The Structure Sensitivity of Cyclohexane Dehydrogenation and Hydrogenolysis Catalyzed by Platinum Single Crystals at Atmospheric Pressure

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The dehydrogenation and hydrogenolysis of cyclohexane catalyzed by platinum single-crystal surfaces has been investigated at total reactant pressures of 115 to 760 Torr and temperatures of 533 to 573 K. The flat (111), stepped (557), and kinked (25, 10, 7) and (10, 8, 7) surfaces used in this study were characterized in ultrahigh vacuum by low-energy electron diffraction and Auger electron spectroscopy, before and after reaction experiments. Benzene, cyclohexene, n-hexane, and alkane fragments with carbon number less than 6 were observed as reaction products. The rate of dehydrogenation to benzene on the four surfaces increased in the order (111) < (557) < (10, 8, 7) < (25, 10, 7). On the other and, the hydrogenolysis rates and the rate of cyclohexene production were highest on the (111) surface. In general, the reaction rates decreased with increasing reaction time. The decrease of the dehydrogenation rates was due to reversible product inhibition by benzene, as well as the irreversible adsorption of tightly bound carbonaceous deposits. The hydrogenolysis rates did not exhibit product inhibition and decreased solely as the result of the irreversibly adsorbed carbonaceous species. The strength of inhibition by benzene increased in the order (25, 10, 7) < (10, 8, 7) < (557) < (111). These high-pressure results using single-crystal catalysts are compared to similar studies previously performed at pressures of less than 10^{-5} Torr. A comparison is also made to studies by others using dispersed platinum catalysts.

INTRODUCTION

The relationship between catalyst structure and catalytic activity, selectivity, and stability is a major concern in the study of heterogeneous catalysis. A catalyzed reaction is considered structure sensitive if its specific rate varies with particle size, and structure insensitive if its specific rate is invariant with changing particle size (*1*). These effects are most apparent in the particle size range of 10–40 Å, where the surface structure is expected to depend most strongly on particle size (*2–5*). Cyclohexane dehydrogenation (*6–9*) and benzene hydrogenation (*10–12*) over platinum have been found to be structure-insensitive reactions. On the other hand, hydrogenolysis

reactions have generally been observed to be structure sensitive (*13–15*). The interpretation of such structure sensitivity studies is difficult since the actual surface structure and composition of the metal particles can only be inferred indirectly. Also, metal-support interactions and nonuniform particle size distributions further add to the difficulties of interpretation.

Single-crystal platinum catalysts offer the distinct advantage of allowing direct determination of surface structure and composition. Such surfaces can be prepared with variable concentrations of low-coordination step and kink sites. These may be the structural features whose concentrations vary as the particle size of dispersed catalysts is varied. Previous studies in this laboratory have demonstrated the importance of these special sites in controlling the activity and selectivity for several catalyzed hydrocarbon reactions (*16–18*). These single-crystal surfaces are amenable

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to direct determination of surface structure by low-energy electron diffraction (LEED) and elemental composition by Auger electron spectroscopy (AES).

We report here a study of cyclohexane dehydrogenation and hydrogenolysis catalyzed by well-characterized platinum single-crystal surfaces. This investigation has been carried out at total reactant pressures of 115 to 760 Torr. This pressure regime will be referred to throughout this paper as high pressure. As a result of the high pressures employed, it is possible to directly compare the rates, selectivities, and deactivation behavior of the single-crystal catalysts of varied atomic structure to similar results with dispersed metal catalysts. Since we have also studied these reactions on platinum single-crystal surfaces at low reactant pressures ($\sim 10^{-8}$–10^{-5} Torr) (16–18), the pressure dependence of cyclohexane dehydrogenation and hydrogenolysis can also be explored. In addition, we have studied the influence of preoxidation of the single-crystal catalysts on the rates and selectivities at high pressure, since previous low-pressure studies (17, 18) revealed important changes in catalytic behavior due to the presence of surface oxide.

EXPERIMENTAL

Apparatus

The experimental apparatus used in the majority of our studies is shown schematically in Fig. 1 and has been described in detail elsewhere (19). Using this system, the single-crystal surfaces are prepared and characterized under ultrahigh vacuum, and catalytic studies performed at pressures up to 1 atm. This is accomplished by means of a movable reaction cell capable of enclosing the sample in a small volume, thus isolating it from the main chamber. Reaction studies are performed by introducing the reactants into this volume and resistively heating the crystal to reaction temperature. The gases are circulated by a metal bellows pump and analyzed by flame ionization gas chromatography. The system operates as a well-stirred batch reactor with a volume of 744 cm^3.

Surface analysis is accomplished by means of a standard Varian four-grid electron optics. This analyzer allows display of the LEED pattern, as well as serving as an electron energy analyzer for AES measurements. Figure 2 illustrates typical AES spectra before and after reaction.

The crystals were mounted in the reactor as depicted in Fig. 1. This arrangement allowed the sample to be heated to greater than 1500 K for cleaning and annealing, did not introduce any contamination to the crystal, and contributed no more than 5% of the total activity. The temperature was monitored by a chromel–alumel thermo-
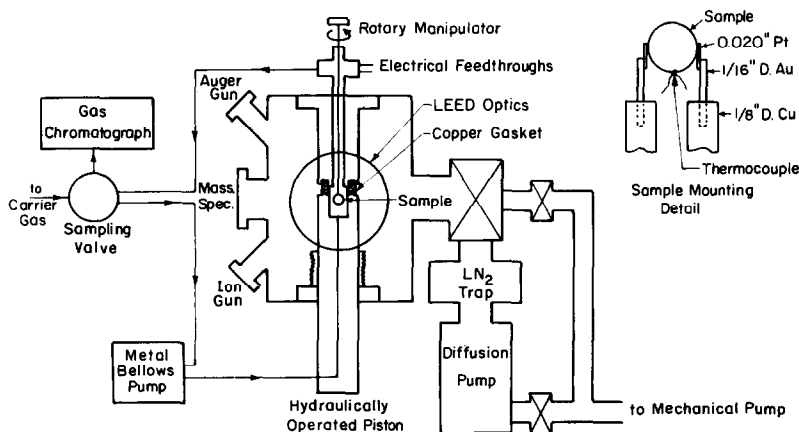

FIG. 1. Schematic diagram of high pressure–low pressure surface analysis reaction apparatus.
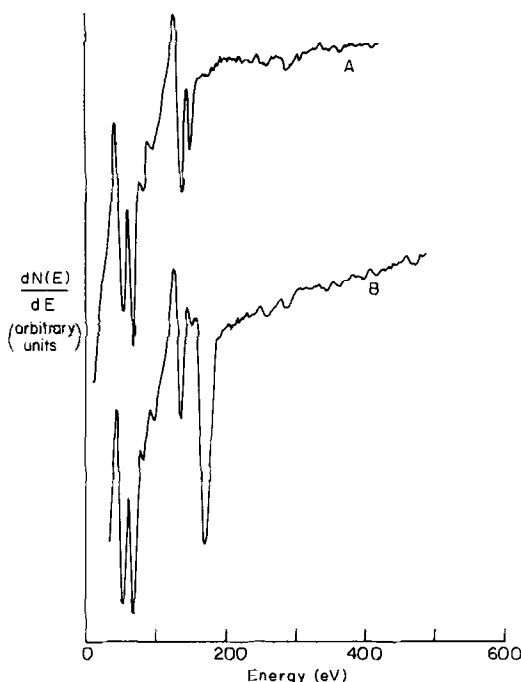
FIG. 2. Typical Auger spectra; (A) clean surface before reaction, (B) surface after reaction covered with about 0.6 monolayer of carbon.

couple spotwelded to the edge of the crystal.

Many of the experiments reported here were also performed in a second high pressure–low pressure reaction apparatus described in detail elsewhere (26, 32). The experiments performed in the second system utilized different reagents, slightly different procedures, and different single-crystal samples. Rather than use the gold–platinum mounting scheme as shown in Fig. 1, the samples were mounted in the second apparatus by spotwelding them directly to tantalum support leads. Comparison of the two sets of data thus affords an excellent check on the reliability of our structure sensitivity studies.

Materials

The 1-mm-thick platinum crystals were prepared by usual metallographic procedures with both faces polished to within 1° of the desired orientation. However, still present are the multifaceted edges which

account for about 25% of the total area of each crystal. It is assumed here that this unoriented area is about the same from crystal to crystal. As a result, differences in results on various surface structures appear smaller than they would be if all the active surface had the same orientation. The surface area used to calculate specific rates is the total macroscopic geometric area of the crystal.

The four surfaces used in this study were the (111), (557), (10, 8, 7), and (25, 10, 7) in simple Miller index notation, or more illustratively (20), the Pt(111), Pt(S) − [5_5(111) + 2_1(100)], Pt(S) − [7_{14}(111) + 1(110) + 2_2(100)], and Pt(S) − [7_{14}(111) + 15_{15}(100) + 3_3(110)] in microfacet notation. Idealized schematic representations of these surfaces are presented in Fig. 3. The (111) surface is a hexagonally close-packed array of atoms. The (557) crystal face is a stepped surface consisting of six-atom-wide terraces of (111) orientation separated by highly unsaturated one-atom-high steps. The other two crystal surfaces have high concentrations of kink sites, which are more highly unsaturated than the step atoms. The (10, 8, 7) surface has approximately seven-atom-wide terraces and steps of (310) orientation resulting in a density of kink sites of about 6% of the total surface atom concentration. The (25, 10, 7) surface has (610) orientation steps, two-atom-wide terraces, and a kink density of about 9%. These surfaces all appear to be structurally stable under the conditions of these experiments.

The cyclohexane was obtained from Phillips Petroleum Company and further purified by repeated freezing–degassing cycles. The resultant hydrocarbon was shown by gas chromatography to have a purity of greater than 99.99%. The hydrogen and nitrogen were both 99.99% pure and used as received.

Procedure

The single-crystal surfaces were cleaned under vacuum prior to reaction studies by

fcc (III)   fcc (10, 8, 7)

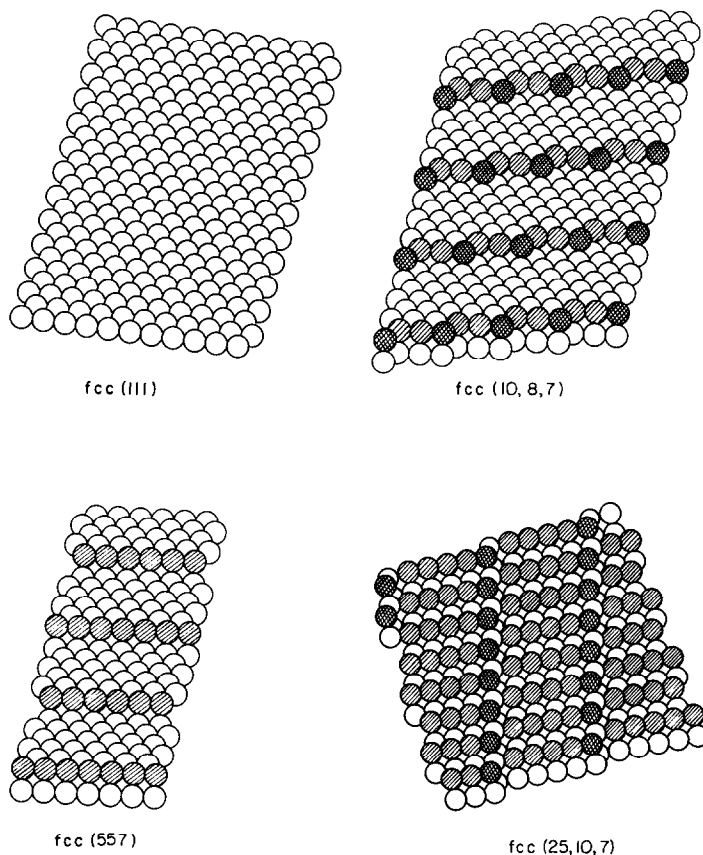fcc (557)   fcc (25, 10, 7)

FIG. 3. Schematic representation of the four surface structures used in this study.

argon ion bombardment and annealing, oxygen treatment at elevated temperatures and annealing, or a combination of these two techniques. The specific method of surface preparation had no influence on catalyst behavior as long as the surfaces were well annealed and judged to be clean by AES.

Once the surface had been prepared and an Auger spectrum obtained of each side, the crystal was flashed to about 1123 K to remove any adsorbed background gases. As the temperature of the crystal decreased below 573 K, the reaction cell was closed and 400-Torr hydrogen was admitted as rapidly as possible to cool the crystal and crystal holders and minimize the adsorption of background gases. The hydrogen was pumped out after the crystal had cooled to below 315 K, and then the reaction mixture

introduced. The order in which the reactants were added did not matter, but generally the cyclohexane was admitted first by evaporation followed by admission of the hydrogen. The total pressure was then increased to 760 Torr by addition of nitrogen as an inert diluent. At least one chromatograph sample was taken before the catalyst was heated to check that no reaction occurred while the crystal remained at room temperature. The catalyst was then heated to reaction temperature in a period of about 2 min and zero time was taken as the time at which the crystal reached this temperature. The temperature was maintained to ± 2 K during kinetic studies. After the reaction had proceeded for the desired length of time, the crystal was cooled in the reaction mixture and then the reactor pumped out. The cell was then opened and the crystal

flashed momentarily to reaction temperature. An Auger spectrum was then recorded as rapidly as possible since the electron beam and the high hydrocarbon background caused deposition of additional carbon. As evidenced by spectrum B in Fig. 2, contamination of the surface by sulfur was not observed.

The calibration used for the quantitative estimation of the concentration of surface carbon is that of Biberian and Somorjai (21). Their method consists of plotting adsorbate Auger peak heights versus substrate Auger peak heights and relating a break in the resulting curve to completion of the first monolayer. Application of this calibration to the present study assumes that no carbon is deposited below the surface.

Initial reaction rates were determined by graphically estimating the initial slopes of product versus time curves. This was not difficult, in general, with the hydrogenolysis data since these curves were nearly linear. However, due to the rapid deactivation of the dehydrogenation rates, this procedure was more uncertain when applied to these data. An attempt was made to find a simple analytical expression to fit the data. No such expression was found which consistently fit all the data. Since the deactivation mechanism is not known in detail, it is more prudent to estimate the initial rates graphically, which introduces an uncertainty of about ±20%.

RESULTS

Initial Rates of Cyclohexane Dehydrogenation and Hydrogenolysis

Reaction studies have been performed at temperatures from 503 to 573 K and total pressures from 115 to 760 Torr. The hydrogen-to-hydrocarbon mole ratio has been varied from 6 to 50. Under these conditions hydrogenolysis, as well as dehydrogenation of cyclohexane, is observed. The major dehydrogenation product is benzene, with cyclohexene produced at rates several or-

ders of magnitude less than benzene formation rates. Cyclohexane hydrogenolysis results in n-hexane formation via ring opening in addition to more extensive degradation to products containing less than six carbon atoms. Products with carbon number less than 6 are summed and considered collectively as one type of hydrogenolysis product. These light alkane fragments have been calibrated as methane. n-Hexane will be considered separately from the other hydrogenolysis products. This separation of the two types of hydrogenolysis products is based on differences in apparent activation energies and hydrogen pressure dependencies. Both hydrogenolysis reactions occur at rates several orders of magnitude slower than benzene production rates. Typical results obtained with the (10, 8, 7) surface depicted in Fig. 4, illustrate the selectivity and deactivation behavior of the four reaction products.

The structure sensitivity of these reactions is illustrated in Figs. 5, 6, 7, and 8. Initial rates based on these data are listed in Table 1. In general, the rate of production of benzene increases and the rate of hydrogenolysis decreases as the surface becomes more coordinatively unsaturated. Cyclohexene production is somewhat higher on the (111) surface than on the other three surfaces. While initial rates vary by factors of 2 to 4, selectivities show a greater structure sensitivity as illustrated in Fig. 9.

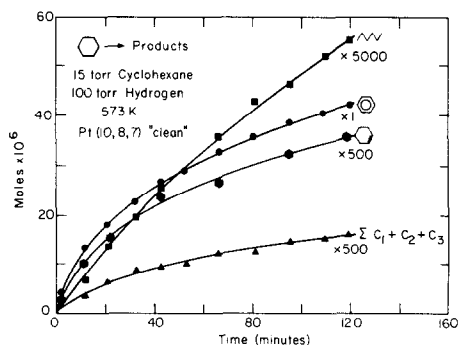The reliability of this structure sensitivity determination is demonstrated by compari-

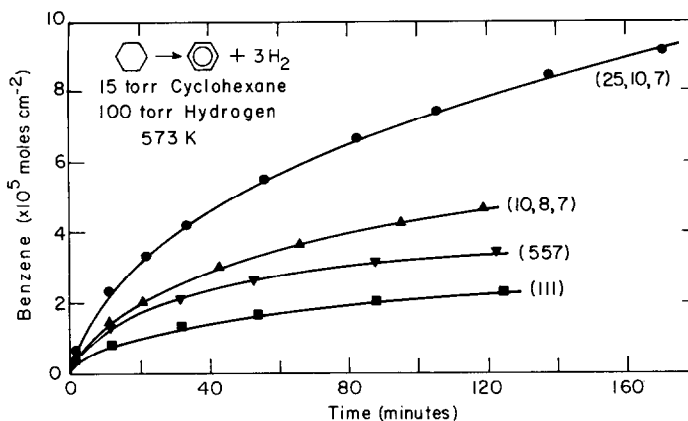FIG. 4. Typical results on the (10, 8, 7) surface.

FIG. 5. Benzene production as a function of surface structure.

son of Fig. 10 to Fig. 5, and Fig. 11 to Fig. 7. The data shown in Figs. 10 and 11 were obtained using the second experimental system and different (111) and (557) single-crystal samples. The (25, 10, 7) crystal was the same in both cases. Dehydrogenation to benzene exhibits excellent reproducibility. The rates of formation of the minor reaction products for the two sets of data do not agree quantitatively as well as the rates of benzene formation do. This is illustrated by Figs. 11 and 7 for hydrogenolysis to n-hexane. However, the same qualitative structure sensitivity is observed, with the (111) surface producing the most n-hexane in both cases. The rate of production of light alkanes shows similar quantitative differences between the two sets of data, but, once again, the qualitative structure sensitivity is reproduced.
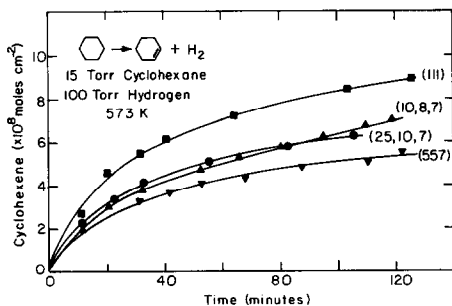
Figures 12 and 13 illustrate the dependence of initial rates on hydrogen pressure on the (111) and (10, 8, 7) surfaces, respectively. On both surfaces, at hydrogen pressures less than 400 Torr, benzene production is positive order in hydrogen. Above 400 Torr the reaction becomes zero order in hydrogen pressure on the (10, 8, 7) surface, but remains positive order up to at least 745 Torr on the (111) surface. Hydrogenolysis leading to ring opening is positive order in hydrogen on both surfaces at low hydrogen pressure, but becomes negative order at pressures greater than 400 Torr. Light alkane production is slightly negative order in hydrogen pressure. Cyclohexene production decreases in all cases as hydrogen pressure increases. Dehydrogenation to
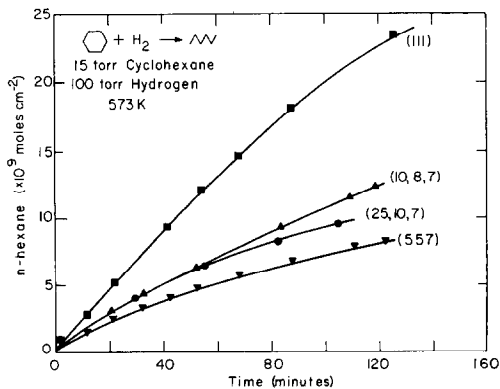

FIG. 6. Cyclohexene production as a function of surface structure.

FIG. 7. n-Hexane production as a function of surface structure.

TABLE 1

Structure Dependence of Initial Rates at 15 Torr Cyclohexane, 100 Torr Hydrogen, and 573 K
(moles/cm^2 min)

Surface	Benzene	Cyclohexene	n-Hexane	Light alkanes
(111)	1.3×10^{-6}	3.1×10^{-9}	2.2×10^{-10}	1.3×10^{-9}
(557)	2.4×10^{-6}	2.1×10^{-9}	9.4×10^{-11}	1.4×10^{-9}
(10, 8, 7)	4.1×10^{-6}	2.9×10^{-9}	1.3×10^{-10}	9.6×10^{-10}
(25, 10, 7)	4.7×10^{-6}	1.9×10^{-9}	9.8×10^{-11}	7.2×10^{-10}

benzene is approximately first order in cyclohexane pressure. The apparent activation energies for benzene production and ring opening are 17 ± 2 and 33 ± 4 kcal/mole, respectively, on both the (111) and (10, 8, 7) surfaces. At temperatures below 573 K the rate for light alkane and cyclohexene production is very low, which results in a large uncertainty in rate measurements for these products. As a consequence, activation energies for these species are not available.

The Effects of Strongly Bound Oxygen

The effect of the presence of strongly bound surface or subsurface oxygen on catalyst activity and selectivity has been investigated. The surfaces were oxidized at 5×10^{-6}-Torr oxygen at 1073 K. Table 2 lists initial rates determined as a function of oxygen concentration on the (10, 8, 7) surface. The effect of the presence of this surface oxide is to decrease the initial rate of dehydrogenation while increasing hydrogenolysis rates at moderate oxygen coverages. At the highest oxygen coverage, the hydrogenolysis rates also decreased. During the course of a reaction experiment the surface remained oxidized as evidenced by AES measurements.

Catalyst Deactivation

Several experiments were performed to identify the deactivation processes. Product inhibition was demonstrated by the addition of toluene to the reactor at the start of a cyclohexane reaction experiment. Toluene produces inhibition similar to that of benzene and is readily separable from benzene by gas chromatography, thus allowing accurate determination of the dehydrogenation rate in the presence of an aromatic inhibitor. Results of such experiments on the Pt(111) surface show that as the toluene concentration is increased from 0 to 0.6 to 2 Torr, the initial
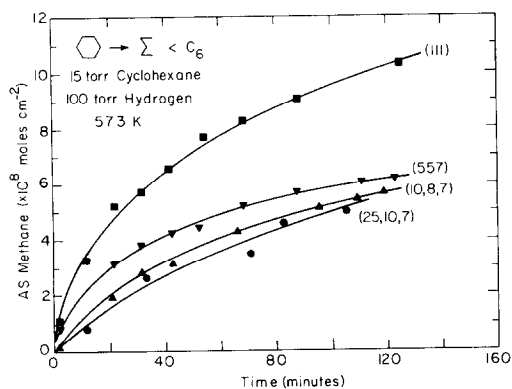
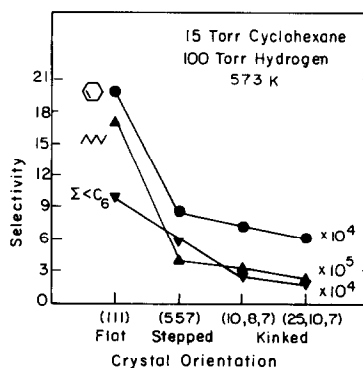FIG. 8. Light alkane production as a function of surface structure.

FIG. 9. Selectivity on the four surface structures for the minor products relative to benzene production.
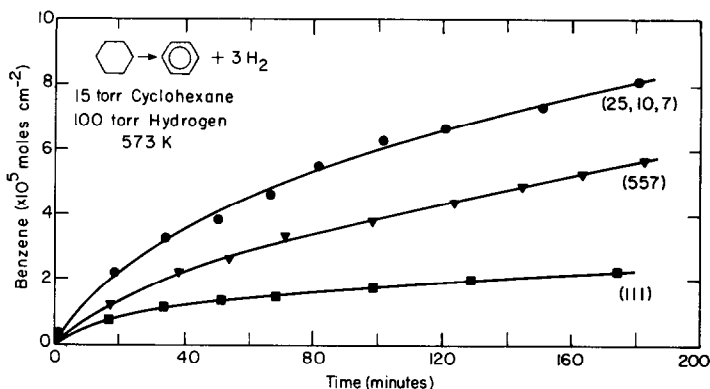
FIG. 10. Benzene production as a function of surface structure as determined in the second reactor system.

rate of benzene formation decreases from 2 to 0.4 to 0.2 μmole min^{-1} cm^{-2}. The addition of toluene had very little effect on hydrogenolysis rates. Figure 14 illustrates a restart experiment in which the reaction is stopped, after about 90 min, by cooling the crystal in the reaction mixture. The cell is then evacuated and a fresh reaction mixture introduced. A run is then started in the normal fashion. In such an experiment, about one-third to one-half of the initial dehydrogenation activity is recovered. Such an experiment also produces a surface with a much higher selectivity for cyclohexene formation.

These experiments demonstrate that the decrease of the dehydrogenation rates with increasing reaction time is due to at least two deactivation processes. The first is reversible and due to inhibition by the aromatic product benzene. The term "reversible" implies that the benzene surface concentration is in equilibrium with the gasphase benzene concentration. Removal of the benzene from the gas phase results in recovery of the reversible part of the deactivation. The second process is irreversible and results from the deposition of strongly adsorbed carbonaceous species. An irreversible loss of activity is defined as a loss
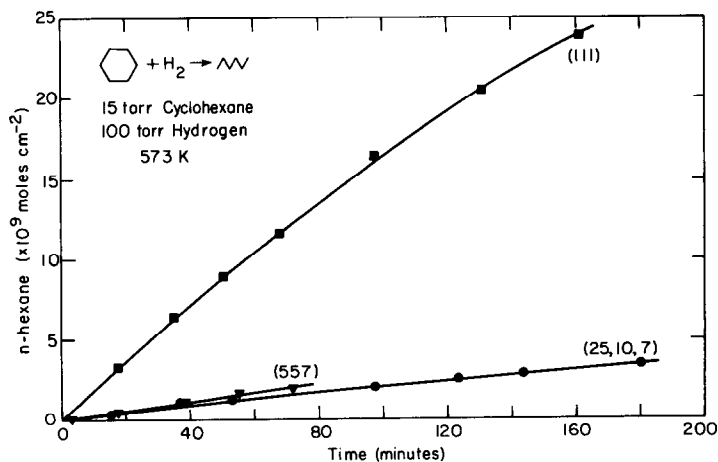

FIG. 11. n-Hexane production as a function of surface structure as determined in the second reactor system.

TABLE 2

Dependence of Initial Rates on Oxygen Coverage for
the (10, 8, 7) Surface at 573 K, 15 Torr
Cyclohexane, and 100 Torr Hydrogen

Oxygen[a] (AES)	Initial rates (moles/cm^2 min)		
	Benzene ($\times 10^6$)	n-Hexane ($\times 10^{10}$)	Light alkanes ($\times 10^{11}$)
0	4.1	1.3	1.0
0.14	3.4	1.2	1.9
0.20	1.4	2.2	1.4
0.59	1.2	1.0	1.9
0.89	0.7	1.3	0.8

[a] Ratio of oxygen 510-eV peak to platinum 237-eV peak.

that cannot be recovered by simply heating the catalyst under vacuum or hydrogen, at or below reaction temperature. The decrease of the hydrogenolysis rates is slower than that of the dehydrogenation rates, is largely irreversible, and does not exhibit product inhibition.

Our experimental results do not allow us to accurately determine the relative contributions of the two deactivation processes to the decrease of the dehydrogenation rates with time. However, estimation of the relative importance of the two processes is possible. After about 2 h of reaction time, at 573 K, the dehydrogenation rates gener-

ally exhibited a decrease of about a factor of 20. At this point the partial pressure of benzene in the reactor was about 1.5 Torr, which represents a conversion of about 10%. As discussed above, experiments were performed in which toluene was added to the reactor at the start of a run. Addition of 2-Torr toluene resulted in a decrease of about a factor of 10 in the initial rate of benzene formation. Assuming that inhibition and irreversible deactivation are separable effects, the irreversible component of dehydrogenation deactivation is roughly a factor of 2 or 3 in a period of 2 h. Also, a restart experiment demonstrated that one-half to one-third of the initial dehydrogenation activity was recovered when benzene was removed from the gas phase. The decrease of the hydrogenolysis rates over a period of 2 h was also about a factor of 2 or 3. It appears that the irreversible component of the dehydrogenation deactivation and the deactivation of hydrogenolysis are of about the same magnitude. Thus it will be assumed throughout the remainder of this paper that the decrease of the hydrogenolysis rates with time is indicative of the general irreversible deactivation of the surface.

The amount of carbon irreversibly adsorbed during a run did not exhibit an obvious dependence on surface structure and exhibited only a weak dependence on reaction conditions. At 15-Torr cyclohex-
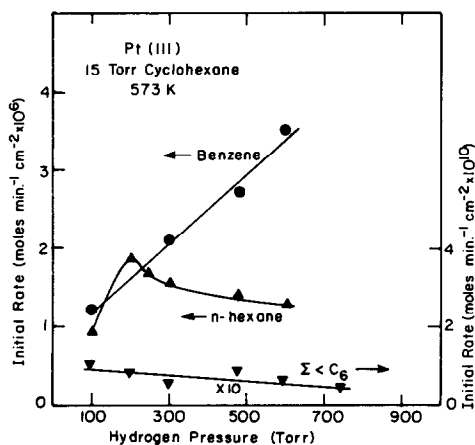

FIG. 12. Effect of hydrogen pressure on dehydrogenation and hydrogenolysis rates on the (111) surface.
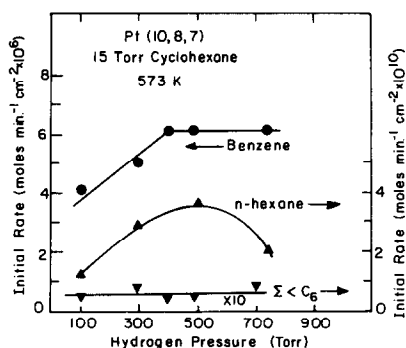

FIG. 13. Effect of hydrogen pressure on dehydrogenation and hydrogenolysis rates on the (10, 8, 7) surface.

15 torr Cyclohexane
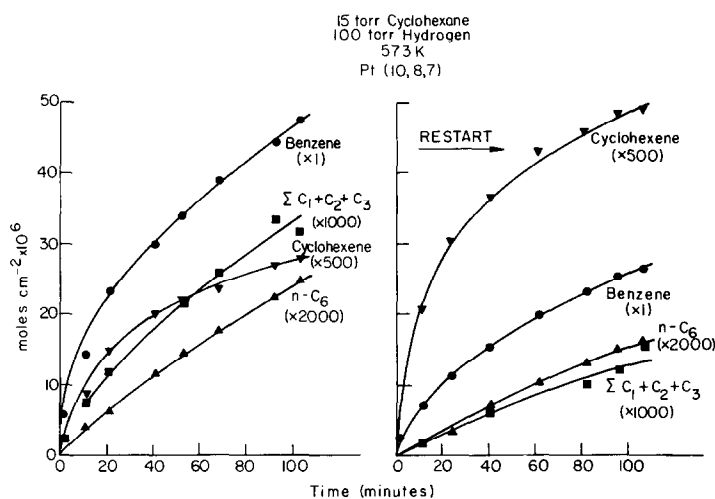100 torr Hydrogen
573 K
Pt (10,8,7)

FIG. 14. Restart of reaction on a partially deactivated surface.

ane pressure, 100- to 745-Torr hydrogen pressure, and 533 to 573 K, the amount of carbon deposited was 0.7 ± 0.2 monolayers. Table 3 lists the carbon coverage as a function of surface structure, while Table 4 lists the carbon coverage as a function of reaction conditions. This strongly bound carbonaceous residue deposited during the reaction forms an amorphous surface layer, as determined by LEED, on all of the surfaces studied. There is no evidence from LEED that this carbon is graphitized. Higher temperatures are required to produce ordered domains of graphite.

As a measure of deactivation, Tables 3 and 4 list the ratio of the initial rate over the rate at 2 h for the various reaction products. A larger ratio indicates a greater amount of deactivation. The ratios for dehydrogenation are difficult to interpret since at 2 h of reaction time, the concentration of benzene in the reactor is not constant as the reaction conditions or the catalyst sample is varied. The (557) crystal was nearly twice as large as the other three crystal samples. Because of the large size of this sample, the amount of benzene in the reactor increased more rapidly causing a larger amount of inhibition. This effect can be seen in the data for the (557) surface in Table 3. The data presented earlier in which toluene was added to the reactor at the start of a run

TABLE 3

Structure Dependence of Deactivation at 573 K, 15 Torr Cyclohexane, and 100 Torr Hydrogen

Surface	Carbon	Final benzene[a]	K^b	Initial rate/Final rate[c]			
				Benzene	Cyclohexene	$n\text{-}C_6$	Light alkanes
(111)	0.65	27.3	1.1	32	47	1.6	3.5
(557)	0.74	72.9	0.63	47	9.4	1.0	11.7
(10, 8, 7)	0.90	55.5	0.38	22	8.8	1.6	4.2
(25, 10, 7)	0.78	101.9	0.17	18	6.3	2.0	3.8

[a] Benzene concentration in the reactor at 2 h in units of μmole · liter^{-1}.
[b] Inhibition parameter as discussed in text.
[c] Rate at 2 h.

TABLE 4

Carbon Coverage and Deactivation of the (10, 8, 7) Surface at Various Temperatures and Hydrogen Pressures

Temp. (K)	Hydrogen pressure (Torr)	Carbon coverage (monolayers)	Final benzene[a]	K^b	Initial rate/Final rate[c]		
					Benzene	n-Hexane	Light alkanes
573	480	0.76	177	0.04	7.8	3.3	3.1
573	400	0.74	171	0.05	10.1	1.0	1.5
573	300	0.74	127	0.06	8.5	2.0	2.9
573	100	0.90	55	0.34	19.7	1.5	2.3
553	300	0.75	111	0.15	17.3	1.9	1.0
533	300	0.53	83	0.24	20.8	1.0	1.2

[a] Benzene concentration at 2 h in units of μmole $\cdot$ liter^{-1}.
[b] Inhibition parameter, K, as discussed in text.
[c] Rate at 2 h.

suggest that inhibition can be modeled by the inhibition expression

$$\text{Rate} = \frac{R_0}{1 + K[\text{Bz}]},$$

where R_0 is the initial rate and [Bz] is the benzene concentration. Also, data obtained at low temperatures could nearly be fit to such an expression. At low temperature, irreversible deactivation is minimized relative to inhibition. Rearranging this expression yields

$$K = \left(\frac{1}{[\text{Bz}]}\right)\left(\frac{R_0}{R} - 1\right),$$

thus allowing calculation of a parameter which compensates for variations in benzene concentration and allows estimation of the dependence of the strength of inhibition on crystal structure, and on reaction conditions. Values of this inhibition parameter are listed in Tables 3 and 4. A larger value of K indicates a greater amount of inhibition. The strength of inhibition as a function of surface structure decreases in the order (111) > (557) > (10, 8, 7) > (25, 10, 7). The data in Table 4 indicate that inhibition becomes less severe with increasing temperature and increasing hydrogen pressure. Irreversible deactivation does not seem to depend on structure and increases with increasing temperature and decreasing hydrogen pressure.

DISCUSSION

Comparison of Cyclohexane Reactions at High and Low Pressures

Somorjai and co-workers have studied the dehydrogenation and hydrogenolysis of cyclohexane catalyzed by platinum single-crystal surfaces at total pressures of less than 10^{-5} Torr (16, 17). Those studies used a standard ultrahigh vacuum chamber as a differential reactor with mass spectrometric detection of reaction products. A comparison of the two pressure extremes yields significant differences in structure sensitivity, activation energies, deactivation behavior, and effect of oxidative pretreatments.

Smith et al. (17) have reported that the specific rate of benzene production at 423 K, 10^{-5}-Torr hydrogen, and 2×10^{-6}-Torr cyclohexane varies by no more than $\pm 15\%$ in a comparison of the (111), (557), and (10, 8, 7) surfaces. The (557) and (10, 8, 7) samples used in that low-pressure study are the same as those used in the present high-pressure study. In contrast to the low-pressure results, we find at high pressure that the initial rate of benzene production does depend significantly on surface structure, with the (10, 8, 7) surface at least a

factor of 3 more active than the (111) surface.

The apparent activation energy of dehydrogenation at low pressure (22) is less than 4 kcal/mole, while at high pressure this parameter is 17 ± 2 kcal/mole, indicating a possible difference in reaction mechanism. The present study has found that dehydrogenation to benzene is approximately first order in cyclohexane pressure and positive fractional order in hydrogen pressure. Similar reaction orders were found at low pressure.

Another significant difference apparent over this large pressure range is the deactivation behavior of the single-crystal catalysts. After an initial induction period at low pressure, the dehydrogenation rate reaches a maximum and then decays approximately exponentially by about an order of magnitude in 2 h of reaction time. Since those experiments were carried out in a differential flow reactor at very low pressure, the dehydrogenation reaction does not exhibit product inhibition, as is the case in the batch reactor at high pressure. As a result, it is not possible to directly compare the deactivation behavior of dehydrogenation at the two pressure extremes. However, as discussed earlier, it is possible to estimate the contribution of product inhibition to the decay of the dehydrogenation rates at high pressure. After this contribution is subtracted out, the residual deactivation is about a factor of 2 or 3. Thus it appears that the deactivation, as measured during the course of a run, is much faster at low pressure, when the comparison is made on a product inhibition-free basis.

At low pressure, preoxidation of the catalyst surface can lead to enhancement of dehydrogenation activity. The degree of enhancement depends on surface structure, and is largest on the (10, 8, 7) surface. A very thorough search was made with all four surfaces used in the present study for the same effect at high pressure. However, no such enhancement was observed.

Finally, there is a marked difference in the structure sensitivity of the hydrogenolysis of cyclohexane in the two pressure regimes. At low pressure n-hexane production from cyclohexane increases with increasing surface kink atom concentration. This is in sharp contrast to high pressure, where hydrogenolysis is fastest on the (111) surface.

Clearly the catalytic behavior of the platinum single crystals is quite different at the two reactant pressure extremes. This different behavior may be the result of large differences in the relative concentrations of adsorbed species over this large pressure range. For example, reversibly adsorbed species with low heats of adsorption (less than 15 kcal/mole) have negligible surface concentrations under low-pressure conditions. Because of the high rate of impingement of molecules on the surface at high pressure, significant steady-state concentrations of such weakly chemisorbed molecules could be present. It is well known that hydrogen has multiple binding states on platinum with heats of adsorption as low as 7–8 kcal/mole and as high as 22–25 kcal/mole (23–25). The weakly bound hydrogen species have been referred to in the literature as reversibly adsorbed hydrogen and have been implicated as the hydrogen species most important in benzene hydrogenation (12). This reversibly adsorbed hydrogen would have negligible surface concentrations at low pressure. The difference in surface concentration of this reversibly adsorbed hydrogen might have a large effect on the rate of catalyst deactivation and might explain some of the selectivity differences observed over this pressure range. The relative concentrations of adsorbed cyclohexane, cyclohexene, and benzene should also be strongly dependent on reactant pressure. The absolute surface coverage by these species should also be greater at high pressure than at low pressure.

We propose that, at high pressure, the surface becomes covered by a complex organic overlayer before the first data point can be taken. This overlayer would be

composed of adsorbed reactants, reaction intermediates, reaction products, and irreversibly adsorbed carbonaceous species. Thus the initial rates reported here were most likely not determined on a "bare" platinum surface. At low pressure the platinum surface remains relatively "clean" as the first data points are taken. This may explain the difference in reaction probability at the two pressure extremes. The reaction probability is simply the specific rate of the reaction divided by the rate of incidence of cyclohexane molecules on the surface. The reaction probability for benzene formation at low pressure is about 10^{-4}, while at high pressure it is about 5×10^{-9}.

The difference in structure sensitivity of dehydrogenation at high and low pressures might be related to the difference in the concentration of adsorbed carbonaceous species at the two pressure extremes. At low pressure, the rate of deactivation is rapid and increases in the order (10, 8, 7) < (557) < (111). After approximately 10 min at low pressure the dehydrogenation activity increases in the order (10, 8, 7) < (555) < (111), which is the same structural ordering observed in the initial rates at high pressure. Possibly the structure-sensitive deactivation, as seen at low pressure, occurs rapidly at high pressure before the first data point can be taken. If this is true, then the structure sensitivity observed at high pressure is not the result of an inherently higher activity of low-coordination step and kink sites versus sites on the (111) terraces. Rather, it results from a decreased tendency for these step and kink sites to be blocked by the carbonaceous overlayer relative to the sites on flat (111) planes. In fact, at high pressure the strength of inhibition by benzene decreases in the order (111) > (557) > (10, 8, 7) > (25, 10, 7), which is exactly the inverse order of the structure sensitivity of the initial rates of dehydrogenation. It is also possible that this difference in structure sensitivity is the result of different rate-determining steps operative at the two pressure extremes. The substan-

tial difference in apparent activation energies at low and high pressures suggests that different reaction steps might be rate limiting in the two cases. Possibly the rate-limiting step at low pressure is structure insensitive, while the rate-limiting step at high pressure is structure sensitive. A detailed discussion of the mechanism of cyclohexane dehydrogenation can be found elsewhere (32).

Comparison of Single-Crystal Studies to Dispersed Catalyst Studies

The dehydrogenation rates obtained on platinum single-crystal surfaces in our studies can be compared to rates on dispersed platinum catalysts using the results obtained by Cusumano et al. (8). By employing a 2 wt% platinum/alumina catalyst, 127-Torr cyclohexane, 633-Torr hydrogen, and 588 K, an activity of 0.59 mole benzene $h^{-1} g^{-1}$ was found at a conversion of 3.3%. Assuming a dispersion of 50%, a turnover number of 3.2 molecules · Pt atom^{-1} · s^{-1} can be calculated from their results. At 80-Torr cyclohexane, 538-Torr hydrogen, and 573 K on the (557) surface a turnover number of 27 was found in the present study. One possible explanation of the much higher rate on single crystals versus supported platinum catalysts is the different methods used to determine the active surface area on the two types of catalysts. It is also possible that the degree of surface cleanliness, or coverage by carbonaceous species, is not the same in the two types of experiments. Initial surface cleanliness is ensured in the case of the single-crystal studies by the use of AES. Kahn et al. (26), using platinum single crystals to catalyze cyclopropane hydrogenolysis, also found specific rates significantly higher than those reported on dispersed platinum catalysts.

Cyclohexane dehydrogenation on supported platinum catalysts has generally been found to be a structure-insensitive reaction (6–9). The present study, however, has found that this reaction does exhibit a certain degree of sensitivity to

surface structure with specific initial rates varying by at least a factor of 4. As discussed earlier the presence of the unoriented edges of the single-crystal catalysts results in smaller experimentally determined differences in rates between different surface structures. If the contribution of the edges could be made negligible, then the difference in initial rates of benzene production would probably be significantly greater than a factor of 4 as the structure is varied from the (111) orientation to the (25, 10, 7) orientation. It is not clear at the present time why this difference in structure sensitivity between single-crystal catalysts and dispersed metal catalysts exists.

The hydrogenolysis of cyclohexane has not been studied as a function of particle size on supported platinum catalysts. However, Lam and Sinfelt (27) have investigated the reaction on ruthenium catalysts of widely varying dispersion and found that the specific rate of methane production increased by over an order of magnitude as the dispersion decreased from close to one to close to zero. On platinum signal crystals, we also found that this reaction structure is sensitive with the highest rate on the (111) surface. Larger crystallites should have relatively more (111) surface area. Although this study was on a different metal, the results correlate well with results obtained on single-crystal surfaces.

Catalyst Deactivation

The strength of inhibition of dehydrogenation by benzene decreases as the surface becomes more coordinatively unsaturated. This result agrees well with a study by Lehwald and Ibach (30), which demonstrated that benzene is adsorbed preferentially on the terraces of a stepped nickel surface. Thus the more highly stepped a surface, the more resistant to inhibition by benzene it should be. Also, Mitrofanova and co-workers (9) determined that on dispersed platinum catalysts product inhibition was stronger on catalysts with large

particle sizes than on those with small particle sizes.

Unlike product inhibition, irreversible deactivation does not exhibit an obvious trend as a function of surface structure. Also, this type of deactivation process does not show a well-defined correlation with the amount of irreversibly adsorbed carbonaceous material. This is in spite of the fact that the concentration of carbonaceous species deposited during reaction is dependent on temperature and hydrogen pressure as demonstrated by the data in Table 4. This could indicate that the structure of the carbonaceous deposit or the types of species forming this deposit are also functions of reaction conditions. No information in this regard could be obtained by LEED or AES.

Our distinction of reversible and irreversible deactivations may not be as clear cut as has been implied thus far. Aromatic molecules have been implicated as precursors to coke formation (28). Thus a high aromatic content in the gas phase may lead to more extensive irreversible deactivation of the catalyst surface. In a study of methylcyclohexane dehydrogenation, Wolf and Petersen (29) concluded that irreversible deactivation occurred through a reversibly adsorbed species. This may explain the high rate of deactivation of light alkane production with the (557) surface as shown in Table 3. The (557) was the large crystal, and thus caused a very rapid buildup of benzene in the reactor relative to the other crystals.

Selectivity for Cyclohexene Formation

The selectivity for cyclohexene versus benzene production appears to be intimately related to the presence of carbonaceous surface deposits. As indicated by Fig. 14, restarting the reaction on a partially deactivated surface resulted in a high selectivity for cyclohexene production. A similar increase in this selectivity could also be produced by pretreating the crystal in a mixture of n-heptane and hydrogen at 573

K to produce an irreversibly adsorbed carbonaceous deposit. At very high space velocities, Haensel *et al.* (*31*) observed an increase in this selectivity as a supported platinum catalyst deactivated under reaction conditions.

This change in selectivity is likely to be related to a change in the bonding of cyclohexene in the presence of a carbonaceous deposit (*32*). Weaker bonding can reduce the residence time of the cyclohexene molecule on the surface, resulting in a higher rate of desorption. Destabilization of the intermediate, adsorbed cyclohexene, could result from a change in the electronic properties of the surface resulting from the presence of the tightly bound carbonaceous species. Alternatively, the size of the site at which the reaction occurs might be important in regulating selectivity for cyclohexane. A larger site may be required to π-bond cyclohexene, π-allylic intermediates, and benzene to the surface than to σ-bond cyclohexane dissociatively (*32*). If the size of a site is limited by the presence of tightly bound carbonaceous species on the surface, the strength of adsorption of π-bonded species might be reduced relative to the strength of adsorption of σ-bonded species, due to steric constraints. Then there might be a greater probability for desorption of cyclohexene than for its further dehydrogenation to benzene. Further studies are needed to clarify the role of surface carbonaceous species on the selectivity of this reaction.

ACKNOWLEDGMENTS

REFERENCES

1. Boudart, M., Aldag, A. W., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6**, 92 (1966).

2. Poltorak, O. M., and Boronin, U. S., *Russ. J. Phys. Chem.* **40**, 1436 (1966).

3. van Hardeveld, R., and Hartog, F., *Surface Sci.* **15**, 189 (1969).

4. Bond, G. C., *in* "Proceedings, 4th International Congress on Catalysis, Moscow, 1968" (B. A. Kazansky, Ed.), Paper 67. Adler, New York, 1968.

5. Anderson, J. R., "Structure of Metallic Catalysts." Academic Press, New York/London, 1975.

6. Maatman, R. W., Mahaffy, P., Hoekstra, P., and Addink, C., *J. Catal.* **23**, 105 (1971).

7. Kraft, M., and Spindler, H., *in* "Proceedings, 4th International Congress on Catalysis, Moscow, 1968" (B. A. Kazansky, Ed.), Paper 69. Adler, New York, 1968.

8. Cusumano, J. A., Dembinski, G. W., and Sinfelt, J. H., *J. Catal.* **5**, 471 (1966).

9. Mitrofanova, A. M., Boronin, V. S., Poltorak, O. M., *Vestn. Mosk. Univ.* **5**, 14 (1966).

10. Dorling, T. A., and Moss, R. L., *J. Catal.* **5**, 11 (1966).

11. Basset, J. M., Dalmai-Imelik, G., Primet, M., and Muten, R., *J. Catal.* **37**, 22 (1975).

12. Aben, P. C., Platteeuw, J. C., and Southhamer, B., Preprints, "Proceedings, 4th International Congress on Catalysis, Moscow, 1968" (B. A. Kazansky, Ed.), Vol. 2, p. 543. Adler, New York, 1968.

13. Maire, G., Corolleur, C., Juttard, D., and Gault, F. G., *J. Catal.* **21**, 250 (1971).

14. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8**, 348 (1967).

15. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24**, 283 (1972).

16. Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976).

17. Smith, C. E., Biberian, J. P., and Somorjai, G. A., *J. Catal.* **57**, 426 (1979).

18. Davis, S. M., and Somorjai, G. A., *Surface Sci.* **91**, 73 (1980).

19. Blakely, D. W., Kozak, E. I., Sexton, B. A., and Somorjai, G. A., *J. Vac. Sci. Technol.*, **13**, 1091 (1976).

20. Van Hove, M. A., and Somrojai, G. A., *Surface Sci.* **92**, 489 (1980).

21. Biberian, J. P., and Somorjai, G. A., *Appl. Surface Sci.* **2**, 352 (1979).

22. Smith, C. E., Ph.D. dissertation, University of California, Berkeley, 1978.

23. Stephan, J. J., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **37**, 81 (1975).

24. Christmann, K., Ertl, G., and Pignet, T., *Surface Sci.* **54**, 365 (1976).

25. McCabe, R. W., and Schmidt, L. D., *in* "Proceedings, 7th Internl. Vac. Congr."; and *in* "Proceedings, 3rd Internl. Conf. Solid Surfaces," 1201. Vienna, 1977.

26. Kahn, D. R., Petersen, E. E., and Somorjai, G. A., *J. Catal.* **34**, 294 (1974).

27. Lam, Y. L., and Sinfelt, J. H., *J. Catal.* **42**, 319 (1976).

28. Muller, J. M., and Gault, F. G., *in* "Proceedings 4th International Congress on Catalysis, Moscow, 1968" (B. A. Kazansky, Ed.), Paper 15. Adler, New York, 1968.

29. Wolf, E. E., and Petersen, E. E., *J. Catal.* **46**, 190 (1977).

30. Lehwald, S., and Ibach, H., *Surface Sci.* **89**, 425 (1979).

31. Haensel, V., Donaldson, G. R., and Riedl, F. J., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," Vol. 1, p. 294. North-Holland, Amsterdam, 1965.

32. Herz, R. K., Ph.D. dissertation, University of California, Berkeley, 1977.