) (moles ( C_3H_8 )/min \cdot cm^2 Pt)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>Run 10A</td>
<td>2.1 \times 10^{-6}</td>
<td>- Rate on Pt(s) - ( [6(111) \times (100)] ) single crystal based on ( E^\theta = 12.2 \text{ kcal/mole} ).</td>
</tr>
<tr>
<td></td>
<td>Run 12A</td>
<td>1.8 \times 10^{-6}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Run 15</td>
<td>1.8 \times 10^{-6}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Run 16</td>
<td>2.1 \times 10^{-6}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.95 \times 10^{-6}</td>
<td>*812</td>
</tr>
</tbody>
</table>

Hegedus\(^{38,49}\)

| Hegedus\(^{38,49}\) | 0.04 Wt\% Pt on \( \eta - \text{Al}_2\text{O}_3 \) | 7.7 \times 10^{-7} | \( \times 410 \) | - Based upon avg. Pt site density of \( 1.12 \times 10^{15} \text{ atoms/cm}^2 \). This value would be nearly equal to average of above values if dispersion was approximately 50%. |

See Table III-5

Boudart et al.\(^{17}\)

\[ \begin{align*}
\text{0.3\% and 2.0\% Pt on } \eta - \text{Al}_2\text{O}_3; \\
\text{0.3\% and 0.6\% Pt on } \gamma - \text{Al}_2\text{O}_3
\end{align*} \]

|                  | 8.9 \times 10^{-7} | 480 | - \( \tau_{CP} = 0.2, E^\theta = 8.5 \text{ kcal/mole} \). |

Dougharty\(^{28}\)

|                  | 2.5 \times 10^{-6} | 1340 | - \( \tau_{CP} = 0.6, E^\theta = 8.5 \text{ kcal/mole} \). (Dougharty reports \( E^\theta = 8.9 \text{ kcal/mole} \) and \( n = 0.2 \) to 0.6) |
Table 4(a). Physical characteristics of the platinum catalyst pellet used by Hegedus^{30,49}

- 0.25 wt% Pt on \( \eta\text{-Al}_2\text{O}_3 \) diluted with \( \eta\text{-Al}_2\text{O}_3 \) to 0.04 wt% Pt
- \( \eta\text{-Al}_2\text{O}_3 \) surface area = 230 m\(^2\)/gram
- Weight of pellet = 0.295 grams
- Pellet density = 1.14 grams/cm\(^3\)

Table 4(b). Initial rate data for the cyclopropane hydrogenolysis using the catalyst pellet of Hegedus^{30,49}

- Catalyst calcined in 3% \( \text{O}_2 \) in \( \text{N}_2 \) @ 400-410°C for 2 hrs.
- Catalyst reduced in \( \text{H}_2 \) @ 300°C for 10 hrs.
- \( C^0_{\text{H}_2} = 41.4 \times 10^{-6} \) moles/cm\(^3\) \( (P^0_{\text{H}_2} = 900 \) torr\)
- \( C^0_{\text{CP}} = 3.45 \times 10^{-6} \) moles/cm\(^3\) \( (P^0_{\text{CP}} = 75.0 \) torr\)
- \( T_{\text{rxn}} = 75°C \)
- \( (k a_0)^1 = 2.61 \) sec\(^{-1}\)
- Reaction found to be first order in cyclopropane concentration.
and assuming a platinum site density of $1.12 \times 10^{15}$ atoms/cm$^2$. To within a factor of two, the 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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FIGURE CAPTIONS

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) Detail of gold O-ring seated in reactor flange wall, tantalum electrodes, and Pt/Pt-10% Rh thermocouple wires.
(b) 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.

Fig. 4. Cyclopropane hydrogenolysis on the Pt(s)-[6(111)×(100)] single crystal surface (Aₜₜ=0.76 cm²). Pₑₑ = 135 torr.
Pₒₒ = 675 torr. Average crystal temperature = 74°C.

Fig. 5. Activation energy for the hydrogenolysis of cyclopropane based upon initial reaction rates on the Pt(s)-[6(111)×(100)] single crystal (Aₜₜ = 0.76 cm²). Pₑₑ = 135 torr. Pₒₒ = 675 torr.
Fig. 1.
Fig. 2
Data corrected for propylene impurity

(Moles Propane per Cm² Platinum x 10⁻⁵)

Elapsed Reaction Time (min.)

Propylene impurity = 1.5 x 10⁻⁵ moles/cm² Pt

Run 10 A
Run 12 A

Fig. 4
Fig. 5
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