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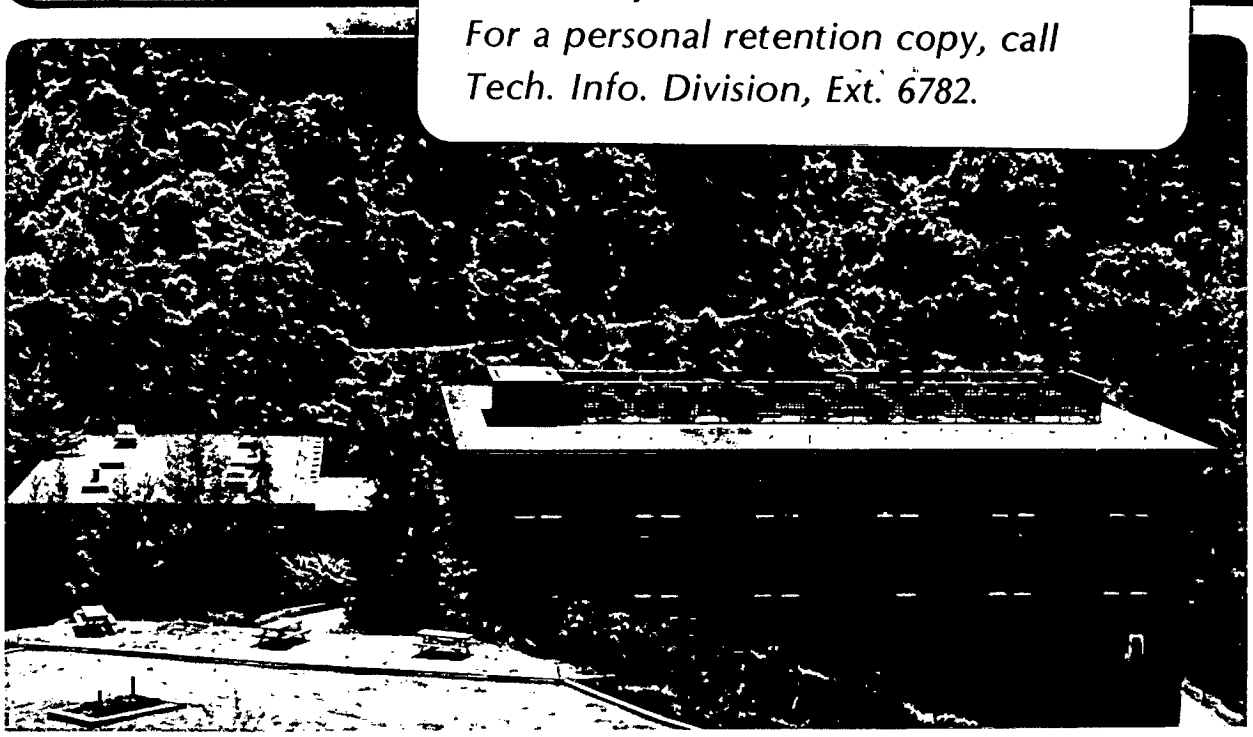

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LBL 13706

The Reactivity and Composition of Strongly Adsorbed Carbonaceous Deposits on Platinum. Model of the Working Hydrocarbon Conversion Catalyst

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Abstract

The role of strongly adsorbed hydrocarbon deposits in reforming catalysis on a series of flat, stepped, and kinked platinum single crystal surfaces at atmospheric pressures and temperatures between 300 and 700K has been established and a model developed for the working structure and composition of the active catalyst surface. Restart reaction studies and reaction rate studies using platinum surfaces precovered with carbonaceous overlayers containing carbon-14 were used to investigate the catalytic activity and selectivity of carbon-covered platinum in hydrocarbon hydrogenation, dehydrogenation, and skeletal rearrangement. Quantitative hydrogen thermal desorption studies were carried out as a function of surface structure and reaction temperature to determine 1) the composition, and 2) the energetics for sequential dehydrogenation of carbonaceous deposits derived from a variety of adsorbed hydrocarbons including isobutane, neopentane, n-hexane, and cyclohexene. Carbon monoxide adsorption thermal desorption methods were developed to titrate uncovered platinum surface sites before and after reaction rate studies. The uncovered site concentrations were correlated with the total surface carbon coverage as determined by Auger electron spectroscopy and the catalytic activity and selectivity of carbon covered platinum. These experiments together with results from related structure sensitivity, thermal desorption, deuterium exchange, and radiotracer studies revealed that the primary role of the disordered carbon deposit is that of a non-selective poison which blocks platinum surface sites from incident reactant molecules. The most important chemical properties of the carbonaceous deposit are its abilities to store and exchange hydrogen with reacting surface species and to provide desorption sites for product molecules. The growth mechanism of this carbonaceous deposit is sensitive to the structure of the reacting hydrocarbon, and its morphology appears to vary continuously from 2-dimensional at low reaction temperatures (< 550K) to 3-dimensional for temperatures higher than about 600 K.

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Introduction

Model catalytic studies using small-area platinum single-crystal surfaces have revealed the special importance of surface structure in controlling the rates and selectivities in many important types of catalyzed hydrocarbon reforming reactions (1-7). The presence of surface irregularities, atomic steps and kinks with fewer nearest neighbors, was essential for high catalytic activity in reactions such as isobutane hydrogenolysis (4), cyclohexane dehydrogenation (1), and n-heptane aromatization (2). Perhaps the most general feature of these reaction rate studies was always the unavoidable build-up of about the equivalent of one monolayer of strongly bound carbonaceous deposit on the catalyst surfaces that is detectable by Auger electron spectroscopy. Gillespie et al (1,2) reported that near atmospheric pressure and 573 K these strongly bound, partially dehydrogenated surface species caused catalyst deactivation with only small changes in reaction selectivity.

The formation and reactivity of surface carbon deposits on high area practical platinum catalysts has also been investigated (8-12). Commercial catalysts that operate selectively for thousands of hours before requiring regeneration are known to accumulate high steady state levels of carbonaceous deposits (5-10% by wt for 1% Pt/ γ -Al_2O_3 or Pt-Re/ γ Al_2O_3) that appear to form almost instantly as the reactions commence (13). The formation of this deposit, its rehydrogenation dynamics, and its interactions with other adsorbates is thus an essential feature of the catalytic chemistry. Expensive regeneration is required only after these surface species are irreversibly transformed into "coke" deposits that block the metal and plug the porous support, rendering the catalyst inactive.

Despite interesting models by Thomson and Webb (14) and Gardner and Hansen (15) which emphasized the dynamic ability of the carbonaceous deposit to undergo hydrogen transfer with reacting surface species, no conclusive evidence exists to accurately describe the nature of the participation of surface carbon deposits in reforming catalysis by metals.

Thus, the two key observations in studies of hydrocarbon conversion reactions over platinum catalysts are: 1) the structure sensitivity of the product distributions and 2) the presence of large amounts of carbonaceous deposit on the surface of the working catalyst.

In this paper we explore the composition and reactivity of the carbonaceous deposits on platinum single crystal surfaces of different atomic surface structure by employing a variety of experimental techniques; restart reaction studies were used to explored the activity of the catalyst in the presence of carbon deposits that were prepared using different adsorbates and the catalytic behavior has been compared with that for initially clean platinum. Carbon-14 labelled deposits were used to ascertain the residence time of the strongly bound carbon. Thermal desorption of hydrogen gave estimates of the (H/C) ratio and CO desorption titrated the concentration of bare metal sites that remained uncovered after the catalytic reactions. As a result of these studies, we propose a molecular model of the working platinum catalyst. Most of its surface is covered by a carbonaceous deposit, partly two-dimensional and partly three-dimensional, that provides sites for desorption of the product molecules and hydrogen transfer to or from the reacting species. Its composition and structure is temperature and hydrogen pressure dependent. Hydrocarbon conversion occurs over the bare metal islands whose structure is predetermined by the catalyst preparation. The reacting molecules may desorb from the

metal sites directly or they may desorb after migration over to the carbonaceous deposit. The accelerated rehydrogenation of the carbonaceous fragments may account for the higher activity of bimetallic catalysts and their increased resistance to deactivation.

Experimental

The experimental apparatus (1,3), materials (3), procedures for thermal desorption studies (16,19) and reaction rate experiments (1,3), and the counting system for carbon-14 radiotracer studies (20) were all described previously. Auger calibrations for surface carbon coverage were derived from radiotracer studies of ^{14}C-benzene chemisorption on Pt(111) and Pt(100); i.e., $C_s/Pt = 0.62(C_{273}/Pt_{237})$ for Pt(111) and $C_s/Pt = 0.74$ (C_{273}/Pt_{237}) for Pt(100) (20,21) [C_s/Pt = carbon atoms per surface platinum atom (±25%)]. Approximate carbon coverages on the stepped (13,1,1) and kinked (10,8,7) platinum surfaces were estimated using the calibrations for Pt(100) and Pt(111), respectively.

Atomic surface structures for the single crystal samples used in this research include the flat (100) and (111) surfaces that are characterized by square and hexagonal close packed atomic arrangements, respectively. The stepped (322), (13,1,1), (557), and (10,8,7) platinum surfaces all have average terrace widths in the range 11-18Å. The (13,1,1) surface has (100) terraces, while the other stepped surfaces have (111) terraces. About 6% of the Pt (10,8,7) surface atoms occupy kink sites.

Two types of experiments were used to investigate the catalytic behavior of carbon covered platinum: 1) reaction rate studies over surfaces precovered with hydrocarbon overlayers, and 2) restart reaction studies.

In the former experiments the initially clean platinum surfaces were pretreated with hydrocarbons at low reactant pressures (~ 10^{-7} Torr) and temperatures between 473 and 673K, the surface coverage by preadsorbed species was determined by AES, and then reaction studies were carried out near atmospheric pressure in the usual manner. Often the preadsorbed layer was labelled with carbon-14 so that its partial removal in subsequent reactions could be detected by radiotracer analysis. In the restart experiments reaction studies were carried out for 90-180 min. starting with an initially clean platinum surface, the reactions were stopped, Auger spectra were recorded for both crystal faces, and then the reactions were restarted using a fresh reaction mixtures, often under exactly the same reaction conditions. These two types of experiments enabled the hydrogen content of the preadsorbed layers and the total surface carbon coverage to be varied independently.

The hydrocarbon reactions studied in this research include cyclohexane hydrogenation and dehydrogenation, isobutane and neopentane isomerization and hydrogenolysis, and n-hexane hydrogenolysis, isomerization, C_5-cyclization (to methylcyclopentane (MCP)), and aromatization. The total reactant pressure was 77-620 Torr and the (H_2/H_C) ratio was varied between 10 and 30. The surface structure and temperature dependence of these reactions catalyzed on initially clean platinum single crystal surfaces has been reported separately in accompanying papers.

Results and Discussion

I. Catalytic Activity and Selectivity of Carbon Covered Platinum: Light Alkane Restart Reactions.

Important information about the catalytic behavior of carbon covered platinum can be determined by pre-

adsorbing one type of hydrocarbon molecule and running a second reaction in the presence of the preadsorbed layer, or by running the reactions continuously, changing the reactant hydrocarbon at periodic intervals. Restart experiments of the latter type reveal how hydrocarbon deposits derived from different molecules influence the activity and selectivity of hydrocarbon conversion reactions. Figure 1 compares product accumulation curves determined as a function of reaction time for isobutane isomerization catalyzed at 573 K over the stepped (13,1,1) platinum surface that was covered with carbon deposits from previous neopentane and n-hexane reactions (lower curves). The initially clean surface was the most active and selective catalyst for this reaction yielding about 97 percent n-butane and 3 percent hydrogenolysis products (4). Because part of the deactivation which occured in the initial reactions was irreversible, the maximum level of activity that could be restored in the restart reactions was always several times less than that for the initially clean platinum surface. The greater deactivation which occurred after the n-hexane reaction correlated with an increased coverage by surface carbon. In Figure 2 initial rates in isobutane and neopentane restart reactions have been divided by initial rates on clean platinum (R_r/R_c) and plotted as a function of the preadsorbed overlayer coverage as determined by AES. Table 1 summarizes reaction conditions and initial rates for the restart experiments. The catalytic activities for isomerization and hydrogenolysis on the (10,8,7) and (13,1,1) platinum surfaces both decreased markedly with increasing carbon coverage. Isomerization was generally suppressed more strongly than hydrogenolysis, particularly during isobutane reactions catalyzed over Pt(10,8,7).

n-Hexane Restart Reactions. A similar series of restart experiments was carried out for n-hexane reactions catalyzed over the (111) and (10,8,7) platinum surfaces. Reaction conditions and initial rates for several of the experiments are summarized in Table 2. The ratio of initial rates (R_r/R_c) is shown as a function of the preadsorbed overlayer coverage for two sets of reaction conditions in Figures 3 and 4. The error bars represent the spread in (R_r/R_c) values measured for parallel hydrogenolysis, isomerization, and cyclization reactions. Again it can be clearly seen the catalytic activity for all reactions decreased with increasing carbon coverage. The deactivation displayed little dependence on platinum surface structure and the hydrocarbon from which the carbon deposit was formed and was roughly first order with increasing surface carbon coverage. Many of the restart experiments were carried out following n-hexane reaction studies using identical experimental conditions. The (R_r/R_c) ratios for these experiments are shown as a function of reaction temperature in Figure 5. It is apparent that the amount of deactivation which occurred in the initial reactions increased with increasing reaction temperature.

A comparison between Figures 2, 3, and 4 reveals that the n-hexane reactions generally displayed less deactivation at a given carbon coverage than the isobutane and neopentane reactions. The activity in light alkane restart reactions approached zero for "carbon coverages" greater than about two carbon atoms per surface platinum atom. By contrast, n-hexane continued to display appreciable activity at carbon coverages equivalent to four or more carbon atoms per surface platinum atom. The reasons for these differences are not certain, but they are likely related to different site requirements for the light alkane and n-hexane reactions or differences in molecular residence times for the reacting species. The longer surface

residence times for n-hexane (19) may enable this molecule to diffuse more efficiently to uncovered platinum sites during a single residence on the surface (ca. 10^{-7} sec at 573 K).

It is clear that the working platinum catalyst can tolerate a substantial accumulation of surface carbon and still exhibit high activity and retain its usual selectivity for the more important reforming reactions of larger alkane molecules. This might be expected if the carbon deposits were to participate in the reforming reactions by hydrogen transfer or other indirect processes. In order for uncovered platinum sites to be totally responsible for the reaction chemistry, the carbon deposit must assume a 3-dimensional morphology which provides a small, steady-state concentration of uncovered platinum surface sites. Carbon monoxide adsorption studies reported below indicate that uncovered platinum sites are indeed present during the restart reactions, and that these sites are responsible for the remaining catalytic activity that is displayed by the carbon covered surfaces.

n-Hexane Reaction Studies on Surfaces Precovered with Overlayers Containing Carbon-14. Reaction rate studies carried over platinum surfaces precovered with hydrocarbon overlayers derived from ^{14}C-benzene and ^{14}C-ethylene were also used to obtain information about the residence times and catalytic behavior of the metal-organic deposit.

Under these conditions, hydrocarbon conversion certainly occurred in the presence of the carbon deposit and perhaps in exchange with the ^{14}C-containing species. Table 3 summarizes initial rates for n-hexane reactions that were catalyzed over the (100) and (111) platinum surfaces following pretreatment with ^{14}C-ethylene and ^{14}C-benzene at 400-670 K. Reaction rates measured in the presence of the preadsorbed overlayers

were always lower than initial rates determined for clean platinum surfaces. No significant changes in reaction selectivity were detected. The fraction of the preadsorbed ^{14}C-containing species which were irreversibly adsorbed is shown as a function of adsorption temperature in Figure 6. Irreversibly adsorbed fraction is defined as the fraction of the initially present ^{14}C-containing species which was not removed during the subsequent n-hexane reactions at 570-670 K. As discussed in the forthcoming paper for ^{14}C-C_2H_4 rehydrogenation reactions (16), the irreversibly adsorbed fraction increased with increasing adsorption temperature and decreasing reaction temperature. At any given pretreatment temperature, ethylene appeared to be adsorbed more irreversibly than benzene. The irreversibly adsorbed fraction displayed an inverse correlation with the hydrogen content of the preadsorbed species (16).

Cyclohexene Hydrogenation and Dehydrogenation. Reaction studies on platinum surfaces covered with preadsorbed overlayers revealed that the strongly adsorbed carbonaceous species which form at low pressures and temperatures between 473 and 523 K act as non-selective poisons for simple hydrogenation and dehydrogenation reactions that can be catalyzed at low temperatures. This is shown in figure 7 for cyclohexene hydrogenation and dehydrogenation catalyzed at 300-425 K over the stepped (322) platinum surface. Ethylene, 1-butene, and benzene were preadsorbed at 473 K ($\theta < 0.5$) or 523 K ($\theta > 0.5$), the surface coverage by preadsorbed species was determined by AES ($\theta = 1$ corresponds to 2 carbon atoms per surface platinum atom ± 25 %), and then the cyclohexene reactions were carried out at a total pressure of 77 Torr (H_2/HC = 10). At 300 K, the preadsorbed species very effectively blocked the sites that were required for cyclohexene hydrogenation. The decline in activity with increasing over-

layer coverage corresponds to a $(1 - \theta)^2$ coverage dependence indicating that two platinum atoms were probably required in the rate determining step of this reaction. Based on the kinetic studies of Segal et al (21) the rate determining step appears to be the dissociative chemisorption of hydrogen molecules on uncovered platinum surface sites. At 425 K the dehydrogenation and hydrogenation reactions were both suppressed strongly by preadsorbed benzene but to a lesser extent by the preadsorbed light olefins.

In order to investigate how hydrogenation and dehydrogenation activity was influenced at higher temperatures, and hydrogen pressures, a couple of cyclohexene restart experiments were carried over the (111) platinum surface at 373-473 K. Results of these reactions are summarized in Table 4. While hydrogenation and dehydrogenation activity was lowered markedly on the carbon-covered surfaces, the rates were still exceedingly high. These reactions were typically 10^2-10^4 times faster than skeletal rearrangement restart reactions catalyzed at 573-673 K. The relative rates for hydrogenation, dehydrogenation, and skeletal rearreangement clearly indicate that platinum is a very effective hydrogenation-dehydrogenation catalyst even when the working catalyst surface is extensively covered by deactivating carbonaceous deposits.

Selectivity of Restart Reactions and Reaction Studies in the Presence of Preadsorbed Overlayers Containing Carbon-14. Only minor changes in reaction selectivity were detected for the carbon-covered platinum surfaces independent of their surface structure, the reaction temperature, the hydrocarbom from which the overlayer was derived, and the hydrogen content of the carbon deposit which was varied continuously between (H/C) = 0 and

(H/C) = 1.5. During the n-hexane reaction studies on carbon-covered Pt(111) and Pt(10,8,7), there was a tendency for aromatization and hydrogenolysis selectivities to be enhanced slightly relative to isomerization and C_5-cyclization (Table 2). Example product distributions illustrating this effect are shown in Figure 8 for n-hexane reactions catalyzed over Pt(111) at 600-700 K. The enhanced aromatization selectivity is highly desirable but not when it arises at the cost of catalytic activity with a concomitant increase in hydrogenolysis selectivity. Within isomerization, the kinetic selectivity for 2-methylpentane formation over 3-methylpentane production was always lowered on the carbon covered surfaces as compared to initially clean platinum. This change in isomerization selectivity would be expected from results presented earlier (3).

The simplest explanation to account for the slightly altered selectivity of the carbon-covered platinum surfaces is that the concentration of surface hydrogen is reduced on the carbon-covered surfaces.

Previous results (3) showed that with increasing temperature and decreasing hydrogen pressure, aromatization and hydrogenolysis selectivities increased at the expense of isomerization and C_5-cyclization. Within isomerization, the kinetic selectivity 2MP/2MP decreased with increasing temperature and decreasing hydrogen pressure. These changes were related to a change in the identity of the most abundant surface intermediate that is caused by a decrease in the surface concentration of chemisorbed hydrogen. Since exactly the same changes in reaction selectivity were observed during the restart experiments, the reduction of hydrogen surface concentration is a meaningful explanation for the slightly altered selectivity of carbon-covered platinum. The surface concentration of hydrogen was reduced in the restart reactions because the sticking coefficient of

hydrogen was reduced on the carbon-covered surfaces (19). Results obtained by Salmeron (22) also indicate that the binding energy of hydrogen is reduced by 2-3 kcal/mole when coadsorbed on platinum in the presence of hydrocarbons.

The increased aromatization selectivity that was detected for the carbon-covered single crystal surfaces corresponds well with results reported by Hughes (23) for commercial Pt/Al_2O_3 and $Pt-Re/Al_2O_3$ catalysts. Supported catalysts that were pretreated with methyl- and dimethylcyclopentanes displayed a 2-10 percent increase in aromatization selectivity that was largest for the bimetallic catalysts. An increase in hydrogenolysis selectivity relative to isomerization and C_5-cyclization, like that observed in this research, was also reported by Karpinski (24) for n-hexane reactions catalyzed over Pt/SiO_2 catalysts that were deliberately deactivated at high temperatures. Paal et al (9) reported the same effect for 3-methylpentane reactions catalyzed over platinum black. Ponec and co-workers (10) recently reported interesting results for n-hexane reactions catalyzed at 500-650 K on a series of Pt/SiO_2 catalysts with average metal particle sizes varied between 20 and 80 Å ($H_2/HC = 16$, $P_{tot} = 1$ atm). The catalytic behavior of freshly reduced catalysts was compared with that for the same catalysts following deliberate deactivation at 720 K. While little or no structure sensitivity was detected for the freshly reduced catalysts, significant structure sensitivity was observed for the catalysts which were modified by carbon deposition at high temperatures. Catalysts with high dispersion were much more resistant to deactivation than catalysts with low dispersion. These results appear to indicate that edge and corner atoms on dispersed crystallites are more resistant to coke depositon than atoms in close packed crystal faces. The Dutch workers also noted that

cyclization selectivity was enhanced relative to isomerization on the deactivated catalysts.

II. Composition and Sequential Dehydrogenation of Hydrocarbon Overlayers Deposited During Reaction Studies at Atmospheric Pressure.

Hydrogen thermal desorption spectra that were recorded following n-hexane reactions which were catalyzed over Pt(111) and Pt(10,8,7) at 573-678K are shown in Figure 9. Also shown is the average (H/C) stoichiometry of the adsorbed layer as determined from the desorption peak areas and the total surface carbon coverage that was in the range 2-5 carbon atoms per surface platinum atom (6,19,20). The spectra represent the sequential dehydrogenation of the strongly adsorbed species that were deposited by the reaction mixture. This process took place in two or more steps with broad hydrogen desorption peaks centered at 440-460 K and 630-660 K. As discussed previously (16), the first desorption peak corresponds to β-hydrogen abstraction, ring metallation, and perhaps other rearrangement processes in alkylidyne, aromatic, and related surface species, respectively. The activation energies for these rearrangements always appear to be in the range 23-29 kcal/mole (16,22). The second desorption peak ($E_a \approx$ 35-45 kcal/mole (16,22)) represents the decomposition of CH fragments (16,22,25) and other C_nH_x groups in which the C-H bonds are not providing easy access to metal sites. The fraction of the total hydrogen which was retained in this chemical state increased with increasing reaction temperature in a manner which was proportional to the total surface carbon coverage. The area of the first desorption peak displayed little dependence or carbon coverage (reaction temperature).

Very similar hydrogen desorption spectra were obtained following the

high pressure reactions of other hydrocarbon molecules including isobutane, n-butane, neopentane, cyclohexane, cyclohexene, and n-heptane. Figure 10 summarizes hydrogen desorption spectra together with (H/C) ratios that were determined following a series of reactions on the (100) platinum surface. The (H/C) ratios and the shapes and positions of the hydrogen desorption peaks were always very similar independent of the platinum surface structure and the nature of the reacting hydrocarbon.

The (H/C) ratios shown in Figures 9 and 10 clearly indicate that the carbonaceous deposit always stores high concentrations of strongly bound hydrogen. For n-hexane reactions catalyzed over Pt(111) and Pt(lo,8,7), the (H/C) ratios decreased slowly with increasing reaction temperature from about 1.6 at 573 K to about 1.0 at 678 K. Following alkane reaction studies on the (100) platinum surface at 573-615 K, the (H/C) ratios were always in the range 1.0-1.6. Under these conditions, the hydrogen which is retained by the carbon deposit can be made to reacting molecules by means of hydrogen transfer reactions (16).

Deuterium exchange also occurred readily within these hydrogen containing carbonaceous depostis at both high and low reactant pressures. Deuterium thermal desorption spectra representing deuterium exchange in carbon deposits derived from n-hexane were reported elsewhere (17). Similar spectra were obtained from isobutane and neopentane reaction studies in the presence of deuterium. Salmeron has shown that ethylidyne species resulting from ethylene adsorption on Pt(111) at 300-450 K exchange deuterium readily even at D_2 pressures as low as 10^{-7} Torr (22). Vibrational ELS studies revealed that CH species also undergo facile deuterium exchange on (111) rhodium and platinum surfaces (25,26).

The amount of hydrogen which was stored by the carbonaceous deposit

represented at least ten times more hydrogen than could be chemisorbed at 300 K on initially clean platinum surfaces (19). Once desorbed, the strongly bound hydrogen could only be partially reintroduced by heating the carbon-covered samples in 200-600 Torr of hydrogen at 423-573 K. The reintroduced hydrogen displayed a single desorption peak at 430-460 K. Very little, if any, of the hydrogen could be reintroduced into the higher energy binding states. Thus, the complete dehydrogenation of the carbonaceous deposits was largely irreversible. This process was accompanied by major restructuring of the surface carbon which resulted in the formation of graphitic carbon islands and perhaps also amorphous carbon deposits. This carbon displayed different hydrogen storage properties as compared to the carbonaceous overlayers that were deposited by the reaction mixtures.

III. Titration of Uncovered Platinum Surface Sites by CO Chemisorption Following Alkane Reaction Studies. The selective chemisorption of carbon monoxide is one of the most reliable experimental methods available for determining the surface area of supported metal catalysts (27). The dispersion of practical platinum catalysts is sometimes determined in this manner (28) by assuming that one CO molecule is chemisorbed per surface platinum atom. Here we show that the same selective adsorption technique can be used to titrate platinum sites on single crystal surfaces that are uncovered by the carbonaceous deposit. Carbon monoxide adsorption -thermal desorption studies were used to determine the concentration of uncovered platinum surface sites which remained following alkane reaction studies that were catalyzed in the temperature range of 540-700 K.

Carbon monoxide adsorption and thermal desorption studies were carried out for the clean (100), (111), and (13,1,1) platinum surfaces,

the same surfaces after pretreatment with n-hexane at low pressures and 673-773 K, and the same surfaces following n-hexane reaction studies that were catalyzed near atmospheric pressure at temperatures between 540 and 700 K. Figure 11 and 12 compare CO thermal desorption spectra obtained under these conditions for the flat (111) and stepped (13,1,1) platinum surfaces. Spectra for Pt(100) were essentially identical to those shown for Pt(13,1,1). All the adsorptions were carried out at 300-310 K, and 36 L represented saturation exposure (IL = 10^{-6} Torr sec.).

The clean (111) platinum surface displayed a single CO desorption peak centered at 440-490 K. Due to repulsive interactions, the temperature of the desorption peak maximum shifted to lower temperatures with increasing CO coverage. The clean (100) and (13,1,1) platinum surfaces exhibited two or more overlapping desorption peaks, th most prominent of which displayed a desorption peak maximum at 560 K.

The CO desorption spectra that were recorded following the n-hexane reaction rate studies always displayed very similar peak shapes and desoption peak temperatures to those determined for the initially clean platinum surfaces. However, the desorption peak areas were reduced markedly indicating that only a small concentration of uncovered sites remained after the high-pressure reactions. It can be seen that the desorption peak areas decreased with increasing surface carbon coverage which is represented by the C_{273}/Pt_{237} AES peak-to-peak height ratio.

A distinctly lower desorption temperature was detected when CO was chemisorbed on the platinum surfaces that were pretreated with n-hexane at 10^{-7} Torr and temperatures between 673 and 773 K. The new desorption peak maxima appeared at about 430 and 490 K for Pt(111) and Pt(13,1,1), respectively. The graphitic-like surface carbon produced under these

conditions reduced both the binding energy and the saturation coverage of the CO molecules.

The concentration of uncovered surface platinum sites which remained after the high-pressure n-hexane reaction studies was estimated by comparing the CO desorption peak areas measured following the reactions with those determined for the clean platinum surfaces. In Figure 13 the CO uptake θ determined following reaction rate studies has been divided by the saturation CO uptake for clean platinum surfaces θo, and the ratio $(\theta / \theta_o)_{CO}$ has been plotted as a function of the total surface carbon deposited by the reaction mixture. For comparison, CO uptake results for the graphite covered (111) and (13,1,1) platinum surfaces are also shown as a function of surface carbon coverage. Two points are important: (1) at any given carbon coverage as determined by AES, much more CO was adsorbed following the high pressure reaction studies than on the graphite-covered surfaces, and (2) the shape of the CO uptake curve determined following the reaction studies displayed a striking resemblance to the restart catalytic activity curves shown in Figures 3 and 4. The formation of 3-dimensional carbonaceous islands during the high pressure reactions affords a simple explanation for the first observation. At elevated temperatures, polymerization of the adsorbed species appears to compete with skeletal rearrangement and leads to the growth of disordered 3-D carbonaceous islands which, upon cooling, display an average hydrogen content in the range (H/C) = 1.0-1.6. The great similarity of the CO uptake and restart catalytic activity curves as a function of surface carbon coverage indicate convincingly that the <u>uncovered platinum atoms are the active sites for all types of catalyzed hydrocarbon conversion reactions</u>. This important conclusion is consistent with the fact that

little change in reaction selectivity was detected in the restart reactions. Uncovered platinum sites that area present in low concentrations do not appear to be affected either structurally or electronically by the presence of the carbon deposit. These sites maintain their normal, unique level of high activity and selectivity even at very high carbon coverages that are equivalent to 3-6 carbon atoms per surface platinum atom.

In the upper frame of Figure 14, the concentration of uncovered platinum sites determined by CO adsorption-desorption is shown as a function of reaction temperature. As expected from the restart reaction studies, the concentration of vacant sites decreased with increasing temperature.

If uncovered platinum sites are the exclusive source of catalytic activity for n-hexane reforming reactions, one would expect that a linear (or higher order) correlation should exist between reaction rates and the concentration of uncovered surface sites. As attempt to establish such a correlation is shown in the lower frame of Figure 14. Final rates determined at the end of the n-hexane reaction studies were divided by initial rates in the same reactions and plotted as a function of the fractional concentration of uncovered sites. All the data fall into a broad envelope corresponding to a fractional (0.6-0.9) order dependence of the final rates on vacant sites. This dependence would be naturally expected if (1) hydrogen transfer reactions between the carbon deposit and reactant molecules contribute to the overall catalytic activity, (2) the concentration of uncovered sites determined by CO adsorption is underestimated, or (3) the initial rates are underestimated because a certain amount of carbon is deposited instantly as the reactions commence.

Background catalytic activity could also contribute to the deviation from first-order behavior. Which of these effects is most important cannot be readily determined from the existing data. Considering the uncertainty involved in the determination of reaction rates and uncovered sites, the deviation from first order behavior cannot be considered very significant.

Selective blocking of step sites by the carbonaceous deposit was detected when CO was chemisorbed on a stepped (557) platinum surface following n-hexane reaction rate studies. As shown in Figure 15, the relative amounts of CO desorbed from step (high T state) and terrace (low T state) sites was altered appreciably as compared to clean platinum. Thus, nucleation and growth of the carbonaceous deposit during n-hexane conversion occurred preferentially at atomic step sites. However, with others reactants including isobutane, neopentane,, and cyclohexane, the site blockage appeared to be largely non-selective (Figure 15). Similar results were obtained on other stepped platinum surfaces. These observations strongly suggest that the growth mechanism of the carbonaceous deposit is sensitive to both surface structure and the structure of the reacting hydrocarbon.

The CO adsorption studies clearly indicate that the growth of 3-dimensional carbonaceous islands takes place during hydrocarbon catalysis over platinum single crystal surfaces. The average thickness of these islands can be roughly estimated using a homogeneous attenuation model for AES peak intensities together with the concentration of uncovered platinum sites that was determined by CO thermal desorption. According to this model the average overlayer thickness is given by

$$Z = \lambda s \left\{ \ln[1 - (\Theta / \Theta_o)_{CO}] - \ln[(I_s/I_s^o) - (\Theta / \Theta_o)_{CO}] \right\} \qquad (1)$$

where λ_s is the attenuation length for the substrate Auger electrons, I_s is the substrate Auger peak intensity, and I° is the AES peak intensity for the initially clean surface. Evaluation of Eq. (1) for the 237 eV platinum Auger transition with λ_s = 7 Å yielded values of the average overlayer thickness which increased with increasing reaction temperature from about 5-7Å at 550 K to 10-14Å at 670-700 K. These figures should not be taken too seriously as it is not known if the carbon deposit assumes a uniform thickness. However, the implication that the average thickness increases with increasing temperature should be noted. The deactivation kinetics reported for alkane reactions catalyzed over initially clean platinum surfaces (3,4) were always well described by the rate equation $R(t) = R(t=0)\exp(-\alpha t^n)$ where n decreased from about one at 540-560 K to 0.3-0.5 at 620-670 K. This change in order for the deactivation reaction with increasing temperature is naturally expected if the structure of the carbon deposit changed from two dimensional at low temperatures to three dimensional at high temperatures (19). The existing experimental data certainly tends to indicate that this change takes place.

The shapes and positions of the CO desorption peaks obtained following the n-hexane reactions also provide important information about the structure of the uncovered platinum sites. At very high carbon coverages the temperature of the CO desorption peak maximum for Pt(111) was about 570 K, whereas at lower carbon coverages the desorption peak maximum was shifted to about 540 K. This shift largely results from repulsive interactions between the adsorbed CO molecules (29). The fact that the CO desorption temperature at high carbon coverages ($C_{273}/Pt_{237} \geq 5$) was very similar to that determined for the clean Pt(111) surface in the limit of

zero CO coverage (~485 K) strongly suggests that the uncovered sites are mostly isolated, i.e., only 1-10 adjacent atoms. By contrast, the CO desorption temperature at lower carbon coverages (C_{273}/Pt_{237} = 1-4) was close to that measured for clean platinum at saturation CO coverage (≃440 K). In this case it appears that the uncovered platinum sites exist in the form of patches which contain enough metal atoms for the lateral interactions to become important. Dipole coupling calculations by Crossley and King (29) suggest that this is possible only if the uncovered patches contain at lest 10-20 contiguous platinum atoms. This apparent change in the size of the available sites with increasing temperature (carbon coverage) may contribute to the small changes in reaction selectivity that were often detected in the restart experiments.

Finally, it must be noted that the CO adsorption results are inconsistent with the idea that carbon may be dissolved into the near surface region. Extensive dissolution of surface carbon during the high pressure reactions would likely result in major restructuring withing the topmost surface layer. Such restructuring would cause the appearance of new adsorbate binding states as observed for CO adsorption on oxidized Pt(111) and Pt(110) (30,31) and sulphidized Pt(110) (32) and Fe(100) (33). No evidence for any such states was ever detected. In addition, the hydrogen TDS results clearly revealed that the carbon deposit is extensively hydrogenated with at least one hydrogen atom per surface carbon atom. It is difficult to imagine a process in which CH_x fragments could be stabilized in the subsurface region. While the possibility that a part of the carbon is dissolved in the near surface region cannot be ruled out, the experimental evidence certainly tends to demonstrate that most of the carbon deposit is formed on the external surface.

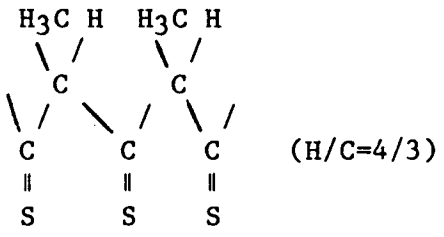
IV. The Composition and Structure of the Working Platinum Hydrocarbon Conversion Catalyst. A model for the working structure and composition of platinum reforming catalysts that emerges from this research is shown in Figure 16. Auger electron spectroscopy revealed that during steady state hydrocarbon conversion, platinum surfaces always become covered with about one or more monolayers of strongly bound carbonaceous deposit. In the absence of other chemical additives, the formation of this carbon deposit must be considered as a fundamental feature of the catalytic hydrocarbon chemistry. The deposit resulted from the activated nucleation and growth ($E_a \sim 10$-20 kcal/mole) (3,19) of unreactive polymeric species with an average hydrogen content of about 1.0-1.5 hydrogen atoms per surface carbon atom. The structure of this deposit varied from two-dimensional at low temperatures (>550 K) to three-dimensional for reaction temperatures higher than about 600 K. Catalyst deactivation kinetics along with restart reaction studies demonstrated that the carbonaceous deposit mainly participates as a non-selective poison; i.e. the deposit simply blocks platinum surface sites from incident reactant molecules. However, radiotracer studies (16) also revealed that the deposit provides sites for hydrogen transfer with reacting surface species. Since the binding energies of chemisorbed hydrocarbons appear to be lowered on carbon covered platinum surfaces (19), it is likely that the deposit can also provide desorption sites for product molecules. Thus, the presence of the carbonaceous deposit makes a catlayst out of platinum that readily exchanges hydrogen with reacting species and facilitates the release of product molecules.

Carbon monoxide adsorption-desorption studies revealed that a small concentration of uncovered platinum surface sites (ca 2-25%) always persists in the presence of this carbon deposit. The uncovered sites appear

to exist in the form of patches or ensembles that contain several contiguous surface atoms. The concentration of these sites decreases with increasing reaction temperature. The existence of these exposed, multiatomic sites is essential to rationalize the high selectivities for hydrogenolysis and aromatization that are displayed by carbon covered platinum. These sites are likely to be continuously regenerated by hydrogenolysis, rehydrogenation, and removal of a part of the carbon deposit by the excess hydrogen that always must be present during hydrocarbon conversion reactions.

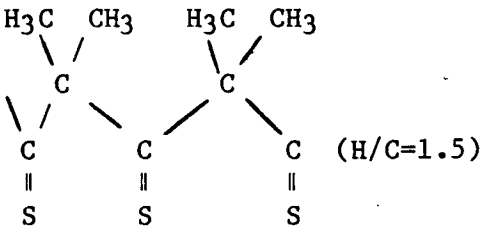
Another important feature of the catalyzed hydrocarbon reactions was the long surface residence times of the dissociatively chemisorbed intermediates which were on the order of seconds (17). Within this residence time the adsorbed species can diffuse over long distances (e.g., 10^{-8}–10^{-3} cm) and visit many different types of surface sites. All sites that are contained in an uncovered patch can therefore become available for sequential bond breaking and skeletal arrangement. It may even be possible for the adsorbed species to visit adjacent ensembles by diffusing over, around, or through the strongly bound carbonaceous deposit. Creative experiments are required to further investigate the mobility of the adsorbed species.

The chemical composition of the carbonaceous deposit was intermediate between that expected for polyacetylene (H/C = 1.0) and polyethylacetylene (H/C = 1.5), or related surface species such as (I) and (II).



(H/C=4/3)

(I)



(H/C=1.5)

(II)

The actual structure of the deposit appears to be heterogeneous and cannot be determined from existing data. However, a polymeric residue is clearly required to account for the low reactivity and high hydrogen content of this surface species. Paal and Tetenyi (11) and others (12) have previously proposed that polylefins are responsible for the catalyst deactivation that is displayed during hydrocarbon skeletal rearrangement on other types of platinum catalysts.

Temperature Dependent Catalytic Behavior of Hydrocarbons Chemisorbed on Platinum. The reaction chemistry of hydrocarbons chemisorbed on platinum is characterized by three distinguishable temperature regimes in which the bond strength, bond-multiplicity, and catalytic behavior of the metal-organic layer are distinctly different;

(1) Low temperatures (<300 K)
Reversible hydrocarbon chemisorption
Clean metal catalysis at high hydrogen pressures

(2) High temperatures (>750 K)
Multilayer carbon build-up
Poisoning by graphitic coke

(3) Medium temperatures (~ 350-750 K)
Reversible (1 atm) or irreversible (10^{-7} Torr) adsorption with sequential bond breaking, skeletal rearrangement and intermolecular hydrogen transfer.
Catalysis by bare platinum islands in the presence of active C_xH_y fragments at high hydrogen pressures (~1 atm)

Provided that the temperature is low enough (<300 K), hydrocarbons chemisorb molecularly, or at least more-or-less reversibly, on any platinum surface. Alkanes are dissociatively adsorbed to a very small extent. Thermal desorption studies (19,22) provided adsorption energies for simple alkanes, olefins, and benzene that varied from about 10 to 20 kcal/mole. In the presence of 1 atm of hydrogen these weakly adsorbed species readily undergo hydrogen addition and deuterium exchange processes

which continuously regenerate the clean metal active sites that are responsible for these reactions (17,34). At the other extreme, if the temperature is higher than about 750 K (700 K, 10^{-7} Torr; ≥ 800 K 1 atm) all hydrocarbons adsorbed dissociatively and irreversibly leading to the growth of graphitic carbon islands that eventually condense into continuous overlayers that poison all catalytic activity. In the most interesting intermediate temperature range of about 350-700 K, the adsorbed species rapidly undergo sequential C-H bond breaking, skeletal rearrangements, and hydrogen transfer processes on the platinum metal islands that produce catalytically active C_xH_y fragments. Over this temperature range, hydrogenation, dehydrogenation, and deuterium exchange all occur at rates that are typically 10-10^3 times faster than skeletal rearrangement. Under these conditions, (1) uncovered metal sites remain available for hydrogen and hydrocarbon chemisorption, and (2) dissociatively adsorbed reaction intermediates exist in quasiequilibrium with gas phase hydrogen. The uncovered platinum sites are responsible for the unique selectivity of platinum catalysis. The existence of these sites also accounts for the structure sensitivities that are often displayed during alkane skeletal rearrangement. Aromatization activity and selectivity was maximized on flat, stepped, and kinked platinum surfaces with (111) terraces (1,3). The low coordination number step and kink atoms were particularly effective for catalyzing cyclohexane (2) and n-heptane (1) aromatization. By contrast, the less important bond shift isomerization reactions of butanes occurred preferentially on platinum surfaces with (100) terraces (4). The specific reaction chemistry that is displayed by each type of site appears to depend strongly on both the local stereochemistry and electronic properties of that site. For certain reactions such as aromatization and bond-shift isomerization,

the reaction selectivity can be predictably tailored by controlling the terrace structure and the concentrations of steps and kinks.

V. Implications for Alloy Catalysis and Hydrocarbon Catalysis by Other Group VIII Metals. As compared to pure platinum, bimetallic alloys such as Pt-Re, Pt-Au, Pt-Ir, Ir-Au, and Pd-Au offer superior activity, selectivity, and poison resistance in catalyzed hydrocarbon reforming reactions (35). The improved stability of the Group VIII-Group IB alloys can be easily rationalized in the context of our model of the working metal catalyst. Since Group IB metals do not form strong bonds with hydrocarbon adsorbates, the concentration of carbonaceous fragments with high metal-organic bond multiplicity is reduced. Polymerization of the adsorbed species that is required for formation of carbonaceous deposits still can can probably does occur at exposed Group VIII metal sites. However, since these sites are isolated and mostly surrounded by a matrix of inactive metal sites, the removal of the carbonaceous deposit by rehydrogenation can be accelerated. In this case, the larger hydrocarbon molecules can easily desorb or "spillover" onto the acid sites of the support where hydrocracking takes place.

It is natural to ask if the same type of stable, strongly bound polymeric residues will be present during hydrocarbon catalysis over other Group VIII metals. While insufficient information now exists for a general conclusion, it appears likely that polymeric carbon deposits should be most prevalent on platinum and palladium catalysts. The reason for suggesting this is shown clearly in Figure 17 where we compare the activities of Group VIII metals for several alkane hydrogenolysis reactions (36). The periodic pattern of reativity displayed for these reactions does

not depend appreciably on the alkane, surface structure, or catalyst type. Within the 4d and 5d series, maximum activity is always observed with ruthenium and osmium catalysts, i.e., in the first subgroup of Group VIII. From rutherium to palladium, and osmium to platinum, the hydrogenolysis activity decreases by 6-9 orders of magnitude. In the first transition series, cobalt and nickel both exhibit comparably high activity. The very low hydrogenolysis activity of platinum catalysts may account in part for the high stability of the carbonaceous deposit, since, once formed, the polymeric residue has only a small probability for undergoing C-C bondbreaking processes that would lead to its continuous rehydrogenation and removal. By contrast, for metals that are very active for hydrogenolysis such as ruthenium, rhodium, osmium, and iridium, it appears likely that continuous hydrogenolysis and decomposition reactions may slow down the formation of polymeric carbonaceous deposits. This proposal could be easily tested by reaction rate studies over single crystal surfaces of other Group VIII metals.

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REFERENCES

1. W.D. Gillespie, R.K. Herz, E.E. Petersen and G.A. Somorjai, J. Catal., 70, 147 (1981)

2. R.K. Herz, W.D. Gillespie, E.E. Petersen and G.A. Somorjai, J. Catal., 67, 371 (1981)

3. S.M. Davis, F. Zaera and G.A. Somorjai, J. Catal., submitted (1st paper of series).

4. S.M. Davis, F. Zaera and G.A. Somorjai, submitted to J. Catal.

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

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

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

8. T. Hattori and R.L. Burwell, Jr, J. Phys. Chem, 83, 241 (1979).

9. Z. Paal, M. Dobrovolszky and P. Tetenyi, J. Catal., 46, 65 (1977).

10. P.P. Lankhorst, H.C. DeJongste and V. Ponec, in Catalyst Deactivation (B. Delmon and G.F. Foment, eds.) Elsevier, Amsterdam, 1980.

11. Z. Paal and P. Tetenyi, J. Catal., 30, 350 (1973).

12. D.L. Trimm, Catal. Rev., 16, 155 (1977), and references cited therein.

13. H. Heinemann, D.W. Blakely and W.C. Baird, Jr., Private communications.

14. S.J. Thomson and G.Webb, J.C.S. Chem Comm., 526 (1976).

15. N.C. Gardner and R.S. Hansen, J. Phys. Chem., 74, 3298 (1970).

16. S.M. Davis, F. Zaera and G.A. Somorjai, J. Catal., to be submitted.

17. S.M. Davis and G.A. Somorjai, J.Phys. Chem in press.

18. S.M. Davis, W.D. Gillespie and G.A. Somorjai, J. Phs. Chem, in press.

19. S.M. Davis, Ph.D. Thesis, University of California, Berkeley, 1981.

20. S.M. Davis, B.E. Gordon, M. Press and G.A. Somorjai, J. Vac. Sci. and Technol., 19, 231 (1981).

21. E. Segal, R.J. Madon and M. Boudart, J. Catal., 52. 45 (1978).

22. M. Salmeron and G.A. Somorjai, J. Phys. Chem. in press.

23. T.R. Hughes. Private communication.

24. Z. Karpinski and T. Koscielski, J. Catal., 63, 313 (1980).

25. A.M. Baro and H. Ibach, J. Chem. Phys., 74, 4194 (1981).

26. L.H. Dubois, Ph.D. Thesis, University of California, Berkeley, 1980.

27. S.J. Gregg and K.S.W. Sing, Adsorption Surface Area and Porosity, Academic Press, New York, 1967, Chpt. 6;

J.H. Sinfelt and D.J.C. Yates, J. Catal., 10, 362 (1968);

M.A. Vannice, J. Catal., 37, 449 (1975);

W.B. Innes, in Experimental Methods in Catalytic Research (R.B. Anderson, Ed.), Vol 1, Academic Press, New York, (1968);

R.L. Moss, in Experimental Methods in Catalytic Research (R.B. Anderson, Ed.) Vol 2, Academic Press, New York, 1972.

28. T.R. Hughes, R.J. Houston and S.P. Sieg, Ind. Eng. Chem. Proc. Design and Develop., 1, 96 (1962).

29. A. Crossley and D.A. King, Surface Sci., 95, 131 (1980).

30. R.W. McCabe and L.D. Schmidt, Surface Sci., 65, 189 (1977).

31. R.W. McCabe and L.D. Schmidt, Surface Sci., 60, 85 (1976).

32. H.P. Bonzel and R. Ku, J. Chem. Phys., 58, 4617 (1973).

33. J. Benziger and R.J. Madix, Surface Sci., 94, 119 (1980).

34. S.M. Davis and G.A. Somorjai, J. Catal., 65, 78 (1980).

J.H. Sinfelt, Catalysis Reviews 9, 147 (1974).

35. see for example V. Ponec, Exchange and Reforming Reactions on Metals and Alloys, in The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 4, Elsevier, Amsterdam, 1981.

J.H. Sinfelt, Adv. in Catalysis 23, 191 (1973).

36. S.M. Davis and G.A. Somorjai, Hydrocarbon Conversion Over Metal Catalysts, in The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 4, Elsevier, Amsterdam, 1981, and references cited therein.

Table 1. Summary of light alkane restart reaction rates and comparisons with clean platinum (a).

Catalyst	T(K)	Pretreatment	$(C/Pt)_i$ (b)	Restart Rates (molec/Pt atom. sec) isom.	Restart Rates (molec/Pt atom. sec) Hydrog.	(R_r/R_c) (c) Isom.	(R_r/R_c) (c) Hydrog.
Isobutane Reactions:							
Pt(10,8,7)	573	neopentane + H_2 563 K	1.0	8×10^{-3}	6×10^{-3}	0.13	0.4
		neopentane + H_2 573 K	1.0	5×10^{-3}	6×10^{-3}	0.08	0.4
	593	n-hexane + H_2 623 K	3.2	——	$\sim3\times10^{-4}$	——	~0.01
Pt(13,1,1)	573	neopentane + H_2 573 K	1.2	0.045	1.4×10^{-3}	0.20	0.25
		n-hexane + H_2 573 K	2.3	7×10^{-3}	7×10^{-4}	0.03	0.13
Neopentane Reactions:							
Pt(10,8,7)	573	n-hexane + H_2 573 K	2.6	4×10^{-3}	1×10^{-3}	0.02	0.04
		n-hexane + H_2 600 K	3.5	2×10^{-3}	1×10^{-3}	0.01	0.04
Pt(13,1,1)	573	isobutane + H_2 573 K	1.2	0.054	7×10^{-3}	0.27	0.30

(a) $H_2/HC = 10$, $P_{tot} = 220$ Torr.

(b) Carbon atoms per surface platinum atom from the initial reaction (±30 percent).

(c) Restart rate over clean platinum rate.

Table 2. Catalytic behavior of platinum in n-hexane restart reactions (a).

Catalyst	T(K)	Pretreatment	$(C/Pt)_i$ (b)	Initial Restart Rate (molec/Pt atom sec)	R_c/R_{Pt} (± 0.05) (c)			
					2MP + 3 MP	$< C_6$	MCP	Bz
Pt(10,8,7)	573	$i-C_4H_{10}$-553 K	0.9	0.025	0.80	0.90	0.70	0.80
Pt(10,8,7)	573	$i-C_4H_{10}$-603 K	2.4	7.1×10^{-3}	0.25	0.35	0.15	0.30
Pt(10,8,7)	573	$n-c_6H_{14}$-573 K	2.1	7.0×10^{-3}	0.27	0.35	0.15	0.30
Pt(111)	573	$n-C_6H_{14}$-533 K	1.4	0.023	0.50	0.40	0.50	0.60
Pt(111)	573	$n-C_6H_{14}$-573 K	2.0	6.4×10^{-3}	0.20	0.20	0.20	0.25
Pt(111)	592	$n-C_6H_{14}$-593 K	2.4	7.4×10^{-3}	0.14	0.14	0.14	0.18
Pt(111)	598 (d)	$n-C_6H_{14}$-598 K	2.6	0.016	0.12	0.14	0.13	0.15
Pt(111)	648 (d)	$n-C_6H_{14}$-648 K	3.8	0.013	0.07	0.09	0.07	0.11

(a) Partial listing; additional data are shown in Figs. 3, 4 and 5.

(b) Carbon atoms per surface platinum atom (±20 percent) from the initial reaction.

(c) Ratio of restart rate to clean platinum rate under the same conditions.

(d) $H_2/HC = 30$, $P_{tot} = 620$ Torr; otherwise $H_2/HC = 10$, P_{tot} 220 = Torr.

Table. 3 Catalytic behavior of platinum in n-hexane reaction studies catalyzed over single crystal surfaces precovered with overlayers containing carbon-14.

Catalyst	Rxn T (K)	Preadsorbed Hydrocarbon (and T_{ads}(K))	R_c/R_{Pt} [a] (±0.1)	(θ/θ_o) [b] (±10 percent)	Initial Coverage (moles/cm^2 ± 30 percent)
Pt(100)	573 (c)	C_6H_6(573)	0.64	46	4×10^{13}
Pt(100)	573 (c)	C_6H_6(639)	0.66	84	5×10^{13}
Pt(100)	673	C_6H_6(639)	0.76	54	5×10^{13}
Pt(111)	573	C_2H_4(413)	0.92	2	4×10^{14}
Pt(111)	573	C_2H_4(523)	0.58	40	4×10^{14}
Pt(111)	573	C_2H_4(573)	0.36	65	1×10^{15}
Pt(111)	623	C_2H_4(523)	0.62	30	5×10^{14}
Pt(111)	623	C_2H_4(623)	0.45	82	1.4×10^{15}
Pt(111)	673	C_6H_6(673)	0.50	70	6×10^{13}

(a) Ratio of reaction rates for the preadsorbed overlayer experiments and clean platinum.

(b) Irreversibly adsorbed fraction of the preadsorbed overlayer.

(c) H_2/HC = 10, P_{tot} = 220 Torr; otherwise H_2/HC = 30, P_{tot} = 620 Torr.

Table 4. Reaction Rates for Cyclohexene Restart Experiments Catalyzed Over Pt(111)[a]

T(K)	Pretreatment	Reaction Rates (molec/Pt atom sec) Hydrogenation	Dehydrogenation	Θ_i [b]
373	clean	>60[c]	~0.18	0
373	n-hexane + H_2 623 K	0.5	~0.05	4.8
473	clean	>200[c]	>18[c]	0
473	n-hexane + H_2 623 K	20	2.3	4.8

(a) $H_2/HC = 30$, $P_{tot} = 620$ Torr

(b) carbon atoms per surface platinum atom (± 20%) at the start of the restart experiment

(c) so rapid that only lower limits could be established.

FIGURE CAPTIONS

Figure 1. Product accumulation curves determined as a function of reaction time at 573 K for isobutane isomerization catalyzed over the clean (13,1,1) platinum surface and in restart reactions catalyzed over carbon covered Pt(13,1,1).

Figure 2. Dependence of restart catalytic activity on surface carbon coverage for isobutane and neopentane restart reactions catalyzed over Pt(13,1,1) and Pt(10,8,7).

Figure 3. Dependence of restart catalytic activity on surface carbon coverage for n-hexane restart reactions catalyzed over Pt(111) and Pt(10,8,7) (H_2/HC = 10, P_{tot} = 220 Torr).

Figure 4. Dependence of restart catalytic activity on surface carbon coverage for n-hexane restart reactions catalyzed over Pt(111) (H_2/HC = 30, P_{tot} = 620 Torr). A few of the data at 573 K represent reaction studies catalyzed over preadsorbed overlayers containing carbon-14.

Figure 5. Dependence of restart catalytic activity on reaction temperature for n-hexane restart reactions catalyzed over Pt(111) and Pt(10,8,7). The initial and restart reactions were carried out using identical experimental conditions.

Figure 6. Dependence of the irreversibly adsorbed fraction on adsorption temperature for n-hexane reaction studies catalyzed on platinum surfaces with preadsorbed overlayers containing carbon-14.

Figure 7. Catalytic activity of the carbon-covered (322) platinum surface for cyclohexene hydrogenation and dehydrogenation. Benzene, ethylene, and 1-butene were preadsorbed at 10^{-7} Torr and 475-525 K, the surface coverage by preadsorbed species was determined by AES, and then the cyclohexene reactions were carried out at 300 or 425 K.

Figure 8. Comparison between product distributions for n-hexane reactions catalyzed at 600-670 K over the initially clean (111) platinum surface and in restart reactions catalyzed over carbon-covered Pt(111).

Figure 9. Hydrogen thermal desorption spectra (lower frame) recorded after n-hexane reaction studies that were carried out at 573-678 K over the flat (111) and kinked (10,8,7) platinum single crystal surfaces. The average hydrogen content of the carbonaceous deposits as determined from the total desorption peak areas is also shown as a function reaction temperature (upper frame) (β = 69-88 K/sec).

Figure 10. Hydrogen thermal desorption spectra recorded following a series of alkane reaction studies on the (100) platinum surface at 573 K (n-hexane, neopentane) and 615 K (isobutane, n-butane). The average hydrogen content of the carbonaceous overlayers is also shown.

Figure 11. Comparison between CO thermal desorption spectra for the clean (111) platinum surface (left frame), Pt(111) following n-hexane reaction rate studies (middle frame); and Pt(111) following the preadsorption of n-hexane at 673 K (right frame). The adsorption temperature was 310-315 K and $\beta \sim 90$ K/sec.

Figure 12. Comparison between CO thermal desorption spectra for the clean (13,1,1) platinum surface (left frame), Pt(13,1,1) following n-hexane reaction rates studies (middle frame), and Pt(13,1,1) following the preadsorption of n-hexane at about 670 K (right frame). The adsorption temperature was 310-315 K and $\beta \sim 80$ K/sec.

Figure 13. Fractional concentrations of uncovered platinum surface sites determined by CO adsorption-desorption as a function of surface carbon coverage on the (100), (111), and (13,1,1) platinum surfaces. A comparison is made between the CO uptake determined following n-hexane reaction studies and CO uptake determined when CO was coadsorbed with "graphitic" surface carbon.

Figure 14. Fractional concentrations of uncovered platinum surface sites determined by CO adsorption-desorption following n-hexane reaction studies on the (100), (111), and (13,1,1) platinum surfaces are shown as a function of reaction temperature (upper frame). Final rates estimated at the end of the n-hexane reaction studies have been divided by initial rates on clean platinum and plotted as a function of the fractional concentration of uncovered sites (lower frame).

Figure 15. Comparison between CO thermal desorption for the clean (557) platinum surface and Pt(557) following hydrocarbon reactions. The adsorption temperature was 310-315 K, $\beta \sim 80$K/sec, and exposure = 36 L.

Figure 16. Model for the working surface composition of platinum reforming catalysts.

Figure 17. Periodic variation in the catalytic activity of metal catalysts for alkane hydrogenolysis reactions catalyzed near atmospheric pressure (36).

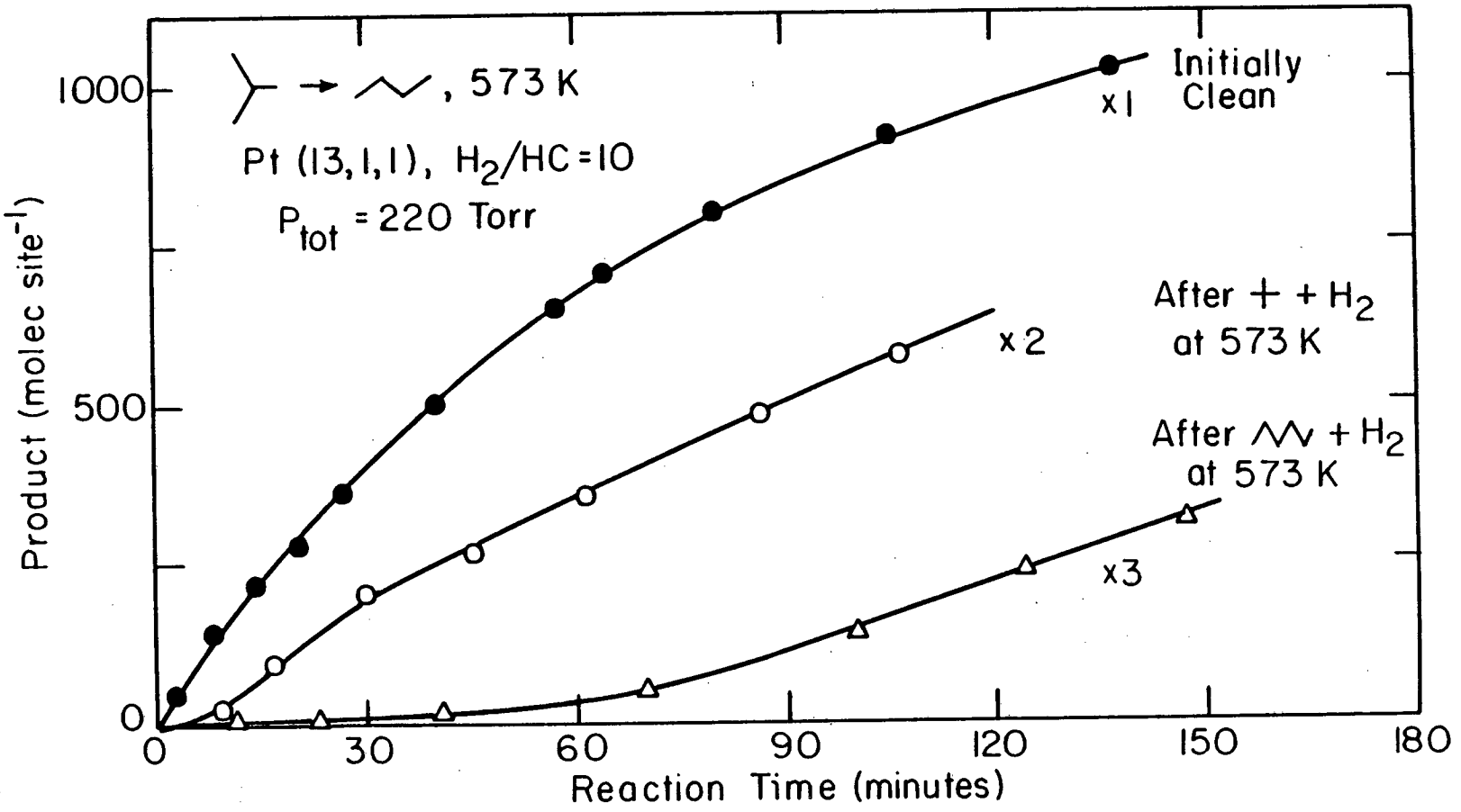

Fig. 1

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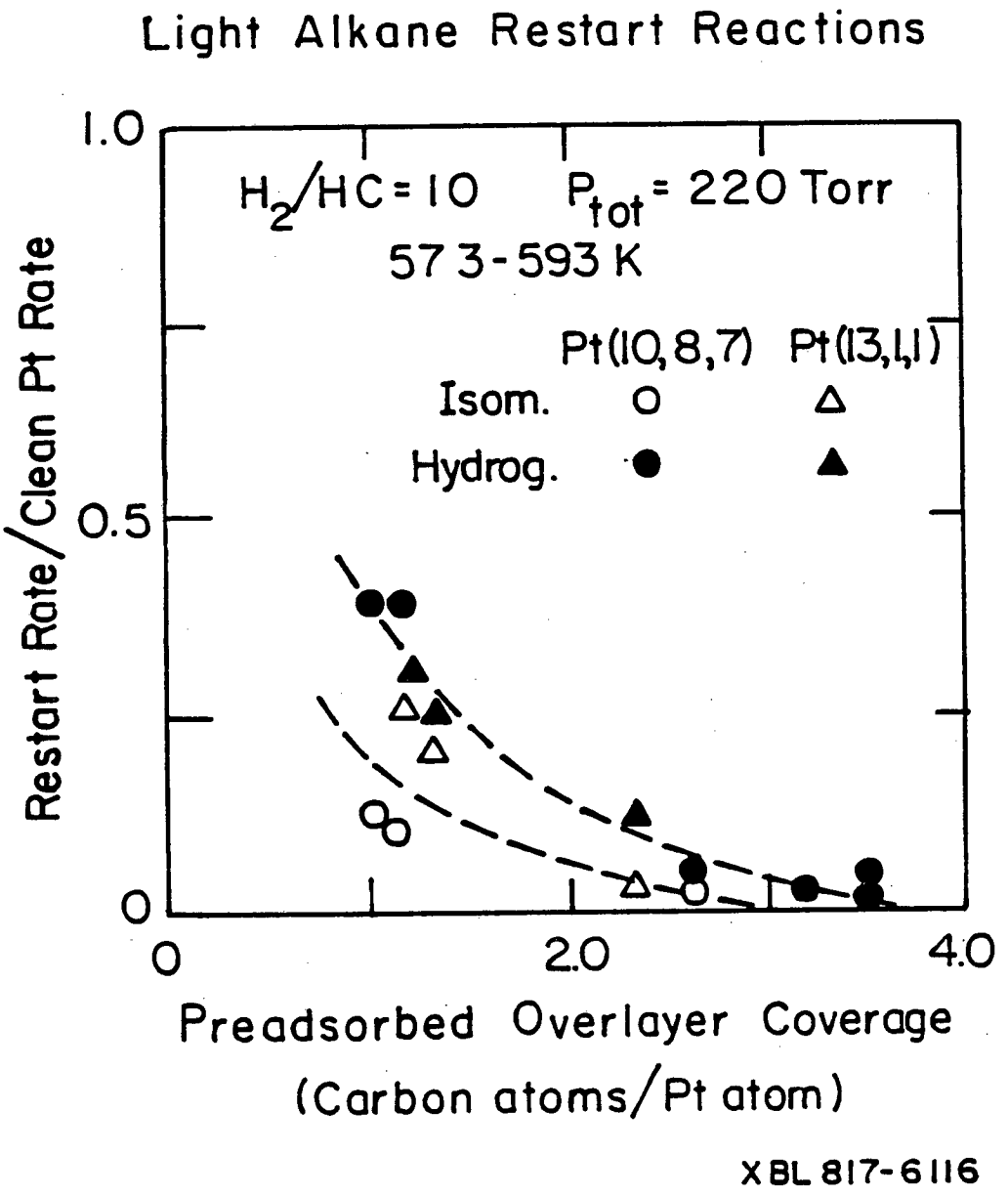

Light Alkane Restart Reactions
H2/HC = 10
Ptot = 220 Torr
573-593 K
Pt(10,8,7)
Pt(13,1,1)
Isom.
Hydrog.
1.0
0.5
0
0
2.0
4.0
Restart Rate/Clean Pt Rate
Preadsorbed Overlayer Coverage
(Carbon atoms/Pt atom)
XBL 817-6116

Fig. 2

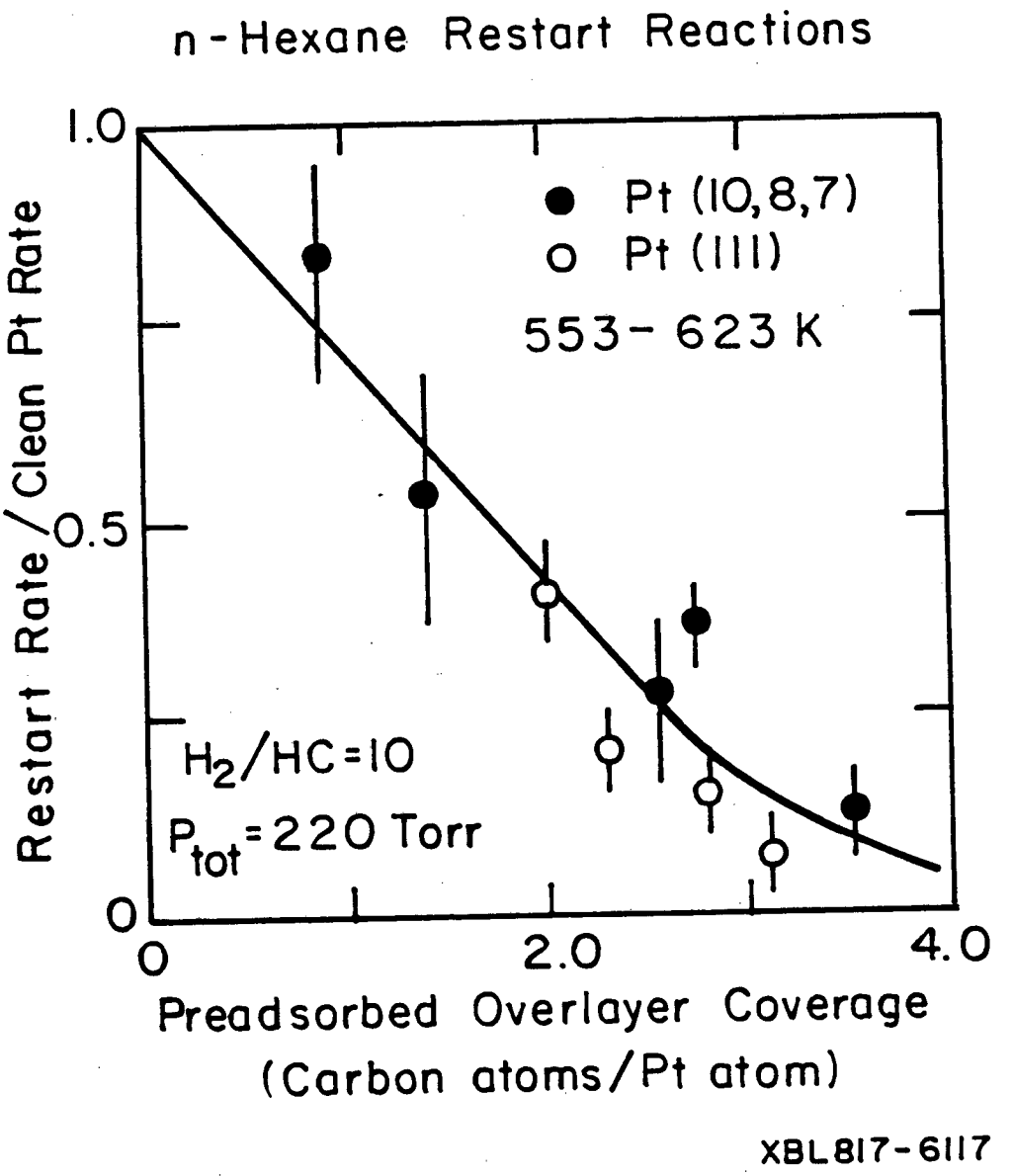
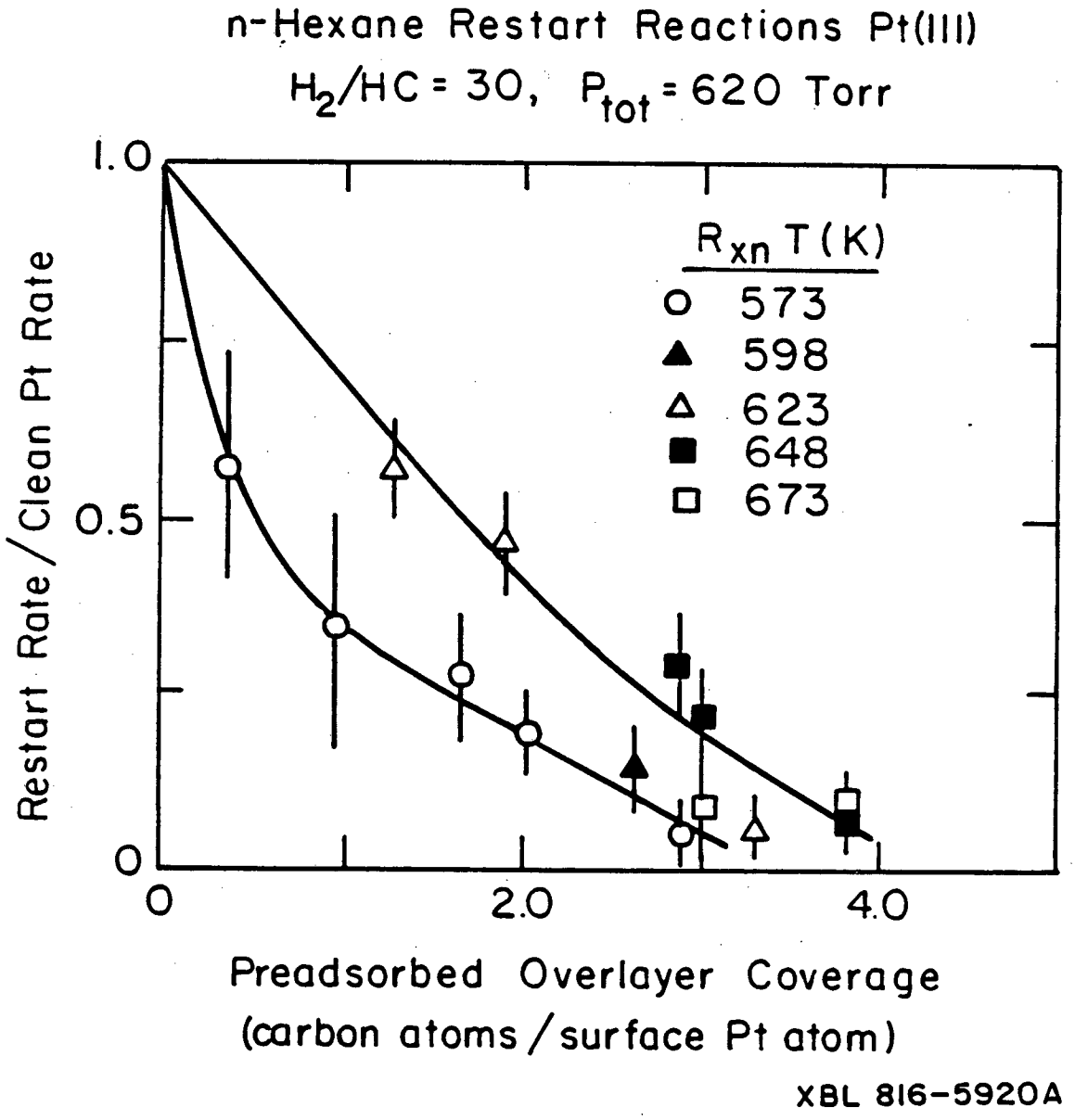

n-Hexane Restart Reactions
1.0
0.5
0
Restart Rate / Clean Pt Rate
Pt (10,8,7)
Pt (111)
553-623 K
H2/HC=10
Ptot=220 Torr
0
2.0
4.0
Preadsorbed Overlayer Coverage
(Carbon atoms/Pt atom)
XBL817-6117

Fig. 3



XBL 816-5920A

Fig. 4

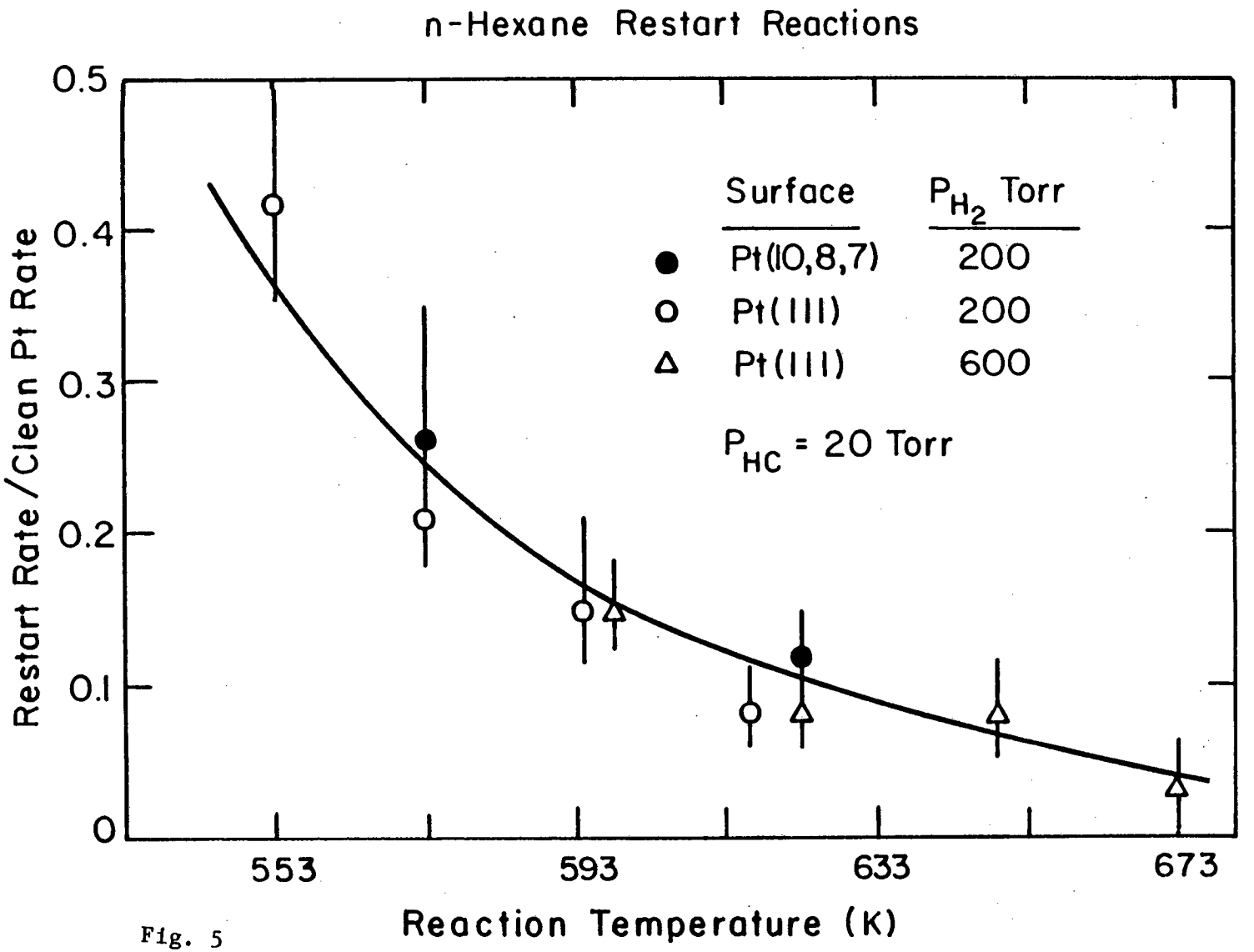
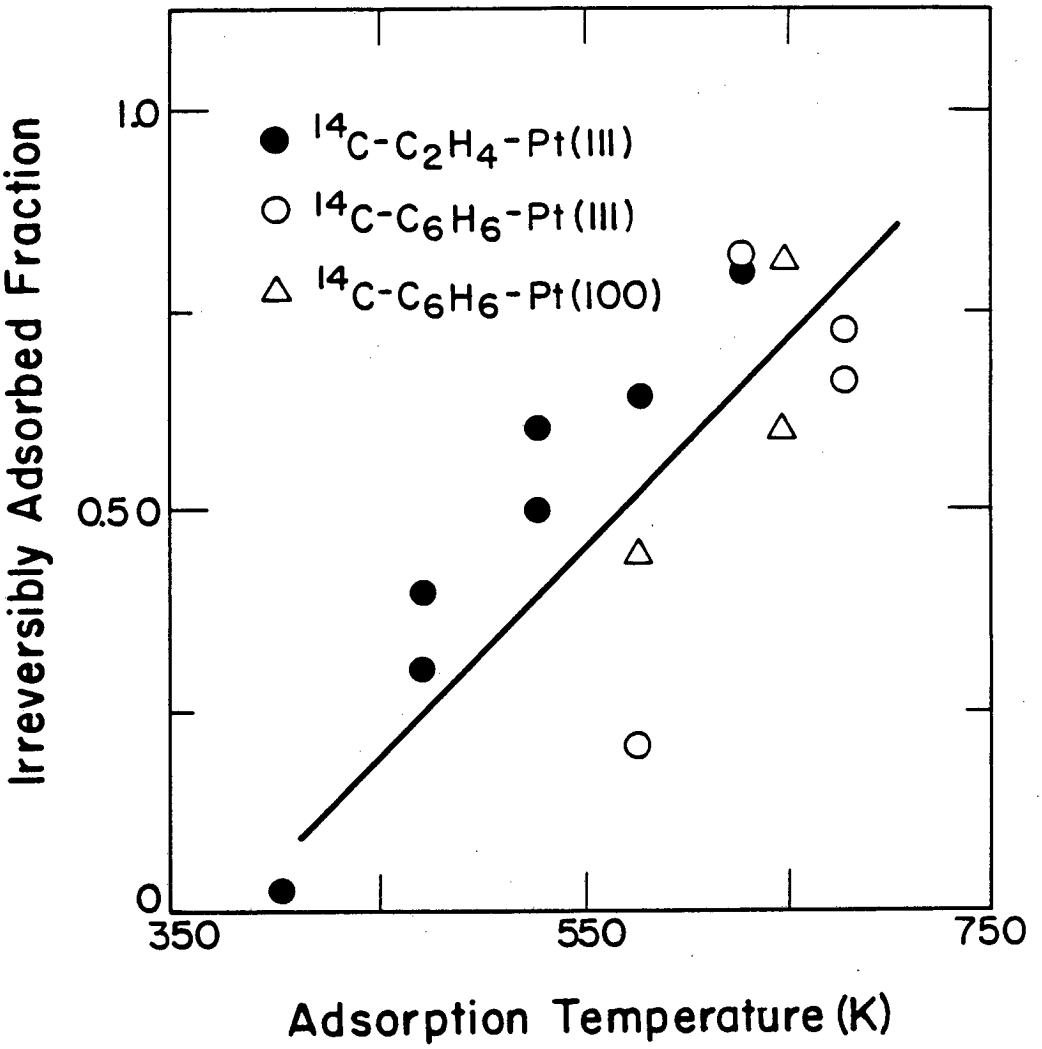


Fig. 5

XBL 817-6118A



XBL 818-1096

Fig. 6

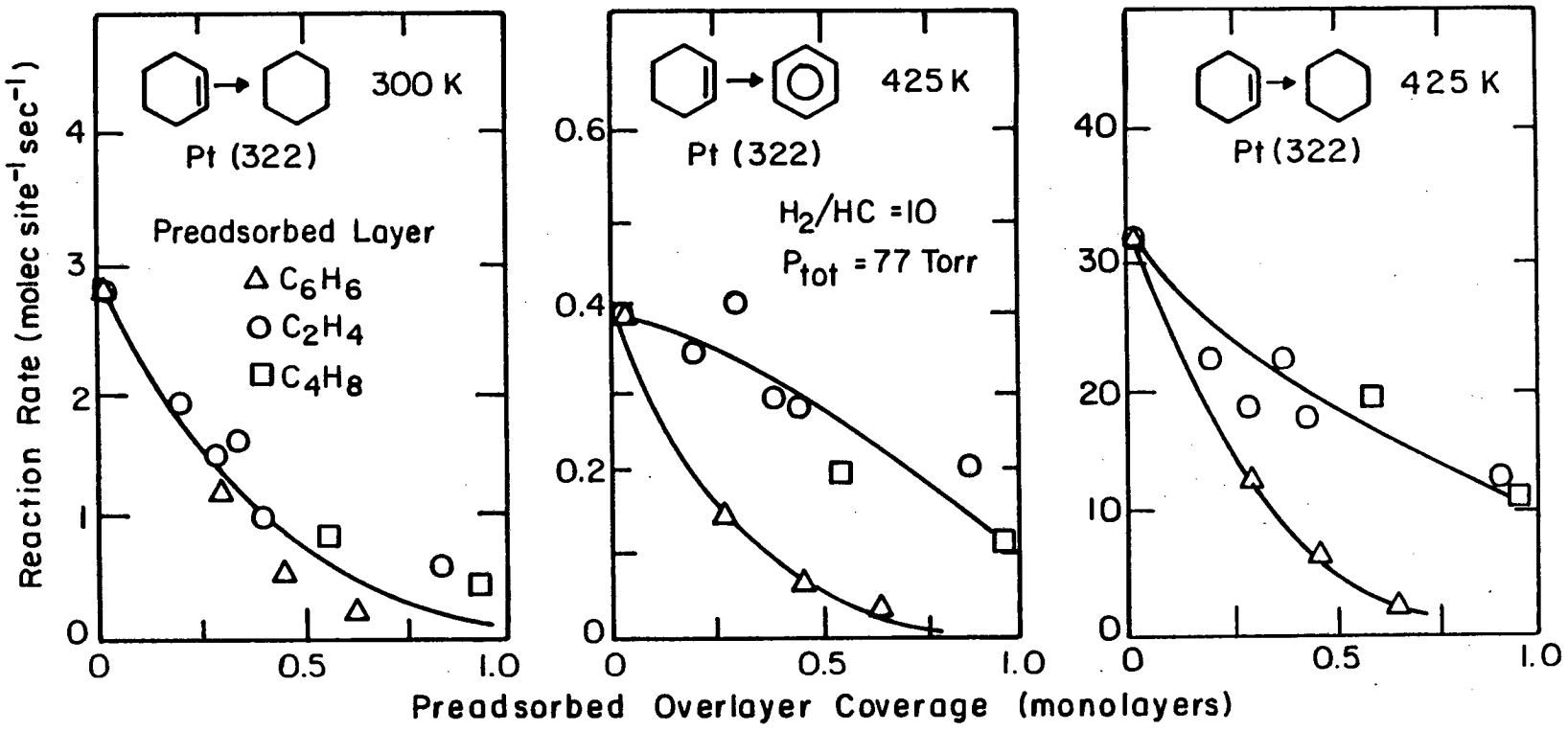


Fig. 7

XBL 812-5156

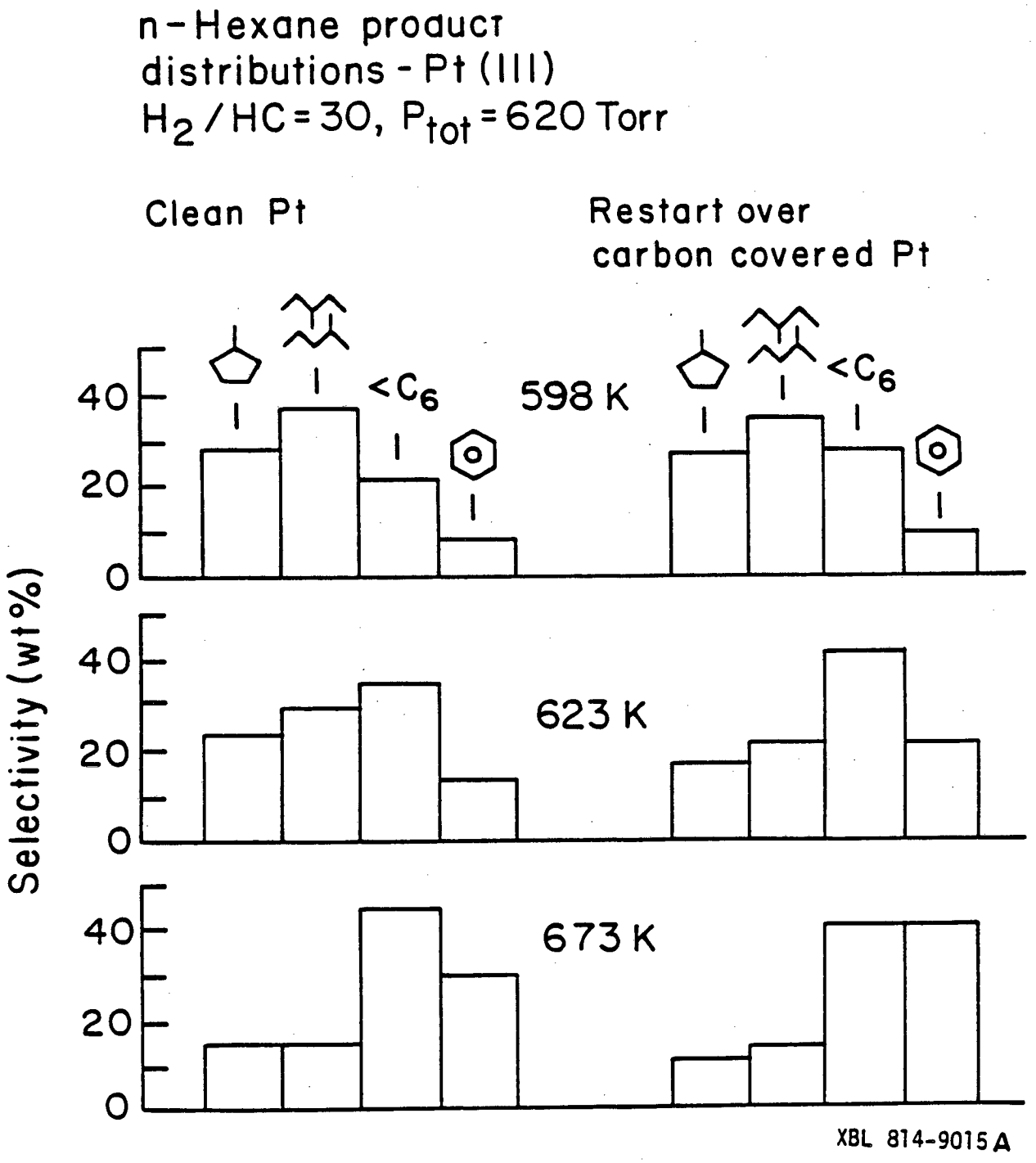

n-Hexane product
distributions - Pt (111)
H2/HC=30, Ptot=620 Torr
Clean Pt
Restart over
carbon covered Pt
<C6
598 K
623 K
673 K
Selectivity (wt%)
40
20
0
XBL 814-9015A

Fig. 8

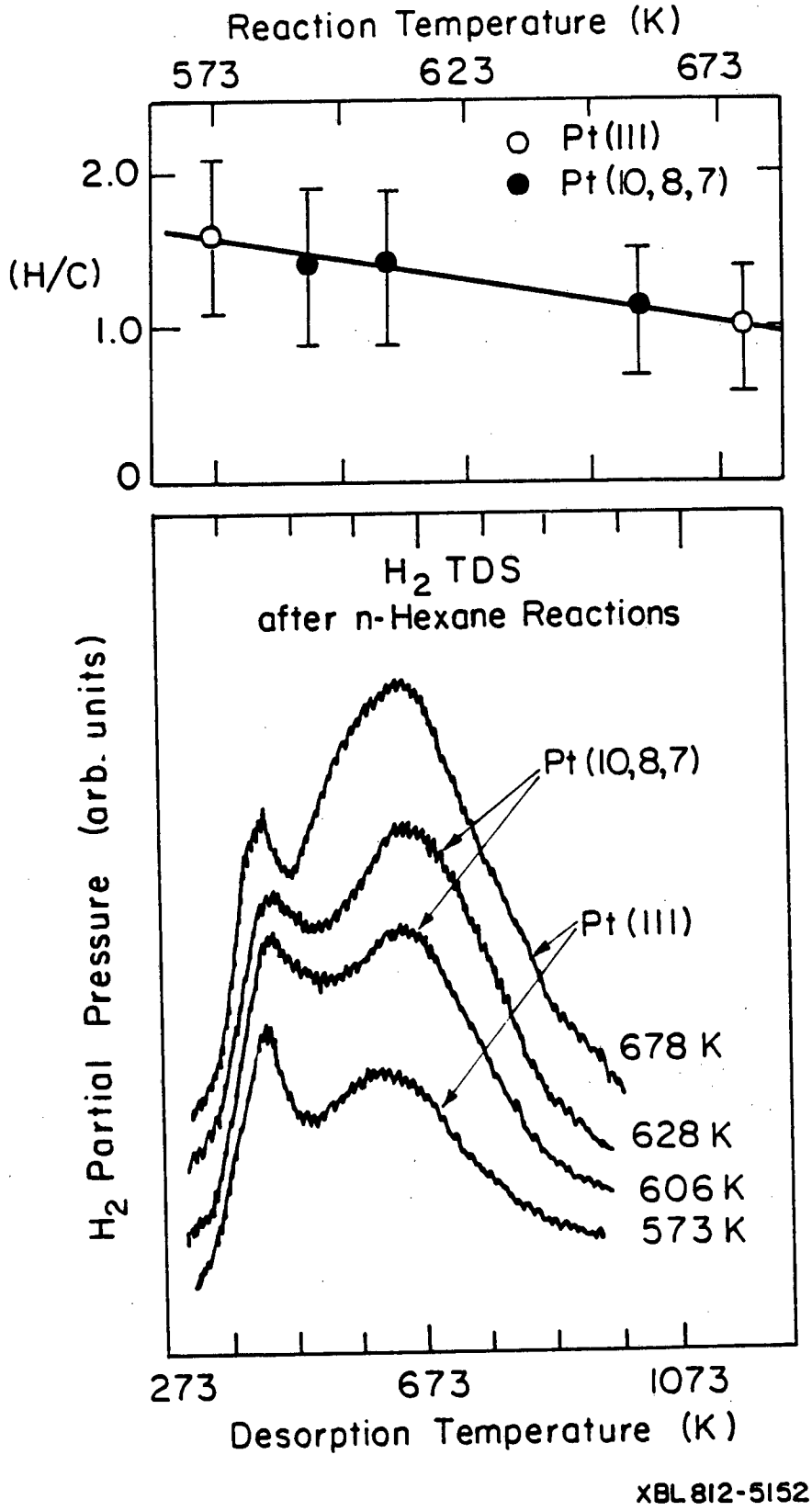

Reaction Temperature (K)
573
623
673
2.0
(H/C)
1.0
0
Pt(111)
Pt(10,8,7)
H2 TDS
after n-Hexane Reactions
H2 Partial Pressure (arb. units)
Pt(10,8,7)
Pt(111)
678 K
628 K
606 K
573 K
273
673
1073
Desorption Temperature (K)
XBL 812-5152

Fig. 9

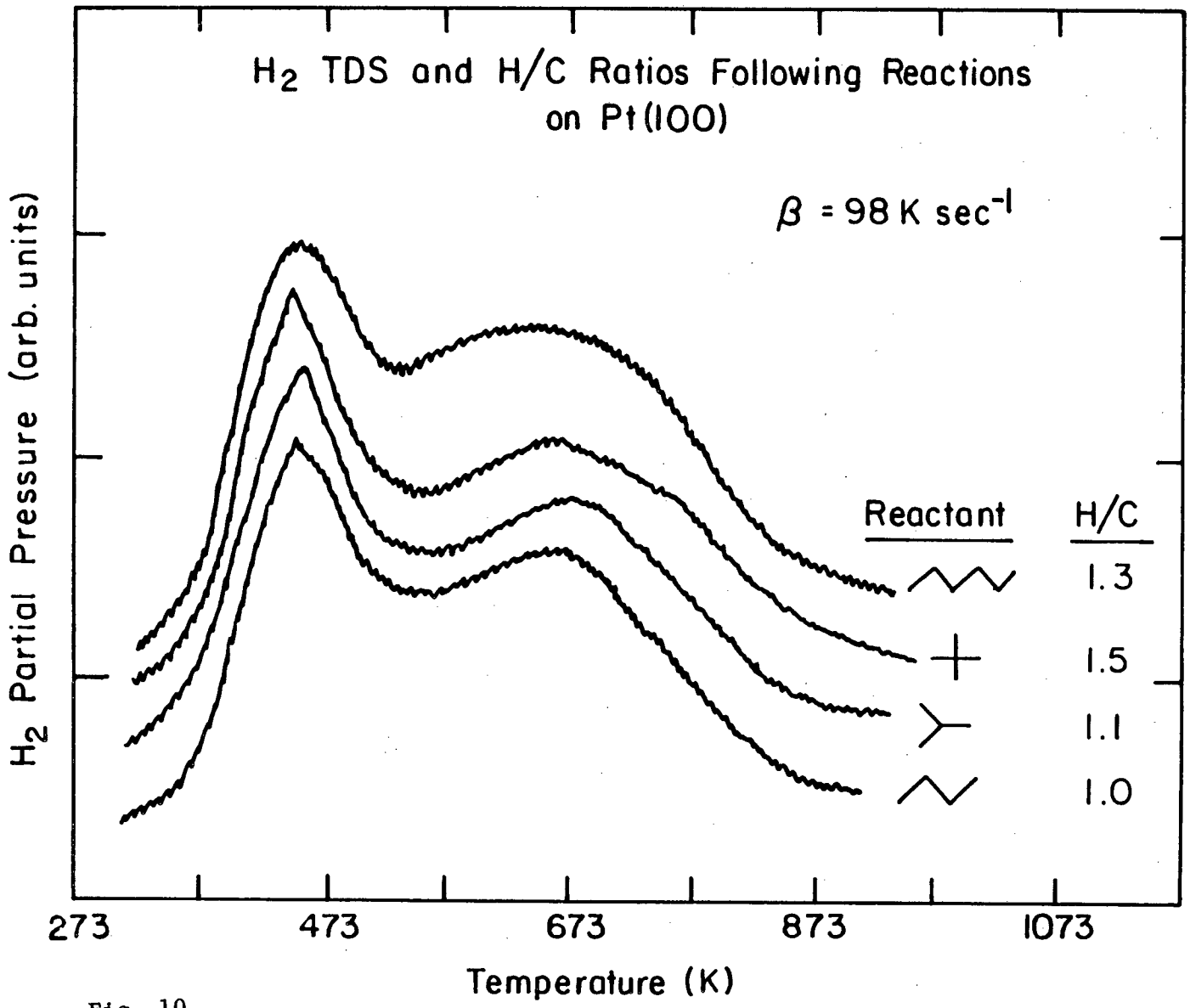


Fig. 10

XBL 817-6104A

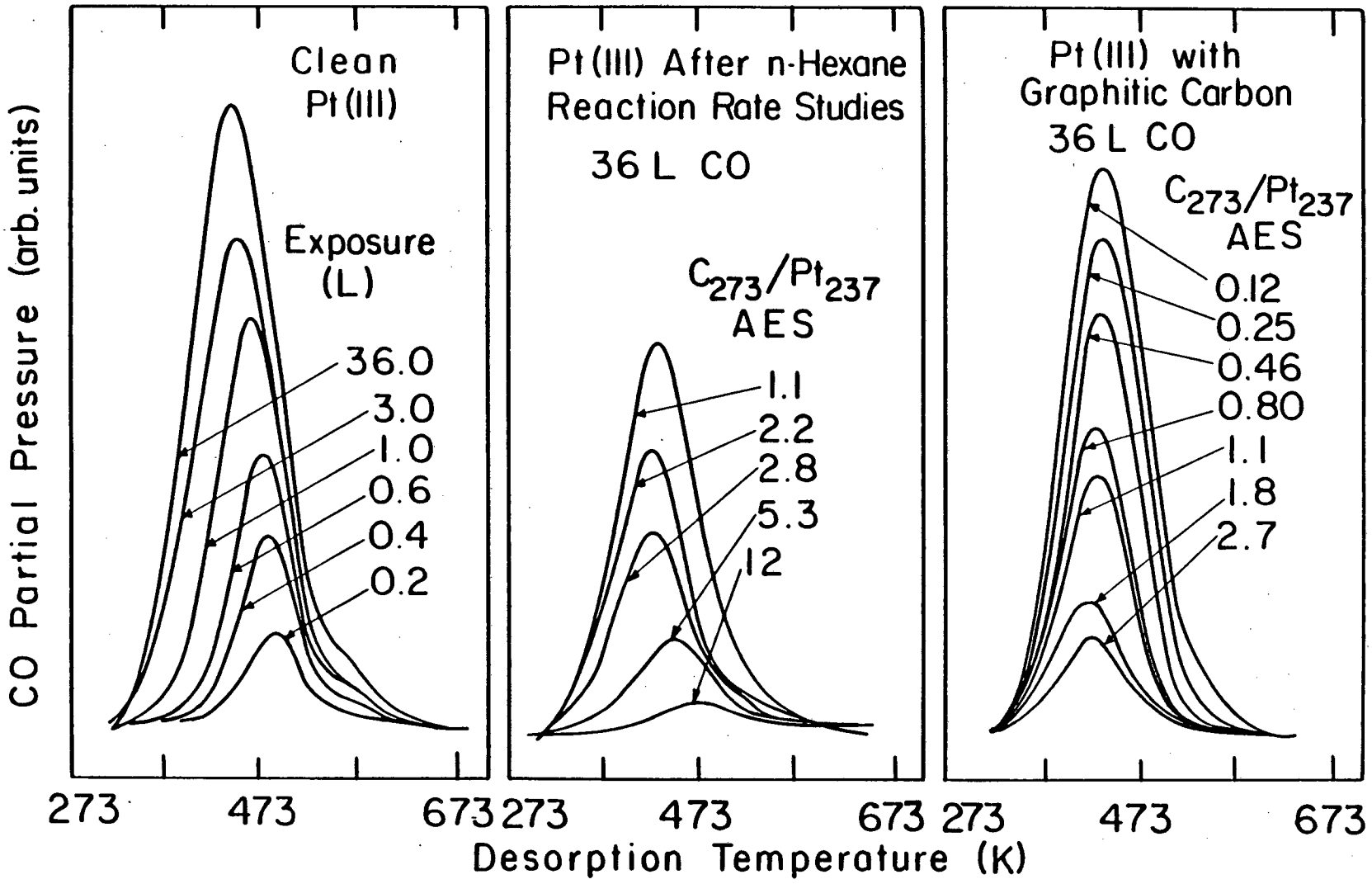


Fig. 11

XBL 815-5661A

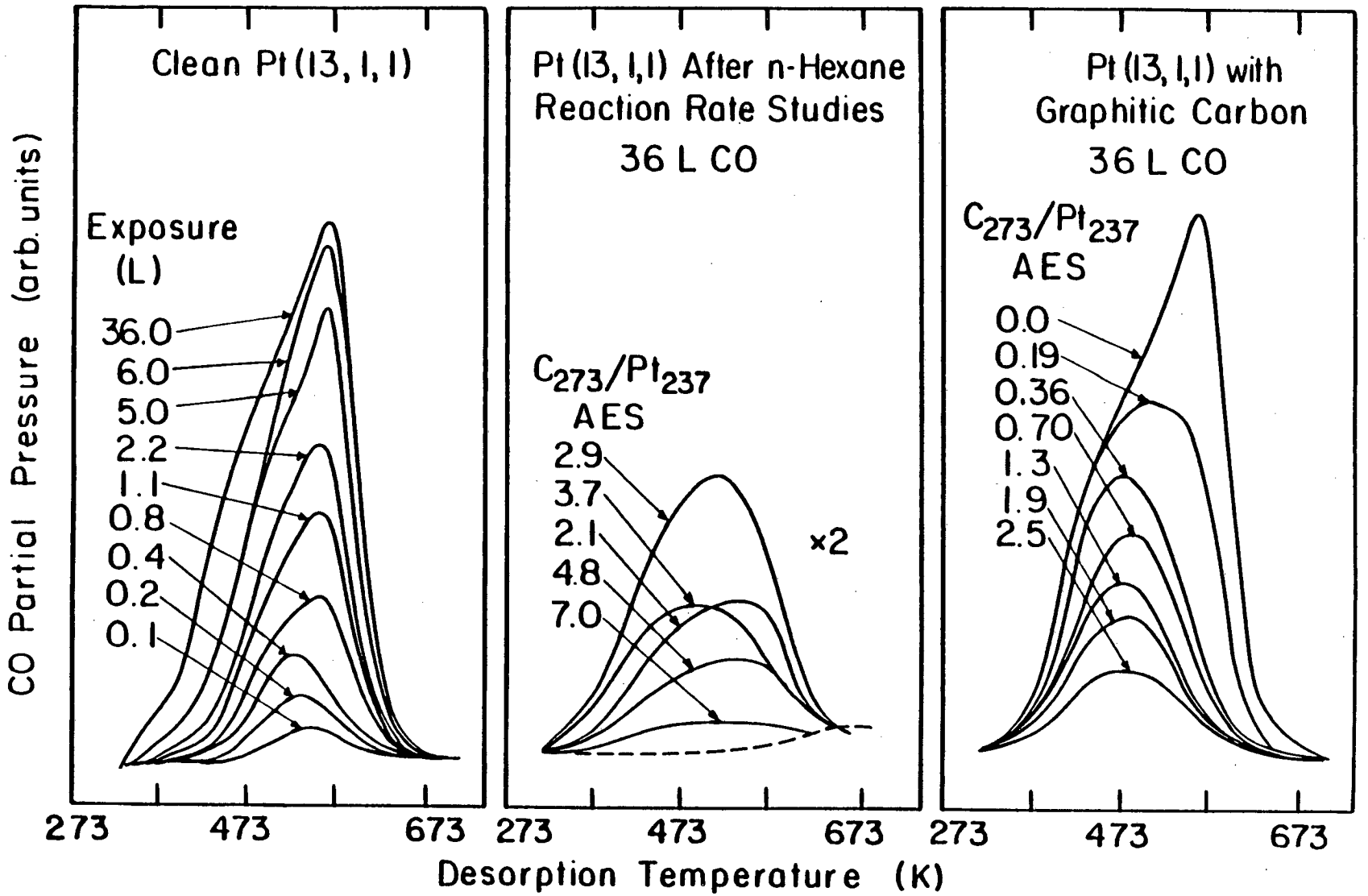


Fig. 12

X BL 815-5662A

CO Chemisorption on Carbon Covered Pt(111), Pt(100) and Pt(13, 1,1)

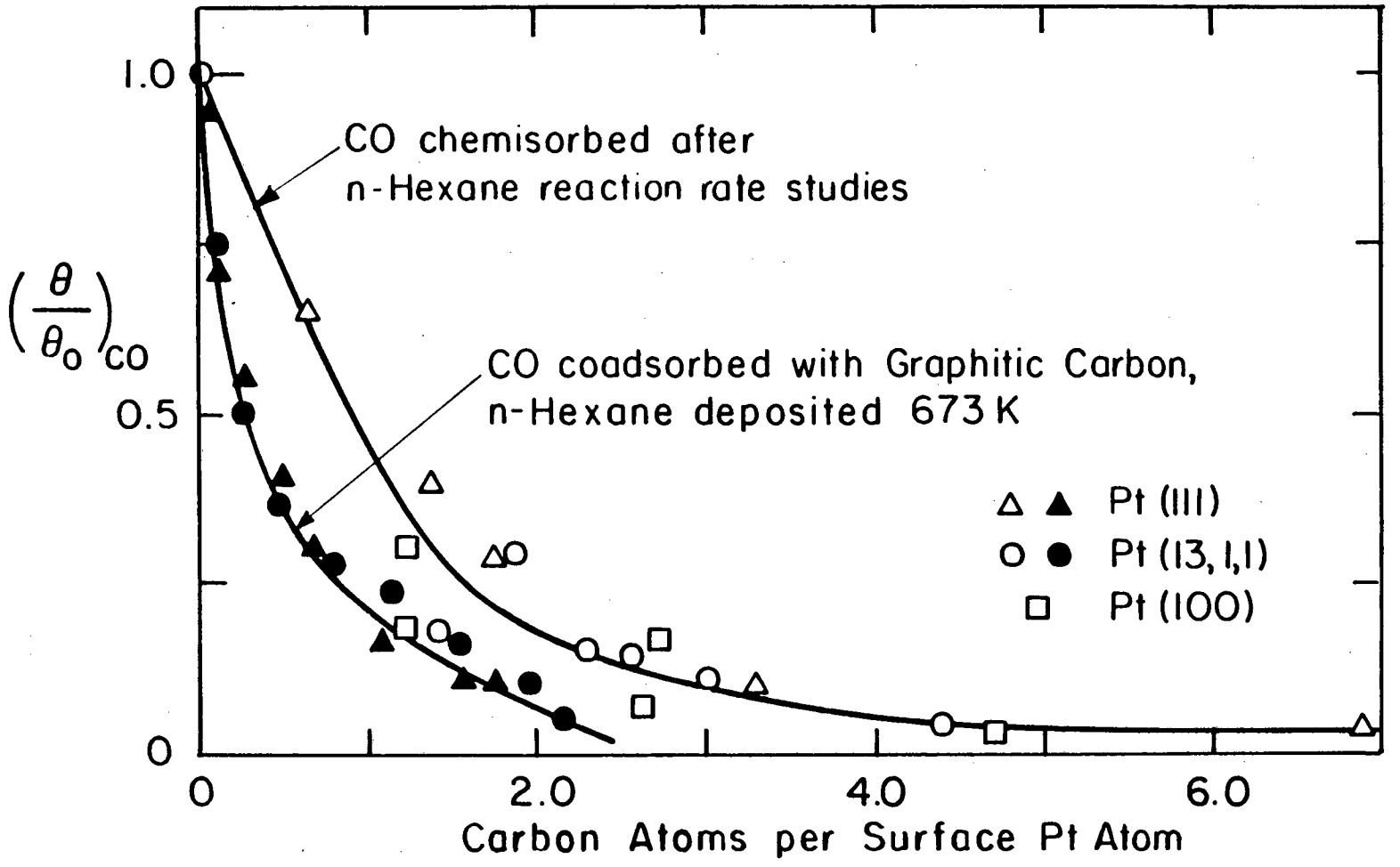
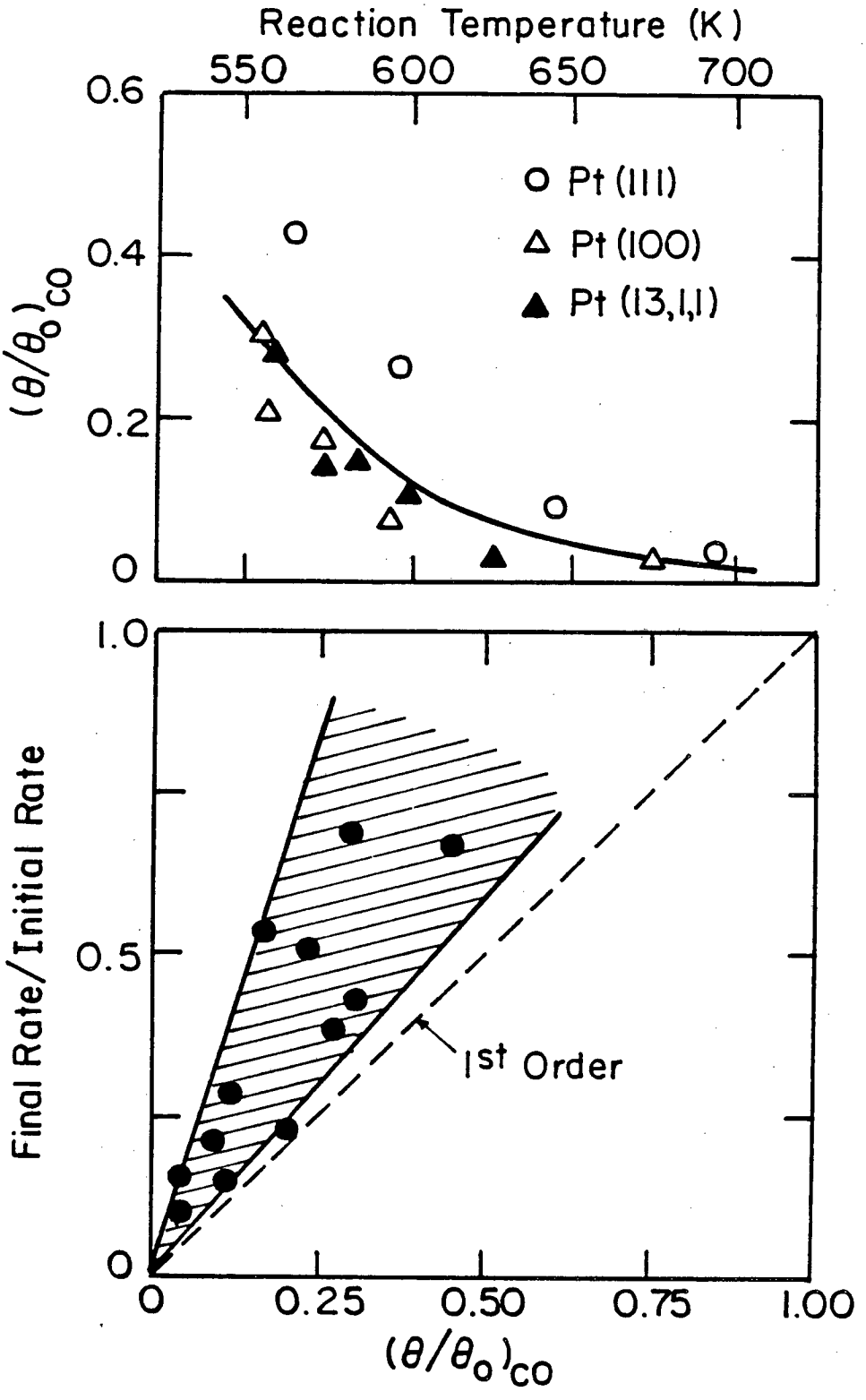


Fig. 13

XBL 816-5851



XBL 817-6115

Fig. 14

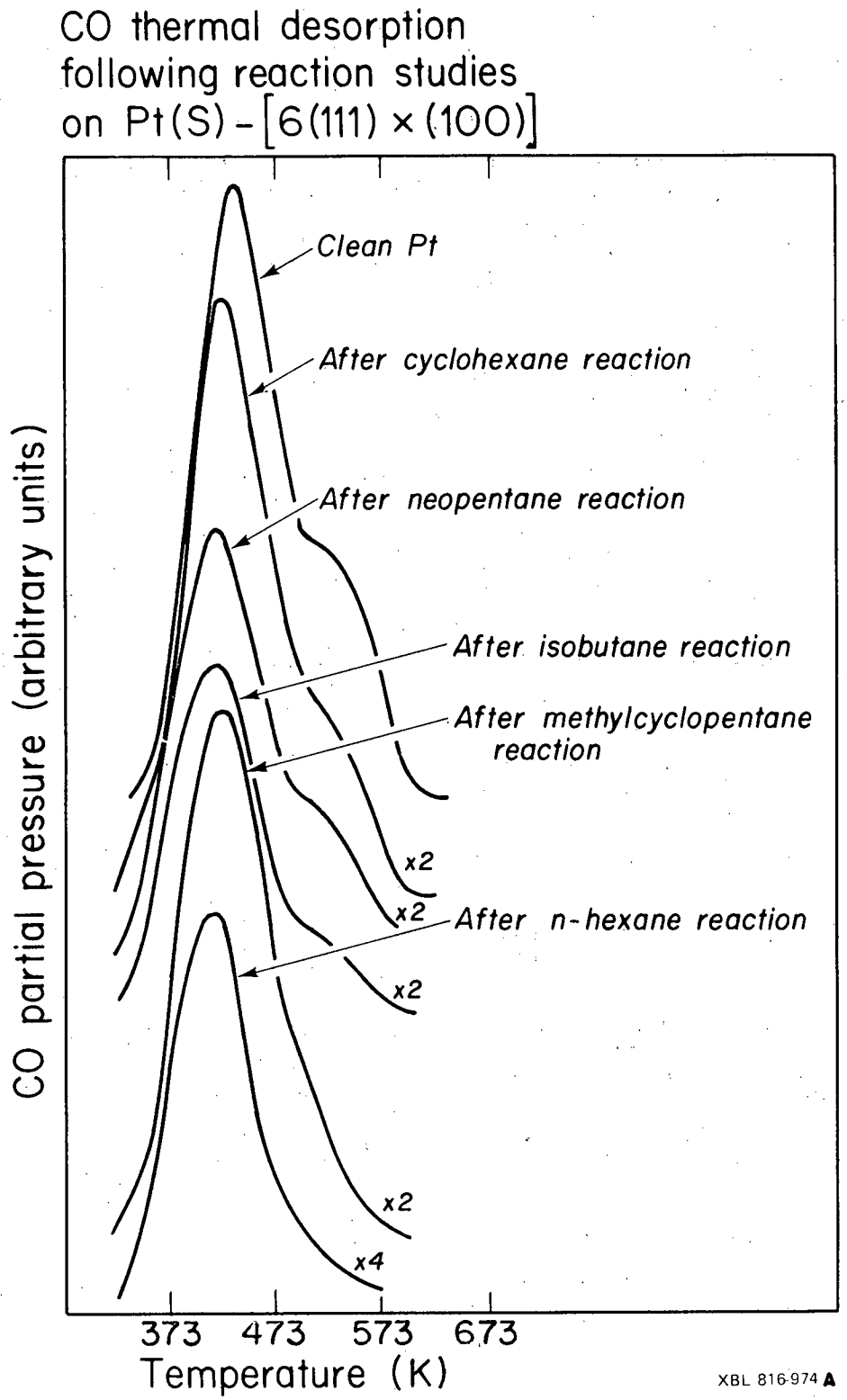
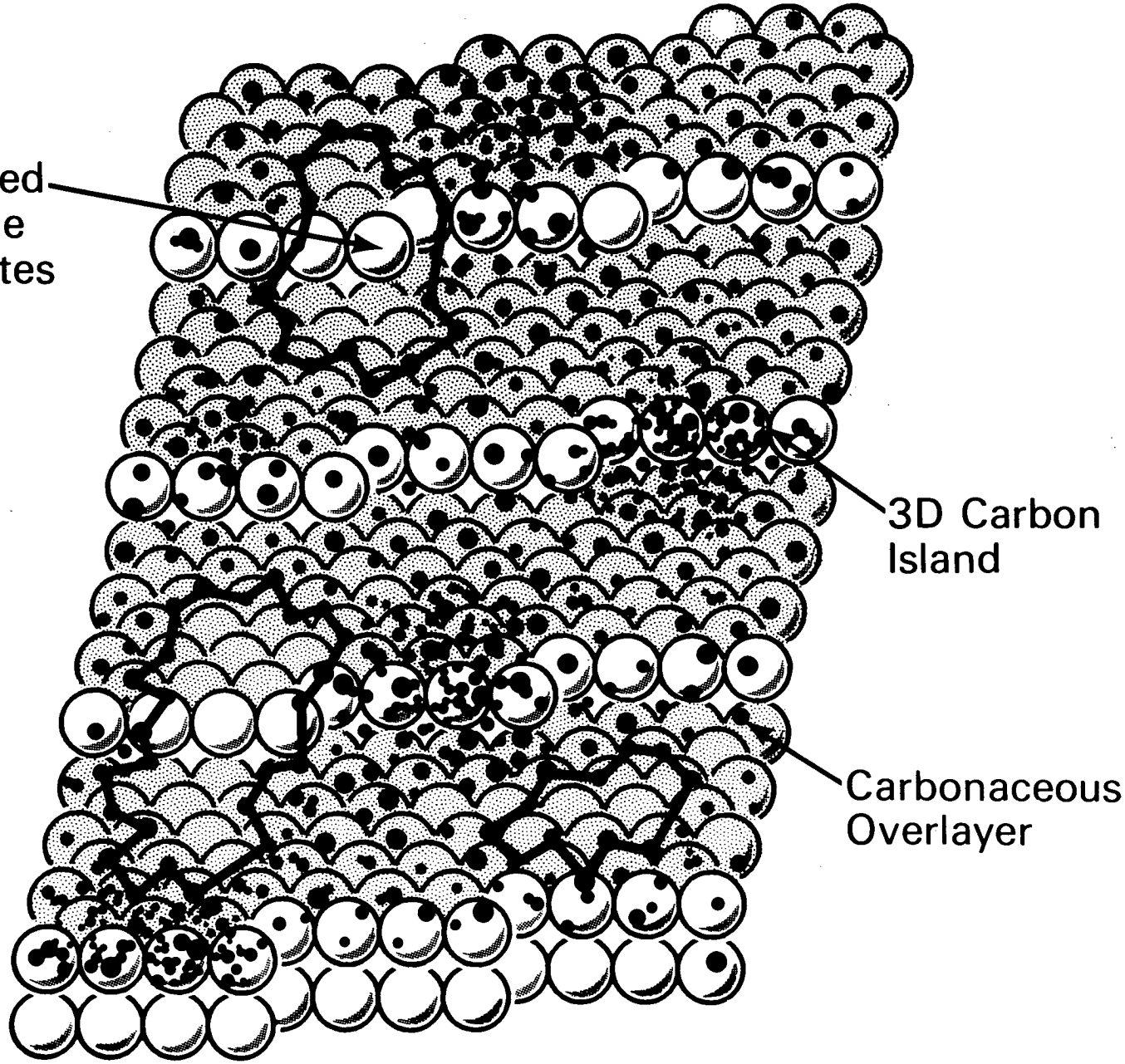

CO thermal desorption
following reaction studies
on Pt(S)-[6(111) × (100)]
Clean Pt
After cyclohexane reaction
After neopentane reaction
After isobutane reaction
After methylcyclopentane reaction
After n-hexane reaction
x2
x2
x2
x2
x4
CO partial pressure (arbitrary units)
373
473
573
673
Temperature (K)
XBL 816-974 A

Fig. 15

MODEL FOR THE WORKING PLATINUM CATALYST



CBB 816-5430

Fig. 16

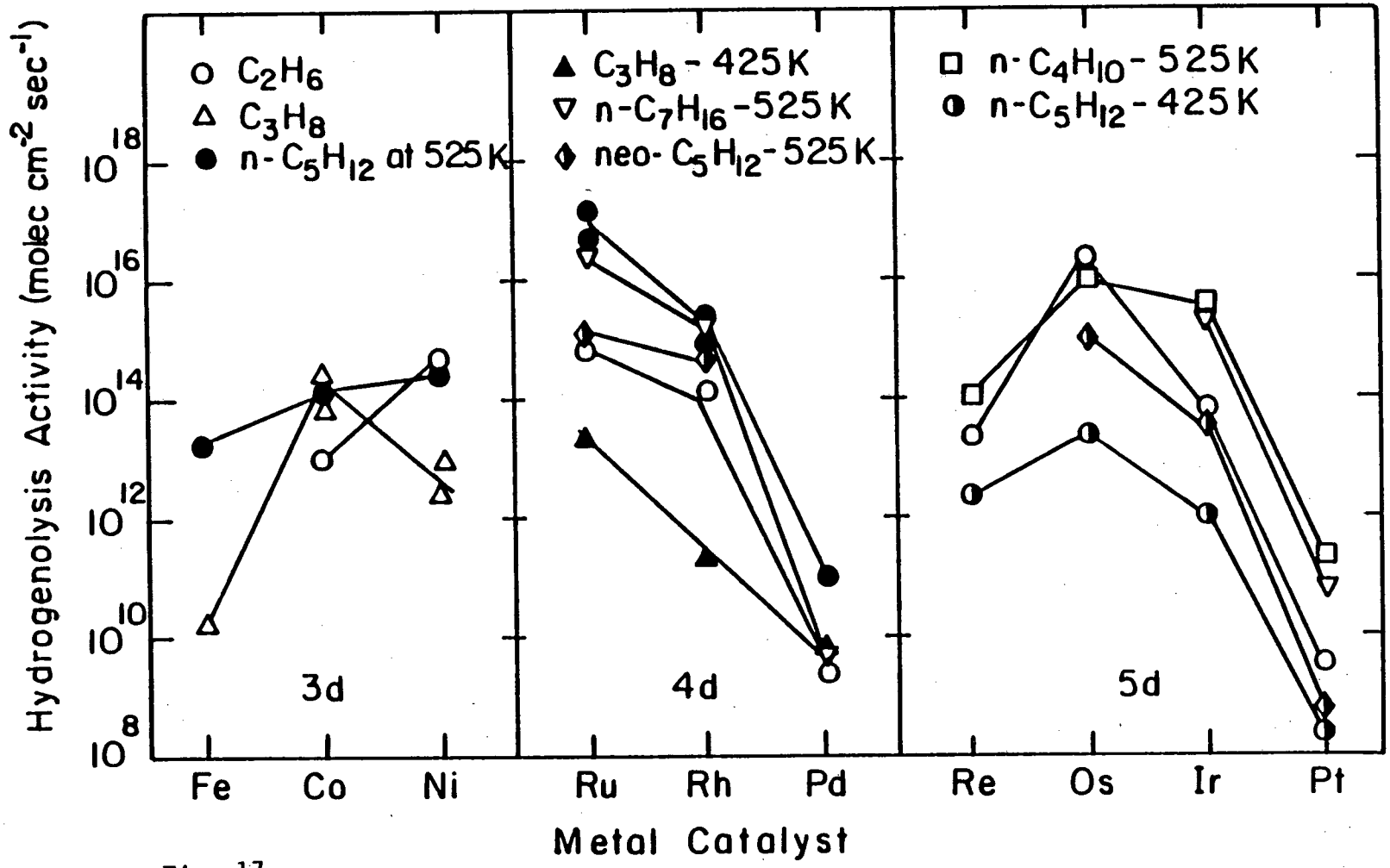


Fig. 17

XBL803-4868

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