

Low-Energy Electron Diffraction, Work Function Change and Mass Spectrometric Studies of Chemisorption and Dehydrogenation of Cyclohexane, Cyclohexene and 1,3-Cyclohexadiene on the Pt(111) Surface

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Adsorption and reaction studies have been carried out using cyclohexane, cyclohexene, 1,3-cyclohexadiene, and benzene on the Pt(111) surface in order to determine the reactivity of the Pt(111) surface and to characterize stable surface species which occur during cyclohexane dehydrogenation. Cyclohexene is a long-lived surface species during the dehydrogenation of cyclohexane on the Pt(111) surface. Cyclohexane conversion to cyclohexene is *not* severely kinetically limited. Dehydrogenation of 1,3-cyclohexadiene to benzene proceeds rapidly to completion on the Pt(111) surface. The slow step in the dehydrogenation of cyclohexane to benzene appears to be the dehydrogenation of the cyclohexene intermediate. The cause of the slow reaction may be the orientation of the adsorbed cyclohexene relative to the catalyst surface.

INTRODUCTION

The dehydrogenation of cyclohexane to benzene has been studied for many years using a variety of catalysts from supported metals to field emission tips. With the availability of commercial systems for examining well-characterized, clean metal surfaces in the form of single crystals a wealth of information has been documented on these surfaces, (1) but only recently have interactions with hydrocarbons been examined (2,3).

Maatman and co-workers (4) studied the dehydrogenation of cyclohexane at 150°C over platinum-alumina catalysts and concluded that the slow step in the reaction cannot be the desorption of benzene but is associated with one or more reactions in which both reactant and product are adsorbed. Kraft and Spindler (5) assumed in their analysis of the kinetics of dehy-

drogenation of cyclohexane over platinum-alumina that benzene adsorption is the slow step. Block (6) studied the dehydrogenation reaction over platinum field emission tips, platinum foil, and platinum-asbestos catalysts. He concluded that the reaction proceeds by the formation of the intermediates, cyclohexene and cyclohexadiene, which were detected in the gas phase. Haensel, Donaldson, and Riedle (7) studied the reaction at 520°C and 20 atm, in the liquid phase, and concluded cyclohexene was an intermediate which was detected as a product at high space velocities; Siegel (8) in 1964, reviews this topic, and devotes a section of his work to the detection of cyclohexene which is an intermediate in the reaction.

Thus, the possible existence of these two cyclic hydrocarbons as intermediates prompted us to include them in a study of the reactivity and chemisorption of cyclohexane over the hexagonal Pt(111) surface using Auger electron spectroscopy (AES)

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to determine surface composition and low-energy electron diffraction (LEED) to determine the structure and degree of order of the clean surface and adsorbed layers. We have also used Work Function Change (WFC) measurements to characterize the adsorbed layer, and Quadrupole Mass Spectrometry (QMS) to analyze the gas phase composition. Using these techniques to uniquely characterize the catalytic system we have studied the reactivity of the surface and correlated the reactivity with physical properties of the surface determined during the adsorption experiments.

Supported catalyst surfaces have a variety of exposed planes available to any reacting species; of these, the low-index planes are often important (9). Thus, we chose to examine the hexagonal Pt(111) surface which is the most dense face in the face-centered cubic system, with surface free energy at a minimum. It must be emphasized that the choice of the orientation of the surface along with the defect density and contamination on the surface profoundly influences the reactivity and chemisorption properties of single crystals.

EXPERIMENTAL

The experimental procedures used for the reaction (10,11) and adsorption (3,12,13) experiments have been outlined elsewhere. Both experimental systems are ultra-high vacuum systems of stainless steel, capable of attaining 2×10^{-9} Torr by ion pumping (and titanium sublimation pumping in the case of the adsorption system). The walls of the reaction chamber were gold-plated to reduce their catalytic reactivity.

Pt(111) single crystals (1 cm² area) were mounted at the center of each chamber and the temperature monitored by a Pt-Pt 10% Rh thermocouple spot welded to the sample. The crystal was spot welded to polycrystalline platinum supports, which, in the reaction system, were shielded by

tight fitting sleeves of high purity alumina, to minimize reaction on the support.

LEED (Varian) and Auger (Vacuum Generators) information was obtained using a four grid system with perpendicular or grazing angle electron beam sources.

Work function change (WFC, $\Delta\phi$), measurements were made using the retarding field method with the LEED gun as the electron beam source. The retarding potentials were used as internal voltage standards. The work function change depends on the density of the adsorbed layer and charge transfer which occurs on adsorption. The WFC observed for π -bonded species is significantly larger than the WFC observed on adsorption of aliphatic molecules since the charge transfer is larger on adsorption (3).

The organic flux was introduced from a capillary tube about 5 mm from the sample surface. The gas phase composition was monitored using a quadrupole mass spectrometer (EAI Quad 200) which was calibrated with an ionization gauge over the pressure range 10^{-9} – 10^{-4} Torr.

Prior to each adsorption and reactivity experiment, the platinum samples were cleaned (O_2 , 3×10^{-5} Torr, 800–1000°C, 30 min) to remove carbon contamination on the surface. This was followed by heat treatment in vacuum (5×10^{-9} Torr, 5 min) to remove adsorbed oxygen.

The exact experimental procedures were as follows:

Adsorption Experiments

1. The single crystal was cleaned using oxygen; Auger spectra, LEED observations and the work function change standards were taken at room temperature.
2. The hydrocarbon was admitted into a steady state flowing system; work function and LEED observations were made.
3. The sample was heated in organic flux to the temperature specified for five minutes then allowed to cool (20–40°C);

work function and LEED data were taken again.

Reaction Experiments

1. The single crystal was cleaned using oxygen; Auger spectra and LEED measurements were taken at room temperature.

2. The 5:1 hydrogen:hydrocarbon was admitted and the vacuum pumps were isolated. A total pressure of 5×10^{-7} Torr was established. The platinum sample was heated to 150°C and the gas phase composition followed continuously.

3. The reaction mixture was pumped out and the temperature reduced to ambient; then LEED and Auger observations were made.

Blank runs were performed for the reaction studies; the same reaction chamber was used without the Pt(111) sample. The polycrystalline holders were spot-welded together, heated resistively, and the temperature monitored with the usual thermocouple.

RESULTS

Prior to each reactivity study, adsorption experiments were carried out using the 5:1 hydrogen:hydrocarbon mixture as an adsorbate. The LEED pattern obtained during the adsorption of the hydrogen-hydrocarbon mixtures agreed with LEED patterns obtained from adsorption of the hydrocarbon alone. That is, the addition of hydrogen does not influence the observed adsorbed structures on the Pt(111) surface. Auger analysis of all of the patterns observed during the adsorption and reactivity studies indicates the surface structures were composed of carbonaceous species. Equilibrium calculations indicate that all hydrocarbons admitted should be converted to benzene at 150°C with a 5:1 hydrogen:hydrocarbon ratio and the total pressure equaling 5×10^{-7} Torr.

Adsorption Studies

The results of the adsorption studies are shown in Table 1. They indicate that all the molecules interact strongly with the Pt(111) surface. Adsorption of 1,3-cyclohexadiene at 20°C leads to the formation of an adsorbed layer which is largely benzene. Cyclohexane interacts with the surface in a different manner than cyclohexene at 20°C, but neither are converted to adsorbed benzene even at 300°C.

1. Cyclohexane Adsorbed on Pt(111)

Cyclohexane (2×10^{-8} Torr) adsorbed on the Pt(111) at 20°C causes little change in the observed hexagonal diffraction pattern due to the Pt(111) surface. The WFC on adsorption is -1.2 V. With increased organic pressure (4×10^{-7} Torr), the WFC becomes -0.7 V and the adsorbed layer becomes poorly ordered. The diffraction pattern shows two faint, concentric, high-order features. With gentle heating to 150°C, the adsorbed layer forms a structure which can be described in a shorthand notation as an apparent $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ structure.

The matrix gives the coefficients of the unit cell vectors of the surface structure with respect to the original platinum surface unit cell vectors (14). A $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ surface structure implies that the adsorbate unit cell vectors are twice as long as the metal unit cell parallel with them. With further heating the adsorbed layer becomes disordered, and the magnitude of the WFC increases to -1.4 V at 300°C. The magnitude of the WFC decreases with further stepwise heating to 600°C.

2. Cyclohexene Adsorbed on Pt(111)

Cyclohexene adsorbed on the Pt(111) surface causes the formation of the ordered $\begin{vmatrix} 2 & 2 \\ 4 & -2 \end{vmatrix}$ structure. The WFC on adsorption is -1.7 V. With increased tem-

TABLE I
 CYCLIC HYDROCARBON ADSORPTION ON THE Pt(111) SURFACE

Absorbate	Temperature (°C)	Pressure (Torr)	Time	Work function change (V)	Surface structure (14)
Benzene	20	4×10^{-7}	initial	-1.8	disordered
	20	4×10^{-7}	5 min	-1.4	$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$
	20	4×10^{-7}	40 min	-0.7	$\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$
1,3-Cyclohexadiene	20	2×10^{-8}	initial	-1.75	disordered
	20	2×10^{-8}	1 hr	-1.3	$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$
	20	2×10^{-8}	5 hr	-0.8	$\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$
Cyclohexene	20	6×10^{-7}	stable	-1.7	$\begin{vmatrix} 2 & 2 \\ 4 & -2 \end{vmatrix}$
	150	6×10^{-7}	stable	-1.7	apparent $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$
	300	6×10^{-7}	stable	-1.55	disordered
Cyclohexane	20	6×10^{-9}	stable	-1.2	$\begin{vmatrix} 1 & 0 \\ 1 & 0 \end{vmatrix}$
	20	4×10^{-7}	stable	-0.7	poorly ordered
	150	4×10^{-7}	stable	-1.1	apparent $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$
	300	4×10^{-7}	stable	-1.4	disordered

perature the WFC remains essentially constant until 200°C where it begins to decrease with stepwise heating to 400°C.

3. 1,3-Cyclohexadiene Adsorption

This hydrocarbon adsorbed on the Pt(111) surface initially forms a poorly ordered layer. With continued exposure this changes with the appearance of the $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure. Further exposure causes the slow appearance of the $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure. The work function shifts which accompany these changes are as follows. On initial adsorption the WFC goes through a minimum (about -1.75 V), then increases slowly towards a higher steady (-0.8 V). The initial order $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ struc-

ture appears at a WFC value of about -1.3 V, after the minimum work function has been passed. The second ordered structure forms after the work function has increased further.

4. Benzene Adsorption

The adsorption of benzene on Pt crystal surfaces has been studied in detail (12) by LEED and WFC measurements and the results of these investigations have been reported elsewhere. It is important, however, to briefly outline the essential features of benzene adsorption inasmuch as it relates to the adsorption of cyclohexene and cyclohexadiene. Benzene forms a poorly ordered layer on Pt(111) at 25°C at low exposures. Continued organic vapor flux causes the appearance of the diffraction pattern resulting from Pt(111)-

$\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ -benzene structure. With continued exposure to the organic, the structure changes to $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure. On initial exposure the work function of the surface decreases rapidly, goes through a minimum (-1.8 V) then increases slowly towards a higher steady-state value of -0.7 V. The initial ordered $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure appears at a WFC of -1.4 V, slightly after the minimum WFC has been obtained. The second ordered $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure appears after the WFC has increased to about -1.0 V.

Reaction Studies

The results of the reactivity experiments are shown in Table 2. Here we have listed initial reaction rates as the production of various species from cyclohexane, cyclohexene, and 1,3-cyclohexadiene under the conditions outlined. Blank runs were carried out on all of the reactants in the absence of the catalyst.

Cyclohexene and cyclohexane are not dehydrogenated extensively, while 1,3-cyclohexadiene is essentially completely converted to benzene. A 5:1 hydrogen:cyclohexane mixture yielded 6% conversion to cyclohexene and a 0.1%

TABLE 2
THE REACTIONS OF CYCLIC HYDROCARBONS
ON Pt(111) SURFACE^{a,b}

Product	Cyclohexane C ₆ H ₁₂	Cyclohexene C ₆ H ₁₀	1,3-Cyclohexadiene C ₆ H ₈	Benzene C ₆ H ₆
Reactant				
C ₆ H ₁₂	90	6	—	0.1
C ₆ H ₁₀	2	95	—	0.4
C ₆ H ₈	—	—	—	80

^a Conditions: 0.83×10^{-7} Torr hydrocarbon, 4.17×10^{-7} Torr H₂, 150°C.

^b Initial reaction rates, units = % conversion in 2 min.

conversion to benzene in 2 min of reaction time with the Pt(111) catalyst at 150°C. It should be pointed out that other reactions that compete with the dehydrogenation reactions may be occurring. The reaction of cyclohexene under the same conditions gives 2% conversion to cyclohexane and 0.4% conversion to benzene in 2 min of reaction time with the Pt(111) catalyst at 150°C. The reaction of 1,3-cyclohexadiene in a 5:1 mixture of hydrogen to the hydrocarbon yields 80% conversion to benzene under the same conditions.

DISCUSSION

Cyclohexane and Cyclohexene

The adsorption data on the Pt(111) surface indicates that at 20°C cyclohexane interacts with the Pt(111) surface in a different manner than cyclohexene. At a pressure of 6×10^{-7} Torr the WFC on adsorption for cyclohexene is -1.7 V. The WFC on adsorption of cyclohexene is similar to the WFC of several π -bonded species such as mesitylene and acetylene. Cyclohexene adsorbed on Pt(111) forms a $\begin{vmatrix} 2 & 2 \\ 4 & -2 \end{vmatrix}$ structure while cyclohexane forms a disordered adsorbed layer. Thus it seems apparent that cyclohexane is *not* doubly dehydrogenated on adsorption at 20°C. It seems likely that cyclohexane interacts with the surface by becoming singly dehydrogenated and σ -bonded to the surface. Cyclohexene appears to form a π -bonded adsorbed specie. With heating to 150°C in flux, both cyclohexane and cyclohexene cause an apparent $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ surface structure with diffuse diffraction features. The magnitude of the WFC increases to -1.1 V for cyclohexane and remains the same for cyclohexene. With further heating to 300°C the magnitudes of the WFC increases to -1.4 V for cyclohexane and decreases to -1.5 V for

cyclohexene. Both adsorbed layer are disordered at 300°C. The marked increase of the magnitude of the WFC for cyclohexane from -0.7 V at 20°C to -1.4 V at 300°C indicates that dehydrogenation is occurring with heating. The fact that the magnitude of the WFC does not increase even further is probably caused by partial decomposition of the adsorbed layer to small fragments or amorphous carbon with heating. The identical diffraction patterns at 150°C are further evidence that dehydrogenation of cyclohexane is occurring with heating. The small change in WFC value for cyclohexene with heating from 20°C to 150°C implies that little change is occurring in the bonding between the adsorbed layer and the substrate for cyclohexene. It seems that the apparent $\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ cyclohexene structure may be a disordered $\begin{vmatrix} 2 & 2 \\ 4 & -2 \end{vmatrix}$ surface structure. Thus it appears that cyclohexane is dehydrogenated on the Pt(111) surface with increased temperature; however, it seems that dehydrogenation may not be complete.

The Adsorption of Benzene and 1,3-Cyclohexadiene

Both benzene and 1,3-cyclohexadiene adsorbed on the Pt(111) surface form a poorly ordered adsorbed layer; the WFC on adsorption is about -1.8 V. With further exposure the $\begin{vmatrix} -2 & 2 \\ 4 & 4 \end{vmatrix}$ structure forms and the magnitude of the WFC decreases to about -1.4 V. With further exposure the $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure forms, and the WFC decreases until it reaches a steady state value of -0.7 V. The $\begin{vmatrix} -2 & 2 \\ 5 & 5 \end{vmatrix}$ structure forms when the WFC is about -1.1 V. Thus 1,3-cyclohexadiene adsorbed on Pt(111) apparently loses two hydrogens and is converted to benzene on the surface. The small deviations between the

values of benzene and 1,3-cyclohexadiene WFC can be explained by considering that part of the surface may be covered with hydrogen from the dehydrogenation of the diene. In fact the transformation takes a significantly longer time for the 1,3-cyclohexadiene than for benzene; this also may be a result of increased surface hydrogen concentration.

The correlation between the benzene surface structure transformation and the change in work function suggests that the orientation of the adsorbed benzene molecules is changing as a function of increased exposure. The initial value of the WFC is similar to that observed for a number of π -bonded species of unsaturated hydrocarbons. This suggests that in the initial state the molecule is π -bonded to the Pt(111) surface. The final value of the WFC, -0.7 V corresponds to the WFC observed on adsorption of cyclohexane and cyclopentane at the same pressure (about -0.7 V). This indicates that the bonding for these two cases (benzene in its final state and the cyclic hexane and pentane) is similar. For cyclopentane or cyclohexane adsorbed on Pt, the bonding appears to involve single dehydrogenation and subsequent binding of the adsorbate to the substrate through the dehydrogenated site.

A likely model consistent with the above observations is that the initial adsorbed state involves benzene adsorbed with its aromatic ring at some small angle or parallel to the metal surface. The final adsorbed state involves reoriented benzene molecules adsorbed, with their rings at some large angle, or perpendicular to the surface. A more complete discussion of benzene adsorption is given elsewhere (12).

The conversion of 1,3-cyclohexadiene to benzene on the Pt(111) surface indicates that the reaction is not kinetically hindered and that the dehydrogenation is complete in the adsorbed layer at 20°C.

The reaction studies with cyclohexane

indicate that cyclohexene is probably present on the catalyst surface during the dehydrogenation reaction since it was detected in the gas phase. The presence of a small amount of benzene product indicates that the sought after reaction is occurring and that the product desired (benzene) is formed over the Pt(111) surface. Further reactions using cyclohexene yielded larger amounts of benzene product. This indicates that there is a feasible catalytic route from adsorbed cyclohexene to benzene; it also indicates that higher concentrations of adsorbed cyclohexene increase the amount of benzene produced. Both of these conclusions lend further credence to the idea that adsorbed cyclohexene is an intermediate in the dehydrogenation of cyclohexane on the Pt(111) surface at 150°C. The reaction path(s) from cyclohexane and cyclohexene to benzene appear to be severely kinetically hindered. However, cyclohexane and cyclohexene appear to be in partial equilibrium at 150°C as indicated by the substantial amount of cyclohexene detected as a product in the dehydrogenation of cyclohexane, and the cyclohexane which appeared as a product of the hydrogenation of cyclohexene.

The large amount of benzene product which results from the dehydrogenation of 1,3-cyclohexadiene indicates that the dehydrogenation of this compound on the Pt(111) surface at 150°C is fast and not kinetically limited.

The Pt(111) Surface and Cyclohexane Conversion to Benzene

The reaction and adsorption studies indicate that the Pt(111) surface is capable of catalyzing the conversion of cyclohexane to cyclohexene. However, the reaction is kinetically hindered and does not proceed to completion at 150°C either on the surface (in the adsorbed state) or in the desorption step (in the gas phase). However, both adsorption and reaction studies indicate that 1,3-cyclohexadiene is

completely converted to benzene over the Pt(111) surface. Thus, the dehydrogenation of cyclohexene is severely kinetically hindered and appears to be the rate limiting step in the dehydrogenation of cyclohexane.

The primary difference between cyclohexane, cyclohexene and 1,3-cyclohexadiene is adsorption geometry. Both cyclohexene and cyclohexane on Pt(111) may have little "contact" with the surface since they may be adsorbed in a perpendicular manner. That is, several of the carbons may be spatially removed from the metal surface because of the conformations of the ring systems. 1,3-Cyclohexadiene, on the other hand, is locked in a planar configuration so that all carbons are in intimate contact with the surface. In essence, the activation barrier may be reduced dramatically for 1,3-cyclohexadiene because the metal can interact with the parts of the molecules where dehydrogenation must occur. This happens because the ring system is rigid and the molecule is π -bonded to the surface. For cyclohexene the activation barrier may be large since the molecules "stand-up" on the surface because of repulsive interactions between adsorbate molecules.

It should be noted that both the adsorption and the surface reaction studies were carried out on one face of a platinum crystal with surface area of less than 1 cm². It is now possible to use well-characterized crystal surfaces of small area as models of polydispersed platinum systems at low pressures or at high pressures. The results cannot only be correlated with real platinum catalyst systems, but the model system permits us to establish correlations between surface structures, composition, and reactivity.

CONCLUSION

Cyclohexane dehydrogenation to benzene over the Pt(111) surface at 150°C is severely kinetically limited. Cyclohexene

is identified as a reaction intermediate during this reaction. Cyclohexane conversion to cyclohexene is *not* severely kinetically limited. Dehydrogenation of 1,3-cyclohexadiene to benzene proceeds rapidly to completion on the Pt(111) surface. The slow step in the dehydrogenation of cyclohexane to benzene appears to be the dehydrogenation of the cyclohexene intermediate. The cause of the slow reaction may be the orientation of the adsorbed cyclohexene relative to the catalyst surface.

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14. The underlying platinum unit cell is described by the matrix $\begin{vmatrix} 1a & 0b \\ 0a & 1b \end{vmatrix}$ or the row vectors $(1a, 0b)$, $(0a, 1b)$ the unit cell of the adsorbed structure $\begin{vmatrix} 2a & 0b \\ 0a & 2b \end{vmatrix}$ is described by the row vectors $(2a, 0b)$, $(0a, 2b)$.