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HYDROGENATION OF CYCLOHEXANE AND DEHYDROCYCLIZATION OF N-HEPTAN--ETC(U)

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Hydrogenation of Cyclohexane and Dehydrocyclization of
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by

B. E. Nieuwenhuys and G. A. Somorjai

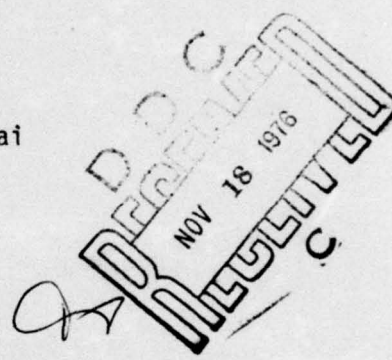
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Hydrogenation of Cyclohexane and Dehydrocyclization of
n-Heptane over Single Crystal Surfaces of Iridium

B. E. Nieuwenhuys and G. A. Somorjai

ABSTRACT

The dehydrogenation of cyclohexane and the dehydrocyclization of n-heptane were investigated at low hydrocarbon pressure ($\sim 10^{-5}$ Torr) on two single crystal surfaces of iridium. The surfaces studied were Ir(111) and Ir(755) or stepped [6(111) $\times$ (100)]. The reaction rates were monitored by a quadrupole mass spectrometer, the surface structure and surface composition were determined by means of low-energy electron diffraction and Auger electron spectroscopy. The results are discussed and compared with similar studies on single crystal surfaces of platinum. The stepped iridium surface appeared to be a factor of 5 more active in dehydrogenation than the iridium (111) surface. The activity of iridium in dehydrocyclization was lower than that for platinum surfaces of the same structure.

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INTRODUCTION

A large number of adsorption studies performed on well-defined crystal surfaces in different laboratories and with various experimental techniques has established a large influence of the crystal surface structure on the adsorption characteristics. This is exhibited by a pronounced crystal face specificity in heat of adsorption, sticking probability, ordering on the surface, dipole moment and decomposition of the adsorbed molecules. For platinum and iridium both metals being active catalysts for a large number of chemical reactions, a striking crystal face effect has been shown to exist in strong chemisorption,¹⁻⁴ weak chemisorption⁵ and physical adsorption.^{6,7}

It may be expected from these adsorption experimental results that the surface structure will also have a significant influence on catalysis. Available data of catalysis studies on various single crystal metal surfaces are, however, still very scarce and limited to the simplest catalytic reactions, such as hydrogen-deuterium equilibration on platinum, studied by Lu and Rye⁸ and decomposition of ammonia, studied on platinum single crystal surfaces by Löffler and Schmidt.⁹ These two studies point indeed to large influence of the surface structure on the activity of the catalyst in low pressure catalysis. Recently more complicated catalytic reactions such as dehydrogenation and hydrogenolysis of some selected hydrocarbons have been investigated on several platinum single crystal surfaces in this laboratory.^{10,11} It was found that the behavior of platinum in these reactions is very sensitive to the presence of imperfections such as steps on the surface. The reaction probability for the dehydrogenation of cyclohexane to benzene appeared to be an order of magnitude higher on a stepped high Miller index

surface than on the platinum (111) surface, a surface with a very low concentration of atomic steps.

In the present paper a similar study performed on iridium surfaces will be described. Two different iridium surfaces have been investigated: the (111) face, that is the atomically most densely packed iridium surface and the high Miller index (755) or Ir(S)-[6(111)×(100)] surface, consisting of terraces of the (111) type with a width of six atoms, separated by steps of the (100) type with monatomic height. The choice of these two surfaces permits a direct examination of the influence of steps on the catalytic activity of iridium. Two reactions were examined, a dehydrogenation reaction, the formation of benzene from cyclohexane and a dehydrocyclization reaction, the formation of toluene from n-heptane.

Another purpose of this study was to compare the behavior of the iridium surfaces in these reactions with the behavior of similar surfaces of platinum which have been studied previously.¹⁰⁻¹² A recent study⁴ has demonstrated the effect of steps on iridium surfaces on the adsorption of hydrocarbons. Further significant differences were found to exist between similar surfaces of iridium and platinum: differences in thermal desorption mass spectra and low-energy electron diffraction observations of the adsorbed species indicated that C-H and possibly also C-C bond breaking occurs more easily on iridium than on platinum. The present study enables a direct comparison of platinum and iridium in catalysis of the same hydrocarbon reactions.

EXPERIMENTAL

The two iridium samples were cut from a single crystal rod of 99.99% nominal purity, purchased from Materials Research Corporation. The main impurities were ruthenium (100 ppm), tungsten (40 ppm), platinum (30 ppm), and iron (15 ppm). Other impurities were stated to have concentrations less than 10 ppm. After orientation of the rod with the aid of the Laue back-reflection X-ray technique the samples were cut from the rod by means of spark erosion to within 1% of the desired angles. The surfaces of the two samples were polished following standard metallographic procedures. The surface area of the samples was approximately 1.0 cm^2 .

The samples spotwelded to tantalum supports were installed in a LEED-AES ultra-high vacuum apparatus. The pumping system consisted of a 140 liter/sec. Vac-Ion pump and a titanium sublimation pump which could be independently isolated from the chamber by gate valves. The system contained four-grid electron optics and was equipped with a quadrupole mass spectrometer and ion bombardment attachment. Typical residual pressures were in the 10^{-10} Torr range (mainly H_2 , H_2O , CO , Ar and CH_4). The samples could be resistively heated through the tantalum supports. Sample temperatures were determined by means of Pt-Pt 10% Rh thermocouples spotwelded near the edges of the samples.

The samples were heated for several days at a temperature of 1200°C for outgassing and surface annealing. After this heating process a small calcium A.E.S. peak was detected, which could be removed from the surface by argon ion bombardment and a subsequent flash to 1200°C in order to restore the surface perfection. This bombardment heating procedure was repeated several times in order to obtain a surface that is free of calcium within

the limits of detection of Auger electron spectroscopy. The main surface contaminant was found to be carbon which could easily be removed by heating the sample to 500-600°C in an oxygen ambient of 5×10^{-7} Torr followed by flashing to 1200°C in order to desorb oxygen from the surface. The surfaces produced in this way were clean within the limits detectable by Auger electron spectroscopy.

The procedure employed during the reaction experiments will be described now. After cleaning the iridium sample was cooled to about 40°C. The vacuum chamber was then isolated from the pumps and hydrogen was admitted into the chamber to the desired pressure, followed by introduction of the hydrocarbon by the use of two variable leak valves. Pressures of the reactant and hydrogen were measured by means of the quadrupole mass spectrometer which was equipped with a thoriated-iridium filament to minimize interaction with the hydrocarbons. The mass spectrometer was calibrated for hydrogen, the reactant and the expected reaction products using an ionization gauge. The ionization gauge was never used during admission of the reactant and during the reaction. The sample was heated to the desired reaction temperature and the partial pressure of reactant and reaction products were continuously monitored with the mass spectrometer. When the experiment was completed, the gases were pumped out and Auger electron spectra were taken and low-energy electron diffraction observations were made in order to investigate the amount and the nature of adsorbates on the surface.

The dehydrogenation of cyclohexane to benzene could easily be followed by using the increase of the parent $m/e = 78$ peak. The dehydrocyclization reaction of n-heptane to toluene was recorded by means of the changes in the $m/e = 91$ and $m/e = 92$ peaks corrected for a small component present in the n-heptane cracking pattern.

RESULTS and DISCUSSION

First we shall describe the dehydrogenation of cyclohexane. The standard conditions for these measurements were a cyclohexane pressure of 1×10^{-5} Torr and a hydrogen pressure of 20×10^{-5} Torr. After cleaning the sample it was cooled to room temperature and hydrogen was introduced into the system and subsequently the hydrocarbon to the desired pressures. The composition of the gas phase was determined by means of the mass spectrometer. No dehydrogenation activity could be detected at this temperature. Then the crystal was heated to the desired temperature and the gas composition was monitored as a function of time. Usually the reaction rate was constant after approximately five minutes and remains constant for at least thirty minutes. This reaction rate was considered to be characteristic of the surface under the experimental conditions used. Separate blank experiments carried out under exactly identical experimental conditions but with the iridium sample replaced by a sheet of tantalum showed no detectable formation of benzene and cyclohexene. However, the rate of hydrogenolysis, as indicated by the increase of $m/e = 15, 16, 29$ and 41 intensities was of the same order of magnitude as in the presence of an iridium sample. It was, therefore, not possible to measure reaction products other than dehydrogenation products.

The main dehydrogenation product was benzene, only minor amounts of cyclohexene, an intermediate in the reaction to benzene, were detected. The results are shown in Table I expressed as turnover numbers for the reactions (the number of benzene or cyclohexene molecules formed per metal atom per second), for two different temperatures viz 150°C and 250°C . The values in the Table are values averaged for three values measured experimentally

at the temperature indicated. The difference between the various rates is less than a factor of two. The stepped iridium surface appears to be more active in dehydrogenation than the (111) surface, the difference is a factor of three at 150°C and a factor of five at 250°C.

An actual metal catalyst in hydrocarbon reactions is always covered with a carbonaceous deposit. The presence of carbon on the surface may drastically change the chemical properties of the metal surface. It was found in our laboratory that carbon monoxide is molecularly adsorbed at room temperature on a clean iridium (110) surface while it is for a large part dissociatively adsorbed at room temperature on an iridium (110) surface covered with carbon.¹³ In the present study the amount of carbon on the surface was measured by means of Auger electron spectroscopy. It appeared that the amount of carbon deposited on the surface after a reaction experiment at 250°C is about twice the amount of carbon after an experiment performed at 150°C. This trend of increasing amount of carbonaceous deposit with increasing temperature has also been observed for platinum.¹⁰ The carbonaceous deposit on the iridium surface is not ordered as judged by LEED. The only effect of the carbon deposit on the LEED pattern is a large increase in the background intensity.

In order to investigate the effect of an ordered carbon layer on the dehydrogenation activity of iridium, the iridium (111) sample was heated for 30 minutes in a cyclohexane ambient of 10^{-7} Torr at a temperature of 900°C. As reported in a previous study⁴ carbon on an iridium (111) surface gives, under these experimental conditions, a LEED pattern corresponding to a (9×9) surface structure. This surface structure may be interpreted as a hexagonal overlayer of carbon similar to the structure of the basal plane of graphite.⁴

Turnover numbers for the dehydrogenation reaction performed on this surface are included in Table I. The activity for benzene formation is not different from that of the initially clean iridium (111) surface within the experimental accuracy. An interesting effect is that the amount of cyclohexene formed is larger than with the initially clean iridium surface. The LEED patterns observed after the reaction reveal that the surface still has a (9x9) structure.

Values of the turnover number for dehydrogenation of cyclohexane on platinum single crystal surfaces have been inserted in Table I. The values were reported by Blakely and Somorjai.¹⁰ The turnover number for the reaction was reported to be an order of magnitude larger on the platinum (S)-[6(111)x(100)] surface than on the platinum (111) surface.

In Table II values of turnover number are given for the dehydrocyclization of n-heptane to toluene on the iridium surface combined with corresponding values of the reaction on single crystal surfaces of platinum as found by Baron et al.¹² and values on polycrystalline iridium and platinum foils as measured by Hagen and Somorjai.¹⁴ The standard conditions of these experiments were: first hydrogen was admitted to a pressure of 2.5×10^{-4} Torr and then n-heptane was introduced into the chamber to a pressure of 5×10^{-5} Torr. The crystal temperature was below 40°C during admission of the n-heptane-hydrogen mixture. The temperature was then increased to the desired temperature and the composition of the gas phase was analyzed continuously. No toluene formation was detected in separate blank runs. The activity of both iridium surfaces was low. A temperature of 400°C was required in order to observe any dehydrocyclization reaction. After approximately five minutes at this temperature the reaction rate became constant and remained constant for at

least twenty minutes. A turnover number of $1 \times 10^{-6} \left(\frac{\text{toluene molecules}}{\text{sec metal atom}} \right)$ was calculated from this rate.

No significant differences in dehydrocyclization activity were detected on the originally clean iridium (111), the originally clean iridium (S)-[6(111)×(100)] and an iridium (111)-(9×9)C surface. This is different from platinum single crystal surfaces where reported values on the turnover number are an order of magnitude larger on stepped than on (111) surfaces.¹² After the experiments a large amount of carbon was deposited on the surfaces, close to a monolayer as judged by A.E.S.-L.E.E.D. observations showed that the carbon deposit was disordered on the iridium surfaces. However, when the experiment was carried out on the Ir(111)-C(9×9) surface, the carbon remains ordered on the surface with the (9×9) surface structure.

The activity of the two iridium surfaces in dehydrocyclization is much lower than that of similar surfaces of platinum. This is consistent with studies by Carter et al.¹⁵ who reported that at atmospheric pressure iridium powder has a much lower activity in dehydrocyclization of n-heptane than platinum powder. However, Hagen and Somorjai¹⁴ found that a polycrystalline iridium foil is more active in low pressure dehydrocyclization studies than a platinum foil. More studies will be required in order to understand these different results. It is possible that one type of stepped iridium surface which is absent on our iridium single crystal surfaces, but is well-represented on the polycrystalline surface, may be very active in the dehydrocyclization reaction.

It is of interest to compare the present results with those of our previous study⁴ on the adsorption of several hydrocarbon, ethylene, acetylene, benzene and cyclohexane, on the same iridium surfaces. It was found that

ordering of the hydrocarbon species is poor on both iridium surfaces. By adsorbing the hydrocarbon at 40°C and subsequently flashing the samples and analyzing the desorbing species it was found that the main desorbing species is hydrogen. After adsorption of acetylene and cyclohexane no desorption of any hydrocarbon could be detected. A few percent of the total amount of adsorbed ethylene could be desorbed by heating while the amount of desorbing benzene was of the same order of magnitude as the amount of desorbing hydrogen. The hydrogen thermal desorption spectra after adsorption of each of these hydrocarbons consists of two main peaks, one around 200°C and the second around 350°C. The relative contribution of these two peaks and the temperature ^{where they appear} structure of the depend slightly on the type of hydrocarbon and strongly on the ^{structure of the} iridium surface. From these observations and from the differences in the LEED patterns it was concluded that C-H bond breaking will occur more easily on a stepped iridium surface than on a iridium (111) surface. The present dehydrogenation study certainly supports this conclusion.

Significant differences in adsorption behavior of hydrocarbons were found to exist between similar surfaces of platinum and iridium.⁴ On Pt(111) the aromatic and unsaturated hydrocarbons are bound at room temperature for a large part undissociatively, as indicated by their thermal desorption and ordering, as found by means of the LEED patterns. On Ir(111) C-H (and possibly C-C) bond breaking occurs more easily than on Pt(111). On the stepped surfaces of platinum C-H bond breaking occurs easily just as on the stepped iridium surfaces. It is, therefore, not surprising that the differences in catalytic activity between a stepped iridium and an (111) iridium surface is smaller than the differences between similar platinum surfaces. The activity of the Ir(111) surface in dehydrogenation is larger than that of the Pt(111) surface.

In conclusion it may be stated that the present study demonstrates the crystal face specificity in low pressure catalysis for iridium. It also shows that the effect of the surface structure may be different for metals that are neighbours in the periodic table of elements in Group VIII.

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Table I

<u>Surface</u>	<u>Temperature (°C)</u>	<u>σ-benzene</u>	<u>σ-cyclohexene</u>
Ir(111)	150	0.3×10^{-5}	$< 0.2 \times 10^{-5}$
	250	0.5×10^{-5}	$< 0.2 \times 10^{-5}$
Ir(S)-[6(111)×(100)]	150	0.9×10^{-5}	$< 0.2 \times 10^{-5}$
		2.3×10^{-5}	$< 0.2 \times 10^{-5}$
Ir(111)-C(9×9)	150	0.3×10^{-5}	0.4×10^{-5}
	250	0.6×10^{-5}	0.3×10^{-5}
Pt(111)	150	0.1×10^{-5}	
Pt(S)-[6(111)×(100)]	150	1.1×10^{-5}	

Values of the turnover number σ (in $\frac{\text{molecules product}}{\text{sec metal atom}}$) for low pressure dehydrogenation of cyclohexane on single crystal surfaces of iridium (this study) and platinum (from ref. 10) for a hydrogen/cyclohexane ratio of 20.

Table II

<u>Surface</u>	<u>T(°C)</u>	<u>σ</u>	<u>Reference</u>
Ir(111)	400	1.8×10^{-6}	This work
Ir(S)-[6(111)×(100)]	400	1.2×10^{-6}	This work
Ir(111)-C(9×9)	400	1.6×10^{-6}	This work
Pt(111)	350	6×10^{-6}	12
Pt(S)-[n(111)×(100)] (n from 5-9)	350	2.10×10^{-5}	12
polycrystalline Pt foil	350	1×10^{-5}	12
polycrystalline Pt foil	400	2×10^{-6}	14
polycrystalline Ir foil	400	1×10^{-5}	14

Values of the turnover number σ (in $\frac{\text{molecules toluene}}{\text{sec metal atom}}$) for dehydrocyclization of n-heptane to toluene on iridium and platinum surfaces. Pressure of n-heptane and hydrogen are 5×10^{-5} Torr and 2.5×10^{-4} Torr, respectively.

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