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Low Pressure Studies of Dehydrocyclization of *n*-Heptane on Platinum Crystal Surfaces Using Mass Spectrometry, Auger Electron Spectroscopy, and Low Energy Electron Diffraction

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The dehydrocyclization of *n*-heptane on platinum crystal surfaces of area less than 1 cm^2 was studied in the temperature range of 100–400°C and at pressures in the 10^{-4} Torr range. The toluene formation rate was monitored in a static system by a mass spectrometer, the surface structure by low energy electron diffraction, and the surface composition by Auger electron spectroscopy. The (111) face and two types of stepped platinum crystal faces were used. The stepped surfaces exhibit a surface structure of ordered steps of monatomic height separated by terraces with (111) orientation for one face and by terraces of (100) orientation for the other. The initial rate of toluene formation on the stepped surface with (111) terraces is twice as fast as on the surface with (100) terraces and the reaction can be sustained in the presence of hydrogen for more than an hour. A new $(\sqrt{3} \times \sqrt{3})$-R30° surface structure which develops in the course of the reaction or a (9×9) surface structure which appears upon heat treatment to 850°C have no detrimental effect on the reactivity. These surface structures can be attributed to the presence of ordered carbon at the platinum surface.

Under identical conditions, the toluene yield of the stepped surface with (100) terraces decreases steadily as a function of the number of doses and reaches the detection limit after about an hour. The low index (111) surface appears to be less reactive than the stepped surface with (111) terraces by at least an order of magnitude. Both of the less reactive surfaces become covered by a disordered carbon-containing layer during the reaction.

The presence of hydrogen during the reaction appears to reduce the rate of dissociative chemisorption of *n*-heptane, so that the dehydrocyclization can successfully compete with it.

INTRODUCTION

The relationship between the structure of solid surfaces and their reactivity is one of the most important questions in modern heterogeneous catalysis. A great deal of experimental evidence (*1–5*) accumulated in recent years which indicates that the atomic structure of the surface has a marked influence on the nature and rate of surface reactions. The broader application of low energy electron diffraction (LEED) as a tool to detect surface structures should have allowed advances in this area. Progress, however, has been retarded for two reasons. The first concerns the very small areas of single crystals which are used in LEED experiments ($\leqslant 1$ cm^2). It was unclear whether the rather low rates of many catalytic processes would yield

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detectable quantities of products. The second problem involves the simulation of the surface structure of small catalyst particles used in most industrial processes. These surfaces may have surface structures which are different from low-index crystal faces of low surface free energy, which were used in most LEED studies. It appears that both of these problems have been overcome in the study reported in this paper. Catalytic reactions of low reaction probability on a single crystal surface of area $\leqslant 1$ cm^2 could be monitored using a mass spectrometer and reactant pressures of $\sim 10^{-4}$ Torr in a modified low-energy electron diffraction chamber. Recent low-energy electron diffraction studies revealed (*6*) that not only low Miller-index crystal faces show sufficient thermal stability to be considered important in catalytic studies, but also certain high Miller index crystal faces which exhibit ordered atomic steps. The properties of the various low index and stepped surfaces differed widely, however, during chemisorption and in the formation of ordered surface structures of chemisorbed gases (*7*). Since catalytic studies utilize small polydispersed particles which are likely to have both low index and stepped surfaces, it would be important to study selectively the catalytic properties of surfaces differing by their atomic structures.

In this paper, we report on an investigation of the dehydrocyclization of *n*-heptane to toluene on a (111) face and two stepped faces of platinum. Platinum was selected since it is one of the most versatile catalysts which is also specific for the dehydrocyclization of *n*-heptane. The surface reaction was studied at 100–400°C in the presence of varying partial pressures of hydrogen. The study was carried out at low total pressure (2×10^{-4} Torr) under static conditions and the formation of toluene was monitored by a quadrupole mass spectrometer (QMS). The surface structures of the platinum and those of the adsorbed gas were monitored by LEED. The surface composition was monitored by Auger electron spectroscopy (AES) which could detect the presence of unwanted impurities in concentrations of about 1% of a monolayer [10^{13} atoms/cm^2]. The reader is referred to recent reviews (*8–10*) for the detailed description of these techniques and their various applications.

We have found the stepped platinum surface with terraces of (111) orientation more reactive for dehydrocyclization than either the stepped platinum surface with terraces of (100) orientation or the Pt(111) face. The sensitivity of the three techniques used to determine the surface structure (LEED), surface composition (AES), and gas phase composition (QMS) makes catalytic reaction studies on single crystal surfaces feasible and permits definitive studies of the correlation between catalytic activity and surface structure.

EXPERIMENTAL

A scheme of the ultra-high vacuum apparatus used in these low-pressure catalytic studies is shown in Fig. 1. The diffraction chamber, which is used as a reaction chamber in this study, is coated with a thin gold film to reduce the rate of wall reactions, which might compete with the surface reaction taking place on the platinum sample of much smaller surface area ($\leqslant 1$ cm^2). The reactant gases are introduced through a needle so that their contact with the platinum crystal surface is assured before any collision with the wall chamber can occur. The gate-valve between the reaction chamber and the ion pump allows the reaction to occur under static conditions or in a controlled flow. It was found that static conditions (closed gate-valve) were necessary in order to monitor the toluene yield reliably using the mass spectrometer. The ambient pressure is in the 10^{-9} Torr range before the introduction of *n*-heptane, the ambient gases being mainly CO and H_2. The crystal sample is heated by resistance through the polycrystalline platinum holder and the temperature is monitored by a thermocouple (Pt–Pt 10% Rh) which is spot-welded to the back of the crystal. The reactivity of the polycrystalline Pt holder is checked in a separate experiment.

The cleaning of the various single-crystal surfaces of platinum has been studied in detail and described elsewhere (*11*). In

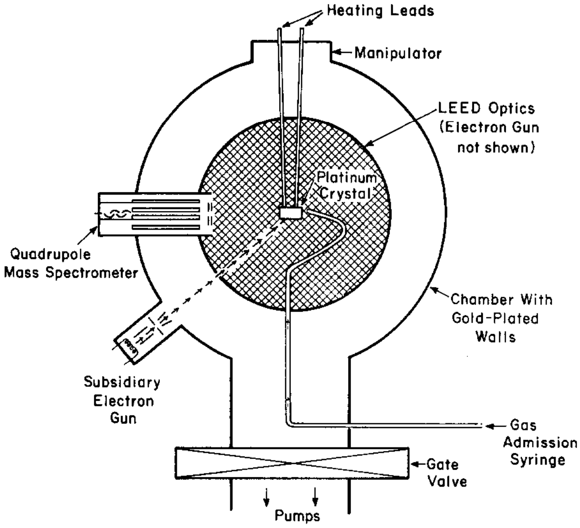

FIG. 1. Schematic diagram of the reaction chamber.

brief, carbon which is the major contaminant in the high-purity single crystal* is removed by heat treatment in oxygen. Any adsorbed oxygen is removed by subsequent heating in vacuum. The surface cleanliness was ascertained by Auger electron spectroscopy, which readily detects carbon, oxygen, and impurities other than hydrogen at the surface. An Auger spectrum, which is characteristic of clean platinum, could be readily obtained after the chemical cleaning and is shown in Fig. 2.

The *n*-heptane exhibits the well-known fragmentation pattern upon electron impact ionization in the QMS, which is published in the API tables (*12*). Toluene, which is the product of the dehydrocyclization of *n*-heptane, can easily be recognized in the mass spectrum by the appearance of the $(m/e) = 91$ and 92 peaks with a known intensity ratio (4:3), since at these masses there are no peaks due to the fragmentation of *n*-heptane. Typical mass spectra of *n*-heptane and toluene are shown in Fig. 3. The surface reaction of *n*-heptane on platinum, which is carried out usually in the temperature range of 250–350°C, yields several other products (e.g., *n*-heptane isomers, dimethylcyclopentanes, etc.) and the existence of some of these is apparent from the mass spectra. No peak of these other products exists in the $(m/e) = 91$–92 region, the closest peaks are located at

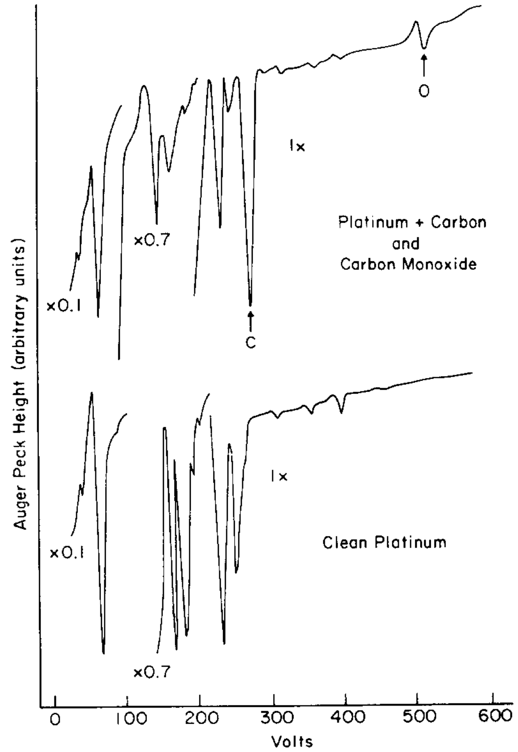

FIG. 2. Auger spectra of platinum with and without carbon.

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* Obtained from Materials Research Corp., Orangeburg, NY.

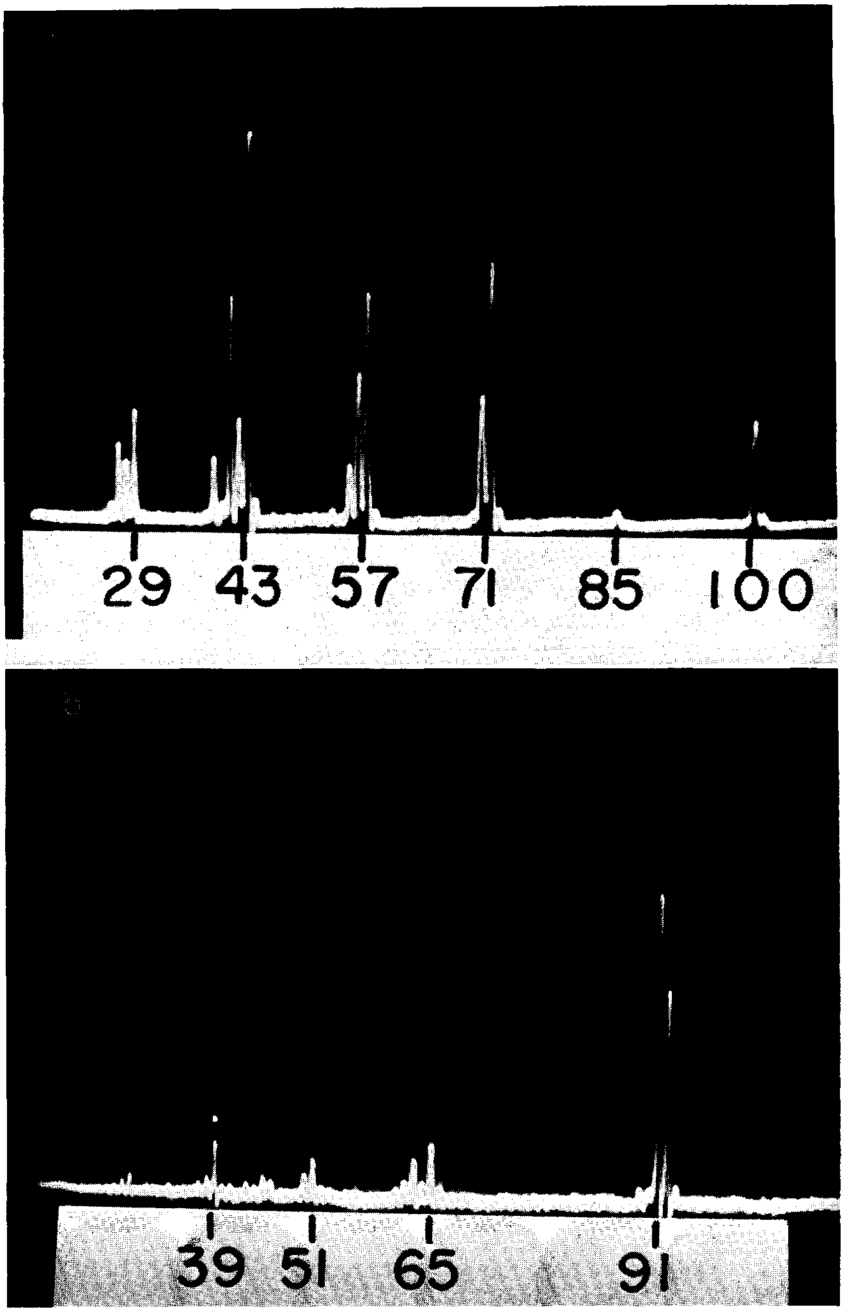

FIG. 3. Mass spectra: a: *n*-heptane; b: toluene.

$(m/e) = 86$ and 98. No attempt was made, however, to sort out the various reaction products as the appearance of toluene was the only surface reaction of interest in this study. The *n*-heptane forms toluene on the platinum surface according to the net reaction:

$$C_7H_{16}(\text{gas}) \rightarrow C_7H_8(\text{gas}) + 4\ H_2(\text{gas})$$

Thus, hydrogen is being produced by this surface chemical reaction.

Studies of the dehydrocyclization of *n*-heptane were carried out in the presence of hydrogen using *n*-heptane–hydrogen mixtures in the ratio of 1:1–1:5. The total pressure was maintained at 2×10^{-4} Torr which gave optimum detection conditions using the mass spectrometer.

It would be important to use the intensities of the toluene peaks detected during the reaction in order to calculate reaction rates. Therefore, the mass spectrometer (EAI Quad 200) was calibrated for toluene. The intensity of the $(m/e) = 91$ toluene peak is measured in arbitrary units with the correspondence $1.0 = 2.0 \times 10^{-8}$ Torr. The minimum partial pressure of toluene which is detectable by our mass spectrometer is $0.2 = 4 \times 10^{-9}$ Torr in the presence of *n*-heptane and other hydrocarbons formed during the reaction of *n*-heptane on platinum. If pure toluene would be present in the vapor phase, a toluene pressure of less than 1×10^{-9} Torr could be detected.

The typical procedure followed in the course of an experiment is as follows:

(1) Cleaning of the platinum surface by oxygen treatment (3×10^{-7} Torr O_2; 850°C; 30 min).

(2) Cooling of the crystal in ultra-high vacuum until its temperature is in the range 120–140°C.

(3) Introduction of the mixture *n*-heptane + hydrogen (ratio in the range 1:1–1:5) while closing the gate valve. A total pressure of 2×10^{-4} Torr is established within 1 min after the closure of the gate-valve and the initial mass spectrum recorded.

(4) Heating of the crystal to a temperature in the range 250–350°C. The maximum of the toluene peak is recorded.

(5) The reaction mixture is pumped, while the crystal is kept at reaction temperature, and then a second dose of the reactant mixture is admitted.

(6) Evacuation and admission of a third dose, etc.

THE STRUCTURE AND CHEMISORPTION CHARACTERISTICS OF STEPPED PLATINUM SURFACES

The stepped platinum surfaces which were used in this study were prepared by cutting a single crystal sample (a) 9.5° from the (111) face towards the (100) face, and (b) 9.0° from the (100) face towards the (111) face (*6*). These crystallographic orientations can be identified by their Miller indices as (755) and (911), respectively. The orientation was determined by the back-reflection Laue technique with an accuracy of ±½°. After placing these samples into the diffraction chamber, cleaning by heating in oxygen and subsequently in vacuum, the diffraction patterns shown in Figs. 4a and b were obtained. The patterns differ from those expected from crystals with low index (111) or (100) faces (Fig. 5) only in that the spots appear as doublets at certain voltages. This splitting was shown to be due to the presence of ordered steps on the surface (*6*). The stepped surface with (111) terraces (Fig. 4a) has the usual (1 × 1) surface structure. The stepped surface with (100) terraces (Fig. 4b) has the (5 × 1) surface structure commonly found on the Pt(100) face with only one domain having its period of 5 normal to the step direction. Detailed analysis of the diffraction features revealed (*6*) that these stepped surfaces consist of terraces of low Miller-index [(111) or (100)] which are linked by steps of monatomic height. The schematic diagrams of the stepped surfaces corresponding to the diffraction patterns of Figs. 4a and b are shown in Figs. 4c and d. Since the indices give little physical insight into the atomic structure of the stepped surface, a suitable nomenclature has been devised (*6*). One of the surfaces can be designated as Pt(S)-[6(111) × (100)]. The postscript (S) indicates a stepped surface, 6(111) designates a terrace of (111) orientation, 6 atomic rows in width, and 1(100), or simply (100), designates a step of (100) orientation and one atomic layer high. In the same manner, the other surface is designated as Pt(S)-[5(100) × (111)].

Platinum surfaces, which possess ordered steps of monatomic height, show remarkable thermal stability (*6*). Ordered arrays of steps were noted on other metals and on semiconductors and thus must be a general structural property of high-index surfaces, regardless of the chemical bonding in the crystal.

Studies of the chemisorption of hydrogen, oxygen, carbon monoxide, ethylene, and

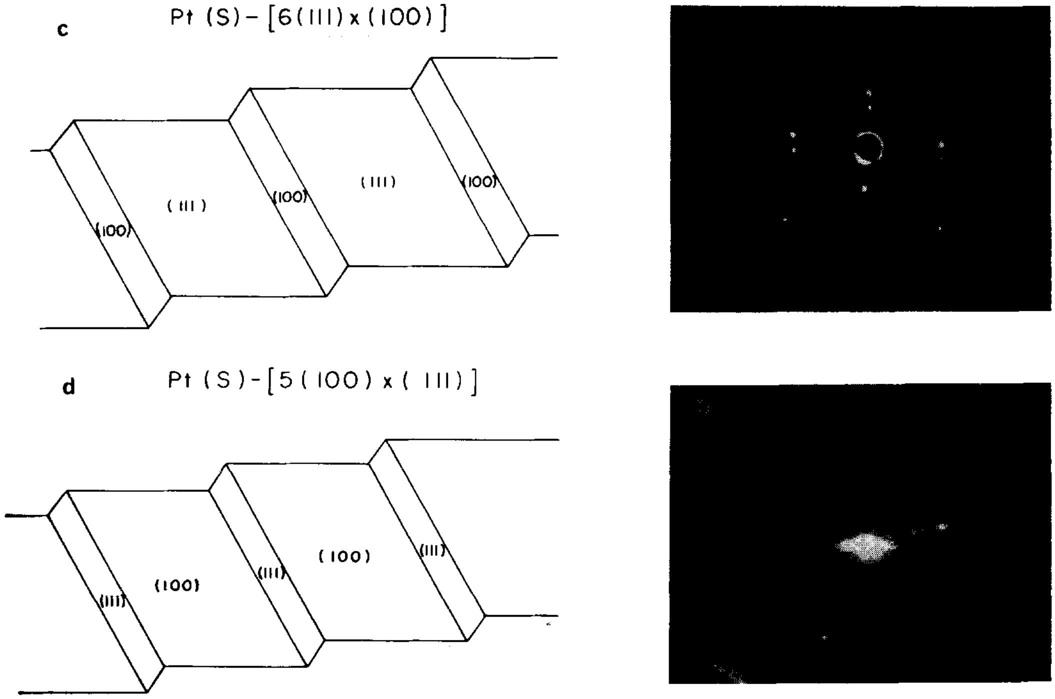

FIG. 4. a: LEED pattern of the Pt(S)-[6(111) × (100)] surface; b: LEED pattern of the Pt(s)-[5(100) × (111)] surface; c: Schematic diagram of the Pt(S)-[6(111) × (100)] surface; d: Schematic diagram of the Pt(S)-[5(100) × (111)] surface.

carbon on stepped surfaces reveal (7) that the chemisorption characteristics are markedly different compared to low-index surfaces. Hydrogen and oxygen, which do not chemisorb easily on the (111) and (100) platinum crystal faces, chemisorb readily at low pressures and temperatures. In the presence of hydrogen, new ordered surface structures form and there is strong evidence for dissociation at the steps and subsequent dissolution in the crystal lattice. In contrast with the ordered adsorption on low-index faces, the adsorption of carbon monoxide and ethylene was disordered on the stepped surfaces and this may be explicable in terms of dissociation of the molecules at the steps. Carbon, which diffused to the surface from the bulk of the crystal or was deposited by heating to high temperatures in the presence of hydrocarbons, also formed several ordered structures which were not observed on low index faces, where it yields directly a disordered graphitic layer. It appears that dissociation of diatomic molecules and breaking of carbon–carbon and carbon–hydrogen bonds occur on stepped surfaces much more readily than on low-index faces, which should have much smaller concentrations of steps.

RESULTS

Dehydrocyclization of n-heptane on the Pt(S)-[6(111) × (100)] Surface

When the *n*-heptane-hydrogen mixture is introduced into the reaction chamber at a total pressure of 2×10^{-4} Torr, as described in the experimental section, the amount of toluene formed is monitored continuously by the mass spectrometer. As the crystal is heated, the toluene peak increases at once and reaches its maximum of 2.2 in about 4 min. The signal height remains unchanged for about 10 min and then decreases slowly with time. After evacuation and the admission of subsequent doses of the reactant mixture, there is little change in the amount of toluene formed. Thus, it appears that this surface retains its activity over a period longer than an hour.

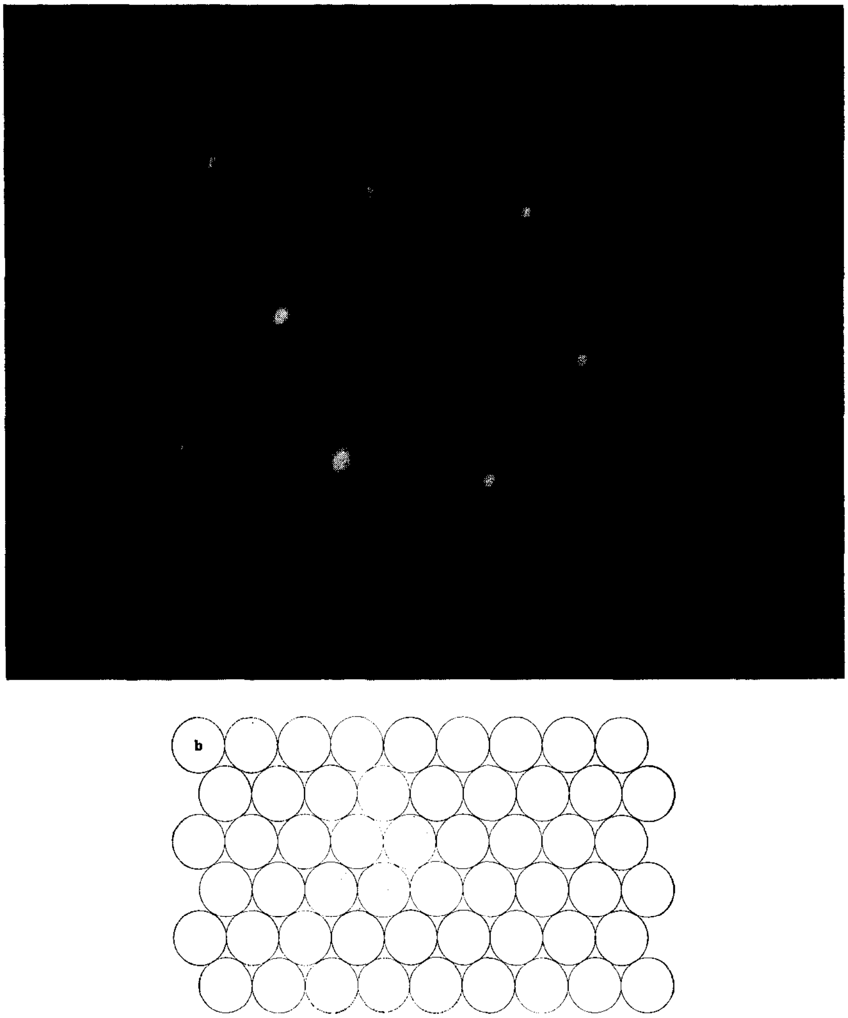

Fig. 5. a: LEED pattern of the Pt(111) face; b: Schematic diagram of the Pt(111) face.

The toluene yield is not affected by either evacuation of the reaction chamber, or by cooling the sample to investigate its diffraction pattern then (after 15 min) reestablishing the conditions of the reaction. The activity is not affected by keeping the sample at 300°C in vacuum for 15 min and drops only slightly after 30 min at this temperature.

Although most of the experiments were carried out in the temperature range 250–350°C, the toluene-forming ability of the crystal could be tested at low temperatures by varying the temperature of the sample (stages 2 and 3 of the experimental procedure). If the initial temperature is only 60°C, the initial peak height is about 3 times lower than at 130°C, but still 3 times higher than the minimum detectable. Thus it appears that platinum shows an appreciable activity for dehydrocyclization even below 100°C.

Since the Pt(S)-[6(111) × (100)] surface showed continued activity in the dehydrocyclization of *n*-heptane, its diffraction pattern was monitored by LEED at various stages of the reaction. These intermittent tests did not appear to have any effect on the catalytic reaction. Before the reaction begins, the surface exhibits the diffraction pattern shown in Fig. 4a: sharp, intense doublets in a dark background indicating well-ordered domains with (1 × 1) unit cell on the (111) terraces. After 15 min of reaction, the substrate diffraction spots are still the only ones visible, but now emerging from a high background intensity, which indicates increased disorder on the surface. After 30 min of reaction (i.e., two doses), new diffraction spots (sharp, but weak) are seen, corresponding to a $(\sqrt{3}\times\sqrt{3})$-R30° unit cell on the (111) terraces. The background intensity is still high. This LEED pattern is unchanged after 60 min of reaction. The diffraction pattern and a schematic representation of one of the surface structures which can give rise to such a pattern are shown in Fig. 6. The stability of this new surface structure has been investigated. It is stable in ultrahigh vacuum for at least 24 hr at 280°C. Increasing the temperature (with short heating times of 3 min) indicates that it is stable below 600°C; it disappears at 650°C, while the array of steps becomes disordered. At 850°C, a new complex pattern appears, which can be indexed (9 × 9). The diffracted intensity is concentrated in those areas of the pattern surrounding the substrate spots and the $(\sqrt{3}\times\sqrt{3})$-R30° spots. The (9 × 9) structure can be interpreted as a coincidence lattice of a layer of graphite on top of a $(\sqrt{3}\times\sqrt{3})$-R30° layer, the unit-cell vectors of the graphite layer being parallel to those of the clean platinum substrate. The ratio of the unit-cell vectors is: $\mathbf{a}(\text{graphite})/\mathbf{a}(\text{Pt}) = 9/10$. The surface, exhibiting either a $(\sqrt{3}\times\sqrt{3})$-R30° or a (9 × 9) LEED pattern, has an activity for toluene formation comparable to that of the clean surface. It is interesting to note that flashing the surface after

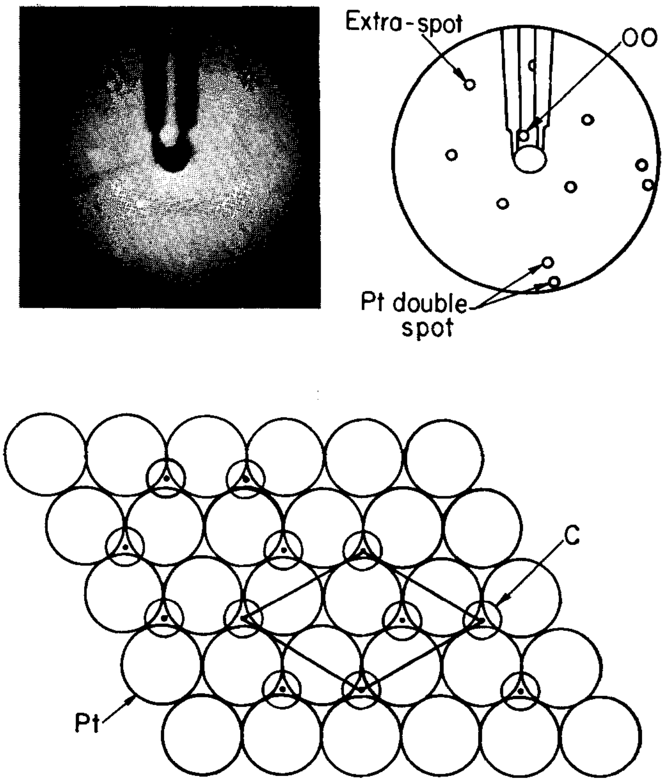

FIG. 6. a: LEED pattern of the Pt(S)-[6(111) × (100)]-$(\sqrt{3}\times\sqrt{3})$-R30° structure, 43 V; b: Schematic diagram of the LEED pattern shown in 6a; c: Schematic diagram of one of the possible surface structures with the $(\sqrt{3}\times\sqrt{3})$-R30° unit cell underlined.

the reaction did not produce the ring-like pattern of rotationally disordered graphite, which is commonly observed on the (111) or (100) faces of platinum. This confirms the tendency of the Pt(S)-[6(111) × (100)] surface to form preferrentially ordered structures when heated in the presence of carbon (7).

Dehydrocyclization of n-Heptane on the Pt(S)-[5(100) × (111)] Surface

Upon heating the crystal in the n-heptane-hydrogen mixture, the toluene signal increases and reaches a maximum of 1.3 in about 8 min. It remains unchanged for 10 min and then decreases slowly with time. There is a decrease by a factor of 2 upon admission of each successive dose, so that, after the third dose, the peak height becomes close to the minimum detectable.

Before the reaction begins, the surface exhibits the LEED pattern shown in Fig. 4b, characteristic of a (5×1) surface structure. As soon as n-heptane is introduced, the extra spots disappear and the pattern reveals only the integral order spots characteristic of the (1×1) surface structure on the (100) terraces. When the diffraction pattern is checked at various stages of the reaction, it shows the same spots, but with a high background intensity. Thus, the surface becomes disordered and there is no indication of the formation of a new surface structure as on the other stepped surface.

Dehydrocyclization of n-Heptane on the Pt(111) Surface

Upon admission of the n-heptane–hydrogen mixture and heating of the crystal, the toluene peak rises and reaches a maximum of 0.5 after about 12 min. The toluene peak is small, however, and when a second dose is admitted, becomes barely detectable.

Although a (2×2) diffraction pattern can be initially detected in the presence of n-heptane, it does not persist when the crystal is brought to the reaction temperature (250–350°C). In the course of the reaction, the only change in the LEED pattern is an increase in background intensity, indicating the presence of a disordered adsorption layer.

Dehydrocyclization of n-Heptane on Polycrystalline Platinum

The reactivity of the polycrystalline platinum strips supporting the single crystal sample has been investigated in a separate experiment. For this particular reaction, the yield appears to be very small. The toluene peak is just above the limit of detection and becomes indistinguishable from the background upon admission of further doses. It should be noted, however, that for other reactions tested (for example, the dehydrogenation of cyclohexane which will be discussed in a subsequent report), the polycrystalline platinum foil has a reactivity comparable to that of a single crystal sample.

DISCUSSION

The results indicate that dehydrocyclization of n-heptane can readily be detected using samples with surface area of the order of 1 cm^2. It is worth noting the potential of this type of study, since toluene formation represents only a few percent of the overall surface reaction (*13*). The study of catalytic reactions on small area single crystals should therefore be very fruitful, regardless of whether the product yield is large or small.

The results also demonstrate an important dependence of toluene yield on surface structure. These are summarized in Table 1. The conditions of the reaction (static system, time-dependent change in the reactant concentration) do not allow, at present, the quantitative determination of reaction rates ($cm^{-2}sec^{-1}$). However, we can estimate the initial rates from the data of Table 1. It appears that the stepped surface with (111) terraces is more reactive by about a factor of 2 than the stepped surface with (100) terraces. As a function of the number of doses, the difference in reactivity becomes much larger (4–5 times) after about an hour reaction time. The stepped surface with (111) terraces ap-

TABLE 1

The Surface Area of the Different Platinum Samples, the Maximum Toluene Peak Intensity, and the Time Necessary to Obtain the Maximum Peak Intensity

Sample structure	Geometrical area (cm^2)	Time to obtain maximum peak intensity (min)	Maximum toluene peak intensity (arbitrary units)		
			1st dose	2nd dose	3rd dose
Pt(S)-[6(111) × (100)]	0.85	4	2.2	2.0	1.5
Pt(S)-[5(100) × (111)]	0.5	8	1.3	0.7	0.4
Pt(111)	1.25	12	0.5	$\leqslant 0.2$	0
Pt polycrystal	1.2	8	0.3	0	0

pears nearly 20 times more reactive than the Pt(111) surface. Thus, the reactivities are in the order:

$$\mathrm{Pt(S)\text{-}[6(111)\times(100)]} > \mathrm{Pt(S)\text{-}[5(100)\times(111)]} > \mathrm{Pt(111)}.$$

So far, the differences in reactivity between our samples have been correlated with the structures of the clean platinum substrates. Clearly, the clean surface condition does not persist during the reaction. The surface becomes covered by a carbon-containing layer, as shown by the presence of a strong carbon Auger peak. The high and relatively constant reactivity of the Pt(S)-[6(111) × (100)] surface can be associated with the presence of an ordered $(\sqrt{3}\times\sqrt{3})$-R30° surface structure, while the less reactive surfaces are covered by a disordered carbonaceous layer. The reactivity is retained in the presence of the (9 × 9) surface structure on the highly reactive surface. Although this (9 × 9) structure is not likely to form under the experimental conditions which are commonly encountered during the dehydrocyclization of *n*-heptane, these results indicate that conversion to toluene may take place in the presence of more than one type of surface structure.

The difference in reactivity between the Pt(S)-[6(111) × (100)] and Pt(111) surfaces can be ascribed to the presence of a high density of ordered steps. Apart from their activity in dissociating diatomic molecules (7), steps appear important in nucleating the formation of ordered carbon-containing structures. The $(\sqrt{3}\times\sqrt{3})$-R30° structure, which does not form on the Pt(111) face, provides an example of ordering induced by the presence of steps. The carbon-containing layer, which forms on the Pt(111) surface at the reaction temperature, is disordered. In addition, previous results (7) indicate that the dissociative chemisorption of hydrogen takes place more easily on stepped than on low-index platinum surfaces. Thus the stepped surface is expected to be more reactive, if hydrogen plays a role in the dehydrocyclization.

The somewhat larger (by a factor of 2) reactivity of the stepped surface with (111) terraces, as compared to the stepped surface with (100) terraces, may be due to the difference in rotational symmetry between the two surfaces. However, the rapid deterioration of the reactivity of the Pt(S)-[5(100) × (111)] surface as a function of time may be due to the formation of a disordered carbon-containing layer, while the reactivity of the Pt(S)-[6(111) × (100)] surface remains virtually unchanged as the ordered carbonaceous $(\sqrt{3}\times\sqrt{3})$-R30° structure forms.

In the absence of hydrogen, the toluene yield is reduced for all of the crystal faces and it appears that toluene formation is reduced more rapidly as a function of time. Although it is difficult to assess the role of hydrogen in this hydrogen-producing reaction, it is likely that the presence of adsorbed hydrogen retards the rate of dehydrogenation of *n*-heptane, so that dehydrocyclization can proceed.

Studies are in progress to determine the reaction rates on the various platinum surfaces, the role of hydrogen, and to further explore the role of ordering in the surface layer during the dehydrocyclization reaction.

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