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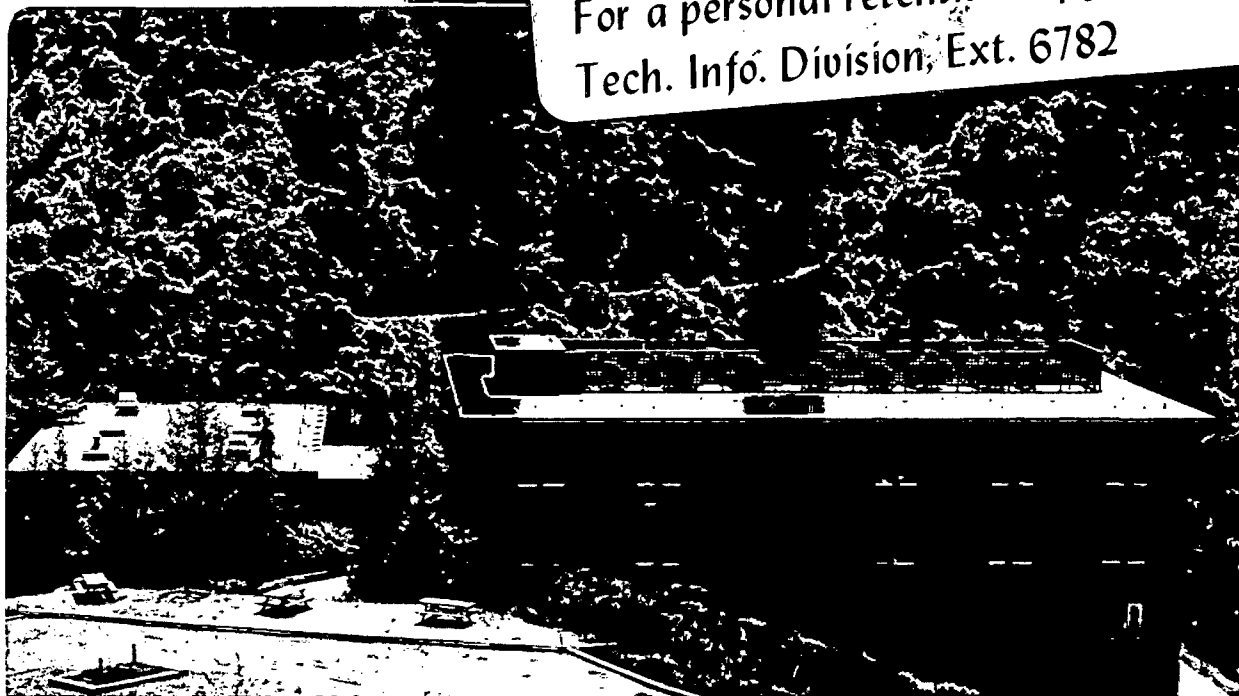
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February 1982

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THE MOLECULAR INGREDIENTS OF HETEROGENEOUS CATALYSIS

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THE MOLECULAR INGREDIENTS OF HETEROGENEOUS CATALYSIS

1. Introduction

In the last 15 years the explosive development in surface science has resulted in the introduction of a multitude of techniques that permit the atomic scale scrutiny of the surface monolayer.⁽¹⁾ The atomic surface structure, the chemical bonding of adsorbates, the composition and oxidation states of surface atoms can all be determined within the sensitivity of less than 1% of a monolayer (about 10^{13} atoms per cm^2). A partial listing of the most frequently employed techniques for surface analysis is displayed in Table 1. We employed many of these techniques for the study of the surface properties of heterogeneous catalysts. We made special use of low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS) for studies of the structure and bonding of hydrocarbon monolayers. LEED, like x-ray diffraction provides details of the molecular structure and because of the very high cross section of low energy electron scattering (about a million times larger than for x-rays) it can detect as little as 10% of a monolayer of ordered adsorbates. HREELS that determines the vibrational spectrum of the adsorbates have also been utilized in combination with LEED to supplement and confirm the surface structures. This technique can be employed to the study of either disordered or ordered monolayers and like infrared spectroscopy it reveals the orientation and symmetry of the adsorbed molecules. Auger electron spectroscopy (AES) was employed to determine the surface composition and photoelectron spectroscopy (XPS) was used to verify the oxidation states of surface atoms.⁽¹⁾

Catalysis is a kinetic phenomenon; reactant molecules adsorb, rearrange and desorb from the surface continuously. It is generally carried out at high

pressures (atmospheres) and the kinetic parameters, rate, activation energy and the product distribution reflect the activity and the selectivity of the catalysts to obtain the desired products. In order to unravel the molecular ingredients of heterogeneous catalysis, we had to combine catalytic reaction rate studies that were carried out at high pressures (several atmospheres) with surface analysis of the catalyst surface that usually required ultra high vacuum conditions. Therefore, we developed techniques⁽²⁾ that permitted us to do both, in the same instrument, in situ. In the low-pressure-high-pressure apparatus (Figure 1) a small area sample was placed in the center of an ultra-high vacuum chamber. Then a small cup with a total volume of 50 cm³ could be placed over the crystal sample to isolate it from the rest of the chamber. This isolation cell could be pressurized to over 100 atmospheres, if desired, using the mixture of gaseous reactants. The pressurized isolation cell served as a high-pressure reaction chamber. It is connected to a gas chromatograph that monitored both the rate and product distributions in this circumstance. The structure and composition of the surface can be determined, in situ, by electron scattering before and after the high pressure experiments once the cup is removed. The crystal sample can be heated during both low and high pressure experiments. Our samples are single crystals or polycrystalline foils of about one cm² in surface area. Such small area catalysts are entirely adequate for surface analysis as well as for detecting the product distributions and the rates obtained during catalytic reaction studies.

The small area single crystals are model catalysts. Models are used frequently in physical sciences to uncover the workings of a complex system. Of course, it must be ascertained that the model system behaves similar to that of the more complex chemical system that is to be ultimately utilized. To obtain credibility the model small area catalysts are compared with dis-

persed high surface area catalyst in the same reaction under identical experimental conditions. The same turnover numbers product distribution and activation energies were obtained for the ring opening of cyclopropane⁽³⁾ and the hydrogenation of benzene over platinum⁽⁴⁾ and for carbon monoxide hydrogenation over rhodium.⁽⁵⁾ It appears that for catalyzed reactions that do not exhibit much structure sensitivity, small area crystal and large area dispersed particles of the same metal yield identical catalytic reaction parameters.

We have concentrated our studies of molecular scale catalysis on transition metals which catalyze hydrocarbon conversion reactions and on the hydrogenation of carbon monoxide. Platinum, an excellent catalyst for dehydrocyclization reactions that produce aromatic molecules from alkanes, or for isomerization, was one of the metals we studied intensively. The other was rhodium, that was found to produce oxygenated organic molecules from carbon monoxide and hydrogen selectively. Iron that carries out ammonia synthesis from nitrogen and hydrogen as well as the CO/H₂ reaction was also the focus of our investigations. Out of these studies came the identification of three necessary ingredients of selective molecular scale catalysis.

- 1) Atomic surface structure.
- 2) An active carbonaceous deposit.
- 3) The proper oxidation state of surface atoms.

Let us review each of these reaction parameters in order to understand how the catalytic reactions occur.

2. Structure Sensitivity of Catalytic Reactions

- a) The structure sensitivity of ammonia synthesis over iron catalysts.

We have studied ammonia synthesis over the (111), (100) and (110) crystal faces of iron at operating pressures approaching those used industrially.

(20 atm).⁽⁶⁾ The structure of these different crystal faces are shown in Figure 2. The Fe(111) face was found to be the most active. It catalyzes the synthesis of ammonia from hydrogen and nitrogen at a rate which is at least 420 times faster than that of the ordered (110) surface. The rate of ammonia synthesis is 32 times faster over the Fe(100) face than that over the ordered (110) surface. These results are consistent with the low pressure chemisorption studies of Ertl and his co-workers⁽⁷⁾ who reported that the rate of dissociative chemisorption of nitrogen is greatest on the (111) phase of iron and least on the (110) phase and with previous suggestions that this step is rate determining in the ammonia synthesis reaction. The (111) plane of iron contains both 7-coordinated and 4-coordinated atoms, whereas the (100) and (110) planes contain only 6-coordinated and 4-coordinated atoms, respectively. The large variation in the rates of ammonia synthesis on the various iron crystal planes lend considerable support to the proposals by Boudart and others⁽⁸⁾ regarding the importance of iron clusters and 7-coordinated iron atoms as components of the active site on the catalyst surface.

b) The structure sensitivity of hydrocarbon conversion reactions on platinum surfaces. Single crystal catalysts can be prepared with a variety of surface structures by cutting the solid along different crystallographic orientations. The surface structures of platinum crystals that display different catalytic behavior are shown in Figure 3. The two flat surfaces, the (111) and (100) crystal faces have hexagonal and square atomic arrangements respectively. Each surface atom is surrounded by six or four nearest neighbors in the surface plane. There are also surfaces with periodic arrays of steps of one atom in height. The structure of the terraces and steps can have the same six-fold or four-fold symmetry as the flat surfaces. The widths of the

terraces are variable depending on the angle of cuts of the single crystal surface which determines the crystallographic orientation of the surface. There may be kinks or ledges in the steps that can be present in large concentrations if the surface is suitably prepared.⁽¹⁾ The step and ledge sites have less nearest neighbors (lower coordination number) and lower symmetry when compared to atoms in the flat surfaces.

Let us compare the activity of these various platinum surfaces for the same hydrocarbon conversion reaction. In Figure 4a, the flat (111) and (100) surfaces are compared for the dehydrocyclization of n-heptane. The hexagonal crystal face is five times more active than the square (100) face for this reaction.⁽⁹⁾ In Figure 4b the stepped platinum surfaces selectivity are compared with the flat ones under identical reaction conditions for the same reaction.⁽¹⁰⁾ The stepped surface with atomic terraces of at least five atom wide and hexagonal orientation was found to be the most active for dehydrocyclization. There is a 5-fold difference in activity for this reaction between the best and least active platinum surfaces that were studied. The hexagonal surface structure enhances the rate and the presence of steps increases further the activity by facilitating C-H bond breaking that is one of the elementary steps of this complex reaction. The presence of kinks was detrimental to the dehydrocyclization activity as it aids both C-C and C-H bond scission (the former is to enhance hydrogenolysis activity that competes with dehydrocyclization). If the terraces are narrower than four-atom wide, reactants or the product molecules cannot fit, the activity declines. Wider than six-atom terraces are less active, probably because the active step concentration is diminished.

For another reaction, the isomerization of isobutane, we found the square and flat (100) surfaces to be more active⁽¹¹⁾ than the flat hexagonal (111)

crystal face as shown in Figure 5. Again, steps seem to further improve the catalytic activity. If one evaluates the selectivity for dehydrocyclization or isomerization we find that there is an order of magnitude variation between crystal faces with the best and worst activity. It is clear that preparation of catalysts with appropriate surface structures allow us to obtain a high degree of reaction selectivity, and optimum activity for hydrocarbon conversion.

3. The Carbonaceous Deposit

When starting with a clean metal surface to study hydrocarbon conversion reactions, within milliseconds after the start of the hydrocarbon reaction at atmospheric pressures an equivalent of a carbonaceous layer is deposited on the surface and the catalytic hydrocarbon reaction then occurs in the presence of this deposit.⁽¹²⁾ Indeed a clean platinum or other clean transition metal surface could not readily catalyze hydrocarbon conversion reactions. Most organic molecules would adsorb irreversibly and form strong metal-carbon bonds. Upon heating, and in the absence of hydrogen, sequential dehydrogenation occurs until a graphitic overlayer remains.⁽¹³⁾ Figure 6 shows the sequential dehydrogenation of several alkenes that were adsorbed on platinum at low temperatures, and then heated.

Our studies using C-14 labeled organic molecules,⁽¹⁴⁾ thermal desorption and hydrogen-deuterium exchange⁽¹⁵⁾ indicate strong temperature dependence for the residence time and the composition of the organic deposit on platinum surfaces. Below about 120°C the layer can be rehydrogenated and removed from the metal surface as rapidly as the turnover time for organic reactants. Thus, at these low temperatures the metal surface remains clean during facile reactions, like the hydrogenation of ethylene that takes place with a low activation energy (less than 15 kcal/mole) at these low temperatures. The temperature programmed thermal desorption⁽¹³⁾ of hydrogen and AES studies indicate that the

stoichiometry of this mobile layer is C_2H_3 . Above $120^\circ C$ with increasing temperature an increasingly larger fraction of the surface carbon becomes irreversibly adsorbed as it loses more hydrogen. That is, this layer resides on the surface much longer than the turnover time of the organic reactants that may undergo isomerization, dehydrocyclization or hydrogenolysis. These reactions have high activation energy (20-45 kcal/mole) and are, therefore, carried out at higher temperatures, in the range of $150-400^\circ C$, to obtain reasonably high turnover numbers. Figure 7 shows the increase of the concentration of an irreversibly adsorbed carbonaceous layer and the simultaneous decline of the amount of reversibly adsorbed mobile organic layer as a function of temperature.⁽¹²⁾ The stoichiometry of this tenacious layer on the catalytically active metal is C_2H . Our detailed investigations exploring the catalytic effect of preparing the carbon deposit from a variety of preadsorbed organic molecules show relatively minor alterations of the selectivity of hydrocarbon conversion reactions. The activity of the catalyzed reaction was inversely proportional to the concentration of the irreversibly adsorbed carbon layer.

The structure of the adsorbed hydrocarbon monolayers was submitted to detailed studies by LEED and HREELS.⁽¹⁶⁾ In the temperature range of 300-400 K the adsorbed alkenes form alkylidyne molecules that are shown in Figure 8. The C-C bond closest to the metal is perpendicular to the surface plane and its length corresponds to a single bond 1.5\AA . The carbon atom that bonds the molecule to the metal is located in a three-fold site equidistant 2.0\AA from the nearest metallic neighbors.⁽¹⁷⁾ This bond is appreciably shorter than the covalent metal-carbon bond (2.2\AA) and is indicative of multiple metal-carbon bonds of the carbene or carbyne type. While this layer is ordered, on heating to about $100^\circ C$ it disorders and hydrogen evolution is detectable by a mass spectrometer that is attached to the system. As the molecules dehydro-

generate the disordered layer is composed of CH_2 , C_2H and CH type fragments that can be identified by HREELS.⁽¹⁶⁾ Only after heating to about 400°C do the fragments loose all their hydrogen and the graphite overlayer forms. These sequential bond breaking processes that occur as a function of temperature is perhaps the most important characteristic of the surface chemical bond that distinguishes it from chemical bonds of other types. While the surface remains active in the presence of organic fragments of C_2H stoichiometry it loses all activity when the graphitic monolayer forms.

Thus, we have two seemingly contradictory experimental informations. On the one hand many catalyzed reactions are strongly dependent on the structure of the surface. On the other hand, the surface that is catalytically active is covered with about a monolayer of carbonaceous deposit that seem to mask the structure of the solid catalyst. In order to sustain the observed structure sensitivity not all the metal surface sites are likely to be covered by the organic layer, but some of them must be available to perform the catalytic function. We have been able to titrate the remaining clean platinum surface sites by CO adsorption⁽¹²⁾ which can be attached readily to the uncovered metal at low pressures, about 10^{-6} torr and 25°C but does not adsorb under these circumstances on the organic overlayer. Figure 9 shows a fraction of the clean platinum surface as a function of the carbon surface concentration. $(\theta/\theta_{\text{clean}})$ is the fraction of bare platinum surface as compared to the site concentration on the initially clean metal surface. This fraction decreases rapidly with increasing temperature as seen in Figure 9. At about 400°C the carbonaceous overlayer that is irreversibly adsorbed gradually loses its remaining hydrogen and becomes graphitized. The graphite layer is a catalyst poison and the catalytic activity is irretrievably lost when this occurs.

Hydrocarbon reactions are always carried out in the presence of excess

hydrogen. Increased hydrogen concentration in the reactant feed helps to rehydrogenate a larger fraction of the irreversibly adsorbed carbonaceous layer and to slow the rate of graphitization. In the absence of excess hydrogen in the reactant mixture a complete monolayer of carbon deposit forms readily at above 400°C where the rate of graphitization is fast.

As a result of these studies a molecular model⁽¹²⁾ of the working platinum catalyst can be proposed and is shown in Figure 10. Most catalyzed reactions could not occur on either the bare metal surface or on the surface that is completely covered by the irreversibly deposited organic layer. Hydrocarbon conversion must occur on the bare metal islands that are kept clean by the presence of hydrogen in the reactant mixture. However, the intermediates or the products that form may not readily desorb from the bare metal sites because they are too strongly bound. It is likely then that these species diffuse over onto the carbonaceous overlayer from which desorption commences perhaps with the additional transfer of hydrogen. By providing sites at which the reaction products are bound only weakly the carbonaceous overlayer facilitates the desorption of the organic molecules. It should be noted that the active carbonaceous deposit that contains CH and CH₂ fragment stores about ten times more hydrogen than the clean metal surface that could be made available to the desorbing organic molecules.

The fractional concentration of the bare metal islands and of the carbonaceous overlayer can be manipulated not only by hydrogen pressure but by additives such as alkali promoters or by other transition metals that are used as alloying agents. Gold and tin were found to beneficially effect the activity, change the selectivity, and surface residence time of adsorbed reaction intermediates and product molecules by: a) alteration of the structure and active site concentration of bare metal islands, b) aiding the rehydrogenation of

the carbonaceous layer on the active catalyst and by c) slowing the rate of its dehydrogenation to the graphitic form that poisons the catalyst surface.

4. The Oxidation State of Surface Atoms

There are several experimental studies published in recent years which clearly indicate the importance of oxidation states other than zero valent metallic state for catalyzed reactions. We shall show two examples of the importance of the presence of higher oxidation states of transition metal ions at the catalyst surface.

a) Carbon monoxide hydrogenation over rhodium. Rhodium was reported to yield predominantly C_2 oxygenated products, acetaldehyde and acetic acid⁽¹⁸⁾ when prepared under appropriate experimental conditions. Our studies using unsupported polycrystalline rhodium foils⁽¹⁹⁾ have detected mostly methane along with small amounts of ethylene and propylene under very similar experimental conditions. This product distribution was identical to that obtained by Vannice⁽²⁰⁾ over supported rhodium catalyst along with the identical activation energies for methanation (about 24 kcal/mole) that we both found. It appears that most of the organic molecules form following the dissociation of CO by the rehydrogenation of CH_x units in the manner similar to alkane and alkene production from CO/ H_2 mixtures over other more active transition metal catalysts (iron, ruthenium and nickel).

However, when rhodium oxide, Rh_2O_3 , was utilized as a catalyst, large concentrations of oxygenated C_2 or C_3 hydrocarbons were produced, including ethanol, acetaldehyde and propionaldehyde.⁽²¹⁾ Furthermore, the addition of C_2H_4 to the CO/ H_2 mixture yielded propionaldehyde, indicating the carbonylation ability of Rh_2O_3 . Under similar experimental conditions over the rhodium metal C_2H_4 was

quantitatively hydrogenated to ethane and carbonylation activity was totally absent. Clearly, higher oxidation state rhodium ions are necessary to produce the oxygenated organic molecules. Unfortunately, Rh_2O_3 reduced rapidly in the CO/H_2 mixture to the metallic state with drastic alteration of the product distribution from oxygenated hydrocarbons to methane. In order to stabilize the rhodium ion, lanthanum rhodate, LaRhO_3 , was prepared by incorporating Rh_2O_3 into La_2O_3 at high temperatures.⁽²²⁾ Over this stable catalyst the formation of oxygenated products from CO/H_2 predominated.

The reason for the change of selectivity in CO/H_2 reactions upon alteration of the oxidation state of the transition metal is due largely to the change of heats of absorption of CO and H_2 as the oxidation state of the transition metal ion is varied.⁽²²⁾ This is demonstrated in Figure 11. The CO adsorption energy is decreased upon oxidation while the heat of adsorption of H_2 is increased, presumably due to the formation of hydroxyl groups. This, in turn, changes the relative surface concentrations of CO and H_2 . In addition, the metal is primarily active for hydrogenation and CO dissociation while the oxide can perform carbonylation and has reduced hydrogenation activity. As shown in Figure 11, the active LaRhO_3 catalyst seems to have both rhodium metal and rhodium ion sites, as indicated by the presence of the thermal desorption peaks of CO and H_2 , to provide both optimum carbonylation as well as hydrogenation activity so necessary to obtain C_2 or C_3 oxygenated hydrocarbon molecules.

We have also found that the product distribution that results from the CO/H_2 reaction at high pressures over LaRhO_3 is highly temperature dependent.⁽²²⁾ At low enough temperatures, below 250°C , the formation of methanol predominates. This can occur by the direct hydrogenation of the undissociated carbon monoxide molecule. As the temperature is increased from 250 to 300°C the formation of C_2 or C_3 oxygenated hydrocarbon molecules ethanol, propanol, acetaldehyde and

propionaldehyde predominate. These molecules need the presence of both CH_x units that form as a result of the dissociation of carbon monoxide followed by the partial rehydrogenation of the surface carbon and the insertion of CO into these fragments to form the oxygenated product. In a finite temperature range between 250 and 350°C the CO dissociation and hydrogenation ability and the carbonylation ability of the catalyst are about identical. As the temperature is increased to above 350°C, the formation of methane predominates. The CO concentration is too low on the surface at these temperatures to produce CO insertion and the rehydrogenation characteristics of the material control the product distribution. (21,22)

One of the difficulties in preparing selective catalysts for hydrocarbon conversion is the poor thermodynamic stability of higher oxidation states of transition metal ions in the reducing reaction environment. It appears that the strong metal support interaction that permits the incorporation of the high oxidation state transition metal ion into the supporting refractory oxide or sulfide crystal lattice often provides for the kinetic stability of the desired oxidation state, as long as the catalytic reaction temperatures are appreciably below the decomposition temperature of the binary oxide so prepared.

b) Photodissociation of water over reduced SrTiO_3 surfaces. When strontium titanate is illuminated with band gap radiation, about 3.1 electron volts in the presence of water vapor or aqueous alkali hydroxide solutions, hydrogen and oxygen evolution are detectable. (23) The presence of Ti^{3+} ions at the surface play a crucial role in dissociating water and is a necessary ingredient of the photocatalytic process. (24) Figure 12 shows the catalytic cycle that explains most of the experimental results found so far. (25) The reduced SrTiO_3 surface that is full of oxygen vacancies and Ti^{3+} ions readily adsorbs water and dissociates

it in the dark. As a result the Ti^{3+} species are oxidized to Ti^{4+} and the oxygen vacancies are filled with the fragmented adsorbates. Upon illumination, the photoelectron so generated is used to reduce H^+ to H and the electron vacancy traps the negative charge of the hydroxyl ion to convert it to OH radical which in turn produces oxygen through, presumably, a peroxide intermediate. As both hydrogen and oxygen desorb after atom recombinations the Ti^{3+} surface sites as well as the oxygen vacancy are regenerated. There is evidence for the rapid exchange of oxygen from the water molecules with the oxygen ions at the surface and for the reduction and oxidation of Ti^{3+} sites during the photochemical reaction.(26) Thus the importance of the proper oxidation state of transition metal ions to carry out catalyzed reactions is again demonstrated.

5. The Building of New High Technology Heterogeneous Catalysts

As a result of combined surface science and catalytic studies on well defined model catalyst systems many of the molecular ingredients of heterogeneous catalysis have been uncovered. The model of the working platinum catalyst reveals not only how selective hydrocarbon catalysis occurs over platinum surfaces but also how we might modify or certainly optimize these working catalyst systems. Once we understand the molecular details of the catalyst operation we can design new high technology catalysts by using the scientific understanding that was obtained on the molecular scale. Indeed, the field of heterogeneous catalysis is ready to be transformed from an art to catalysis science that permits the fabrication of high technology catalyst systems.

There exists, already, a group of high technology catalysts that has been in use in the chemical technology over the past 12 years. These are the zeolites(27), and one of them is shown in Figure 13. Zeolites are aluminum silicates that can be prepared with variable pore sizes that have molecular dimen-

sions. This gives rise to shape selectivity in hydrocarbon conversion reactions as molecules that are small enough to enter the pores can undergo catalyzed reactions. In addition, by controlling the silicon to aluminum ratio of the zeolite crystallite the catalytic behavior of these aluminum silicates can be drastically altered. Zeolites, at present, are the largest volume heterogeneous catalysts used in technology.

Using the molecular ingredients of heterogeneous catalysis that were described above we may control the structure, the concentration of the carbonaceous deposit and the oxidation states of atoms on the catalysts surface. The structure of the catalyst may be controlled by epitaxial deposition of one metal on top of another metal or on an oxide or a sulfide that serve as suitably structured supports. The concentration and hydrogen content of the carbonaceous deposits in hydrocarbon conversion reactions or of oxide layers under oxidizing conditions can be altered by the addition of other metals, transition and alkali. And finally, the oxidation state of surface ions may be stabilized by incorporation of the transition metal ion into the crystal lattice of refractory oxides or by the addition of electron acceptors, halogens, etc. Below we shall give brief descriptions of several attempts to build a new catalyst.

a) The catalytic activity of the gold-platinum system. Bimetallic alloy systems are noted for their higher activity and selectivity for many hydrocarbon reactions as compared to single metal component catalysts. In order to explore the reasons for this we studied the gold-platinum system.^(28,29) Gold was epitaxially deposited on the (100) or (111) crystal faces of platinum and the structure of the monolayer and the activity for various hydrocarbon reactions as a function of gold surface concentration was monitored. Then by heating the system gold was diffused into platinum and the catalytic activity of the freshly

formed alloy was again determined for the same chemical reaction as that used in the presence of the gold overlayer on platinum. Gold forms an ordered overlayer on the platinum surface.⁽²⁸⁾ Figure 14 shows the activity for dehydrogenation, hydrogenolysis and isomerization of n-hexane as a function of gold coverage in the epitaxial case. It appears that the activity of platinum is linearly decreased by the presence of a gold overlayer at high reactant pressures. This result, of course, is not surprising as gold is inactive for all these catalytic reactions.⁽²⁹⁾

Very different results are obtained when gold was diffused into platinum at elevated temperatures. The gold-platinum alloy that forms showed a much higher activity for isomerization than clean platinum.⁽²⁹⁾ Simultaneously the activity for dehydrocyclization and hydrogenolysis is declined exponentially with gold coverage. As a result, the selectivity for isomerization became very large. Gold tends to break up the large coordination number sites by substitution more than the lower coordination number sites; thus reactions that require three-fold sites are more likely to be affected by the presence of gold in the crystal lattice than those reactions involving one or two neighboring platinum atoms. This simple argument can explain the observed selectivity.⁽²⁹⁾ However, this cannot explain the observed increase in chemical activity; the gold alloy is a more active catalyst than clean platinum for isomerization. The presence of gold may decrease the concentration of the carbonaceous deposit and the residence times of the reaction intermediates. By breaking up the carbonaceous polymers by the presence of gold it can be more rapidly rehydrogenated. This can certainly account for the increased rates obtained on the gold alloy surface for isomerization. It is also known that bimetallic alloys poison more slowly than pure metallic catalyst in many hydrocarbon conversion reactions. Perhaps the presence of a second component metal also decreases the rate of conversion

of the active carbonaceous fragments to the inactive graphitic phase.

Atomic scale studies of several bimetallic systems including platinum-iridium, iridium-gold and platinum-rhenium systems are in progress and no doubt will help to elucidate the important effects of bimetallic catalysis; the increased activity, higher selectivity and greater resistance to poisoning.

b) The effect of alkali metals on the chemisorption of CO and on the reactivity of surface carbon. Alkali metals are frequently used as promoters in many catalyzed surface reactions. These include the ammonia synthesis on iron, the catalyzed hydrogenation of carbon monoxide on various transition metal surfaces and coal gasification in the presence of water. Alkali metals when present on transition metal surfaces affect the catalytic activity in several ways. One important effect is their influence on the heats of absorption of adsorbates such as carbon monoxide. HREELS and TDS studies showed⁽³⁰⁾ that the coadsorption of potassium and carbon monoxide on platinum surfaces has decreased the CO stretching frequency by about 400 wave numbers as compared to the stretching frequency on the clean platinum, in the absence of potassium. This effect is shown in Figure 15. A decreased CO stretching frequency indicates a weakening of the CO bond and simultaneously it implies an increased metal-carbon bond strength. Thus, potassium seems to increase the bonding energy of CO to the surface, thereby improving the dissociation probability significantly. During ammonia synthesis the presence of potassium on the iron surface increases the binding energy of dinitrogen and reduces the activation energy for its dissociation to produce atomic nitrogen on the surface.⁽⁷⁾ Since the dissociation of dinitrogen is the rate limiting step the ammonia synthesis rate is accelerated.

Another effect is due to the alkali metal catalyzed interaction of water

vapor with carbon at the surface. It was reported recently⁽³¹⁾ that when alkali hydroxides or carbonates are adsorbed on the surface of graphite they catalyze its reaction with water vapor. At low temperature in the range 200-250°C methane and carbon dioxide are produced. This reaction is an alternate route for the gasification of carbon that is usually carried out without a catalyst around 1000°C with water vapor to produce carbon monoxide and oxygen. It is clear that by the low temperature reaction alkali hydroxides (potassium, lithium, etc.) act as catalysts for both the reduction of carbon to CH₄ and for its oxidation to CO₂ or CO. This reaction involves ionic intermediates, the formation of H⁺ and OH⁻, that are catalyzed by the alkali hydroxides. These then, by a series of complex reactions that follow, can hydrogenate and oxidize the surface carbon. This low temperature reaction has an activation energy of about 11 kcal/mole and can be responsible for the removal of the carbonaceous deposit from various transition metal surfaces when water vapor is present.

c) Strong metal-support interaction. A control of the oxidation state of the surface transition metal ions has been reported by Tauster and coworkers.⁽³²⁾ By using relatively basic oxides, titanium oxide, zirconium oxide, etc. they find very different chemisorption and reactivity properties of transition metal ions. The influence of these refractory oxide supports on the catalytic activity was called "strong metals support interaction" (SMSI). Thus, using the support, higher oxidation state transition metal ions can be stabilized in addition to the presence of the same transition metals in the zero valent state.

Undoubtedly there will be many attempts in the future to build new metal catalysts using the molecular ingredients of heterogeneous catalysis that were uncovered. Indeed, it appears that the art of catalysis is rapidly becoming high technology catalysis science.

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FIGURE CAPTIONS

- Figure 1: Schematic diagram of the low pressure-high pressure apparatus for combined surface analysis and catalysis studies.
- Figure 2: Idealized atomic surface structure for the low-index planes of Iron Fe(100, Fe(111) and Fe(110).
- Figure 3: Idealized atomic surface structures for the flat Pt(111) and Pt(100), the stepped Pt(755) and the kinked Pt(10,8,7) surfaces.
- Figure 4: a) Toluene accumulation curve measured as a function of reaction time for n-heptane conversion over Pt(111) and Pt(100) surfaces.
b) Dependence of dehydrocyclization selectivities at 15 torr n-heptane, 480 torr hydrogen and 573 K, as a function of surface structure.
- Figure 5: Structure sensitivity of alkane isomerization reactions catalyzed over platinum single crystal surfaces.
- Figure 6: Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of ethylene, propylene, and cis-2-butene chemisorbed on Pt(111) at about 120 K ($\beta = 12$ K/sec).
- Figure 7: Composition and reactivity of ^{14}C -ethylene chemisorbed on Pt(111) at temperatures between 320 and 670 K; the irreversibly adsorbed fraction determined by radiotracer analysis displays an excellent correlation with the average hydrogen content (H/C) of the strongly adsorbed species.
- Figure 8: Atomic surface structure for alkylidyne species chemisorbed on Pt(111).
- Figure 9: 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 "graphite" surface carbon.

Figure 10: Model for the working surface composition of platinum reforming catalysts.

Figure 11: Heat of desorption (kcal/mole) of CO and D₂ from La₂O₃ fresh and used LaRhO₃, used rhodium oxide and rhodium metal. The spread of each value represents the variation with surface coverage rather than experimental uncertainty.

Figure 12: The suggested mechanism for the catalyzed photodissociation of water on Titanium oxide surfaces.

Figure 13: One of the important zeolites, mordenite, Na₈ Al₈ Si₄₀ O₉₆ · 24 H₂O, viewed along (001) axis.

Figure 14: Activity for n-hexane conversion as a function of gold coverage in the gold Pt(111) system.

Figure 15: Vibrational spectra of the saturation CO coverage chemisorbed on Pt(111) at 300 K as a function of preadsorbed potassium.

TABLE I

Table of some of the frequently utilized surface characterization techniques to determine the structure and composition of solid surfaces. Adsorbed species present at concentrations of 1% of a monolayer can be readily detected.

SURFACE ANALYSIS METHOD	ACRONYM	PHYSICAL BASIS	TYPE OF INFORMATION OBTAINED
Low energy electron diffraction	LEED	Elastic backscattering of low energy electrons	atomic surface structure of surfaces and of adsorbed gases
Auger electron spectroscopy	AES	Electron emission from surface atoms excited by electron x-ray or ion bombardment	surface composition
High resolution electron energy loss spectroscopy	HREELS	Vibartional excitation of surface atoms by inelastic reflection of low energy electrons	Structure and bonding of surface atoms and adsorbed species
Infrared spectroscopy	IRS	Vibrational excitation of surface atoms by absorption of infrared radiation	Structure and bonding of adsorbed gases
X-ray and ultraviolet photoelectron spectroscopy	XPS UPS	Electron emission from atoms	Electronic structure and oxidation state of surface atoms and adsorbed species
Ion scattering spectroscopy	ISS	Inelastic reflection of inert gas ions	Atomic structure and composition of solid surfaces
Secondary ion mass spectroscopy	SIMS	Ion beam induced ejection of surface atoms as positive & negative ions	surface composition
Extended X-ray absorption fine structure analysis	EXAFS	Interference effects during x-ray emission	atomic structure of surfaces and adsorbed gases
Thermal desorption spectroscopy	TDS	Thermally induced desorption or decomposition of adsorbed species	Adsorption energetics composition of adsorbed species

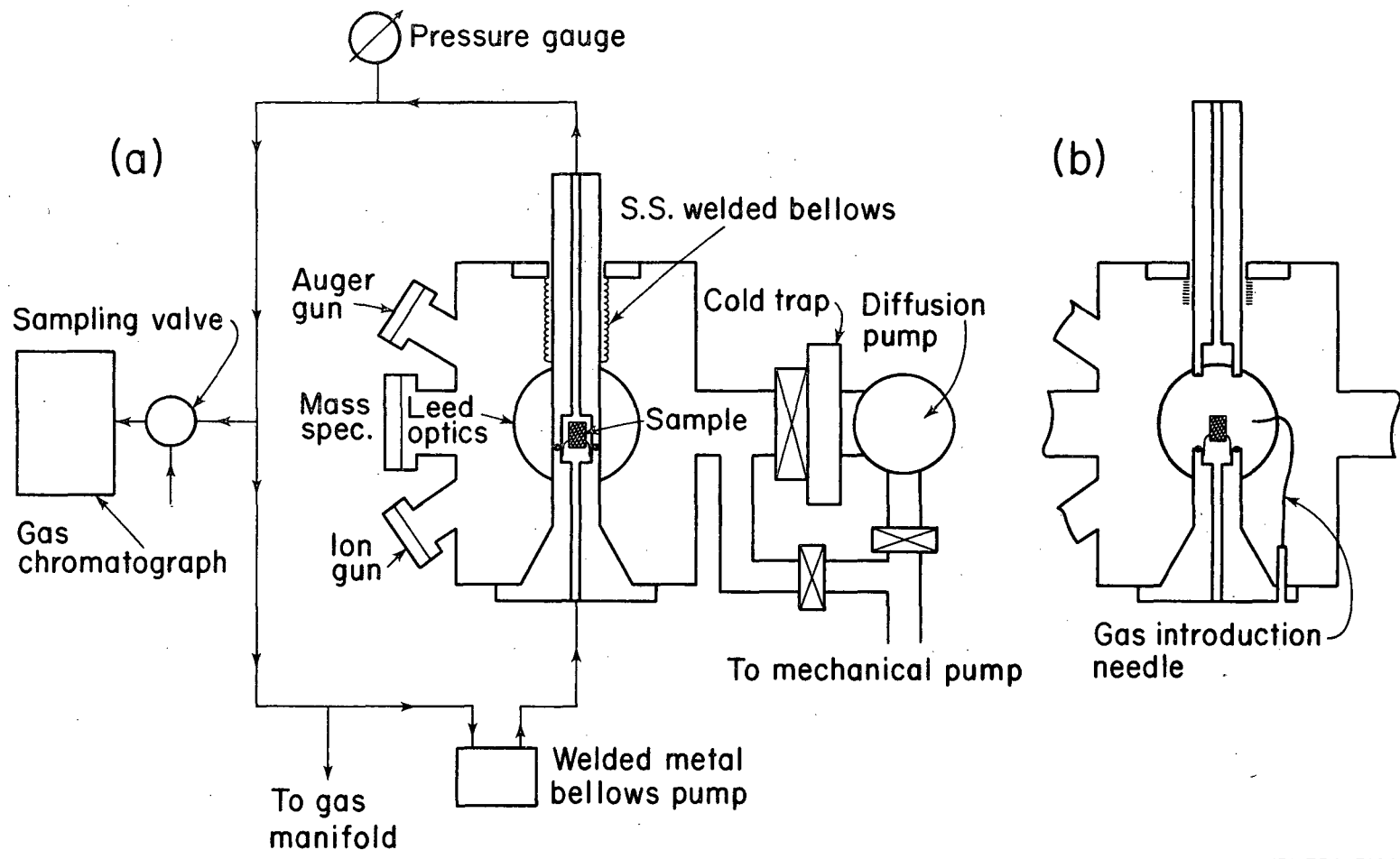


Fig. 1

XBL 756-3160

LOW-INDEX PLANES OF IRON

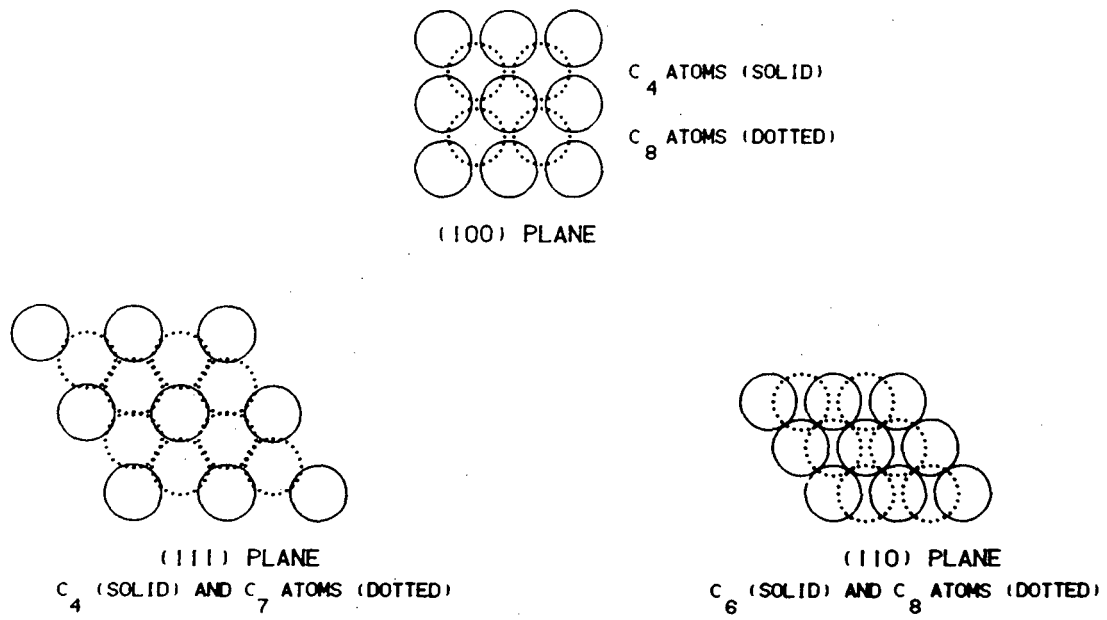
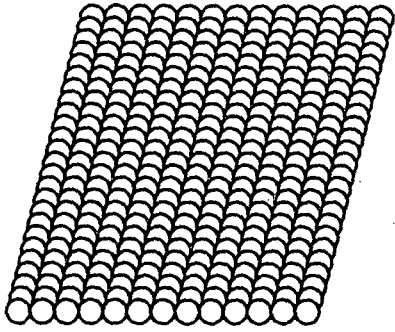
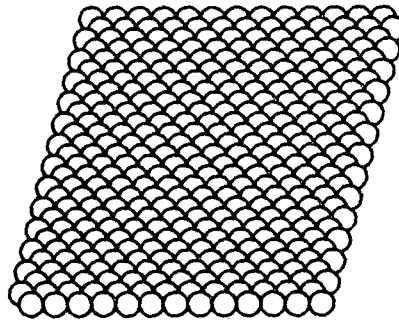


Fig. 2

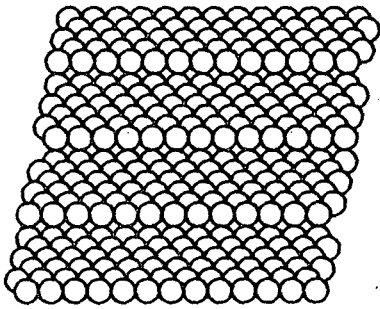
XBL 819-1842



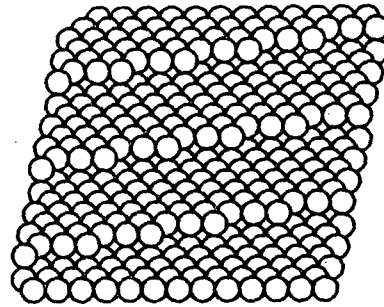
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fcc (111)



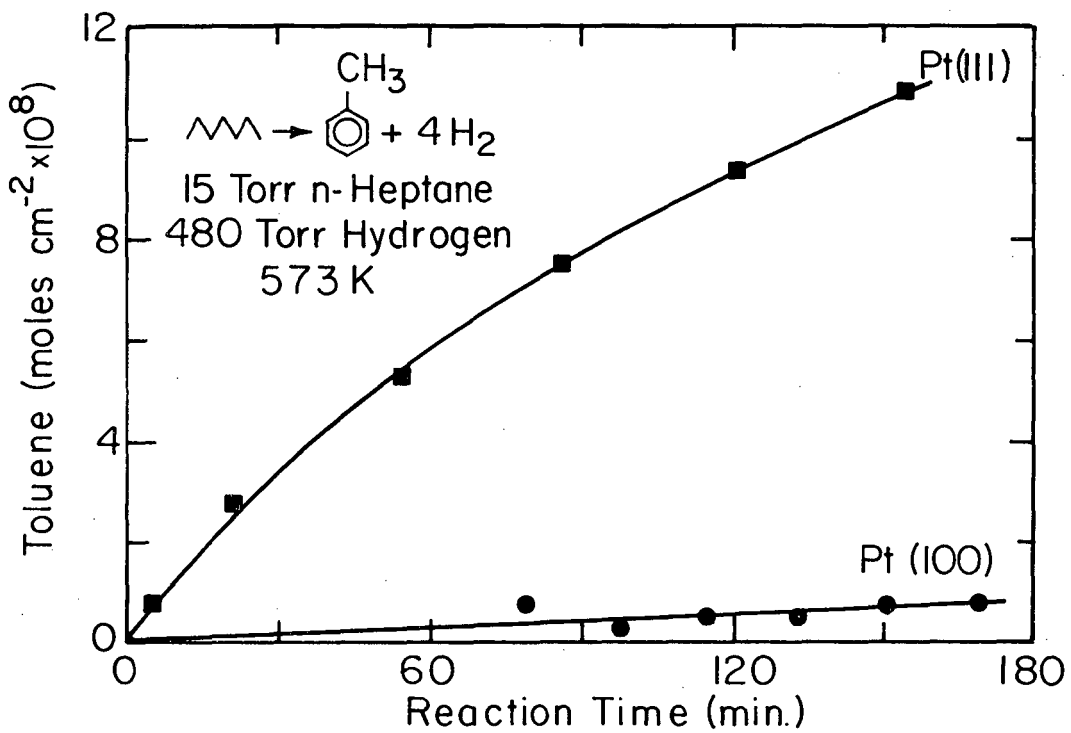
fcc (110)



fcc (110.0.7)

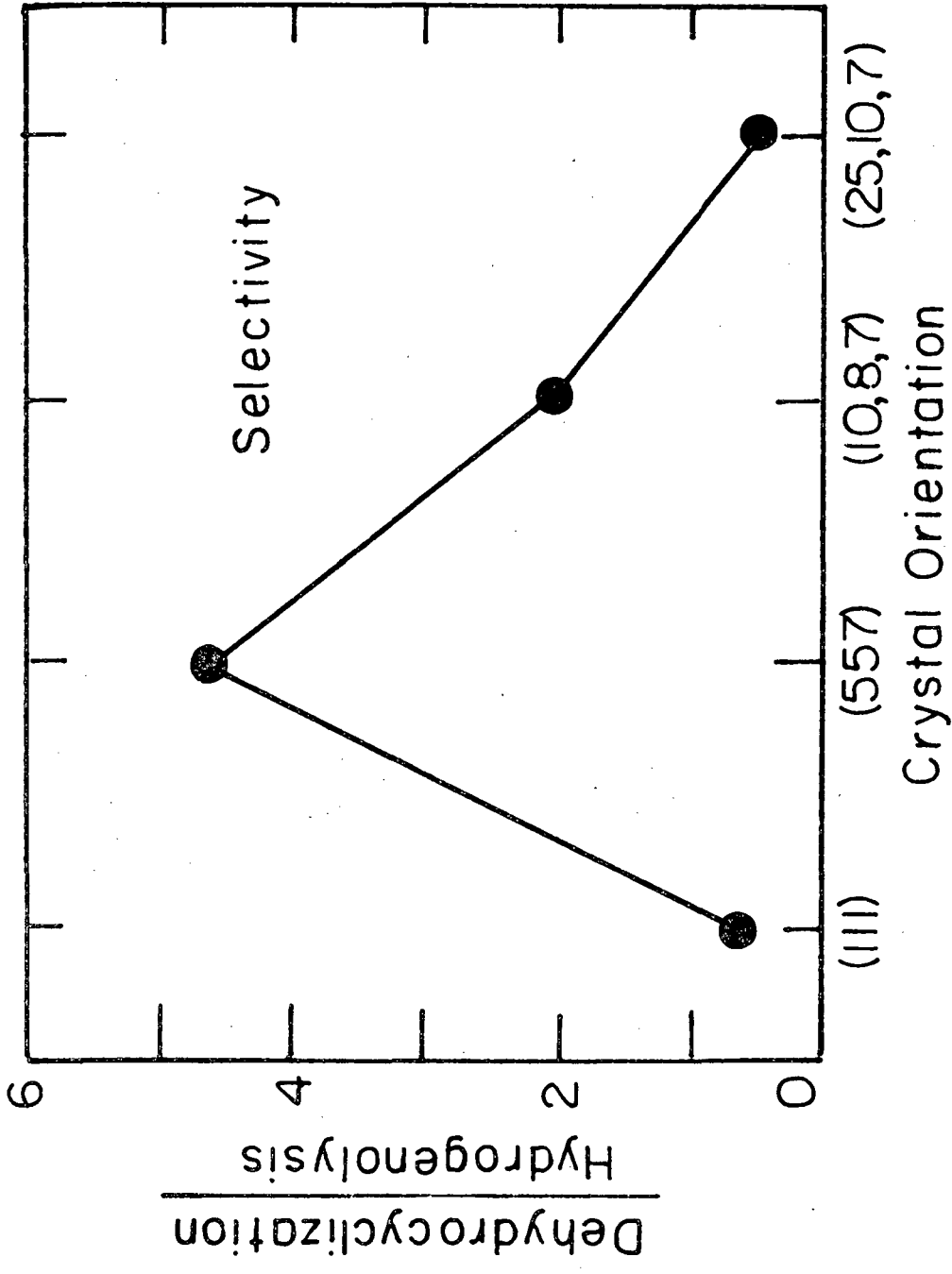
XBL 8112-13009

Fig. 3



XBL 813-5435

Fig. 4a



XBL 807 5520A

Fig. 4b

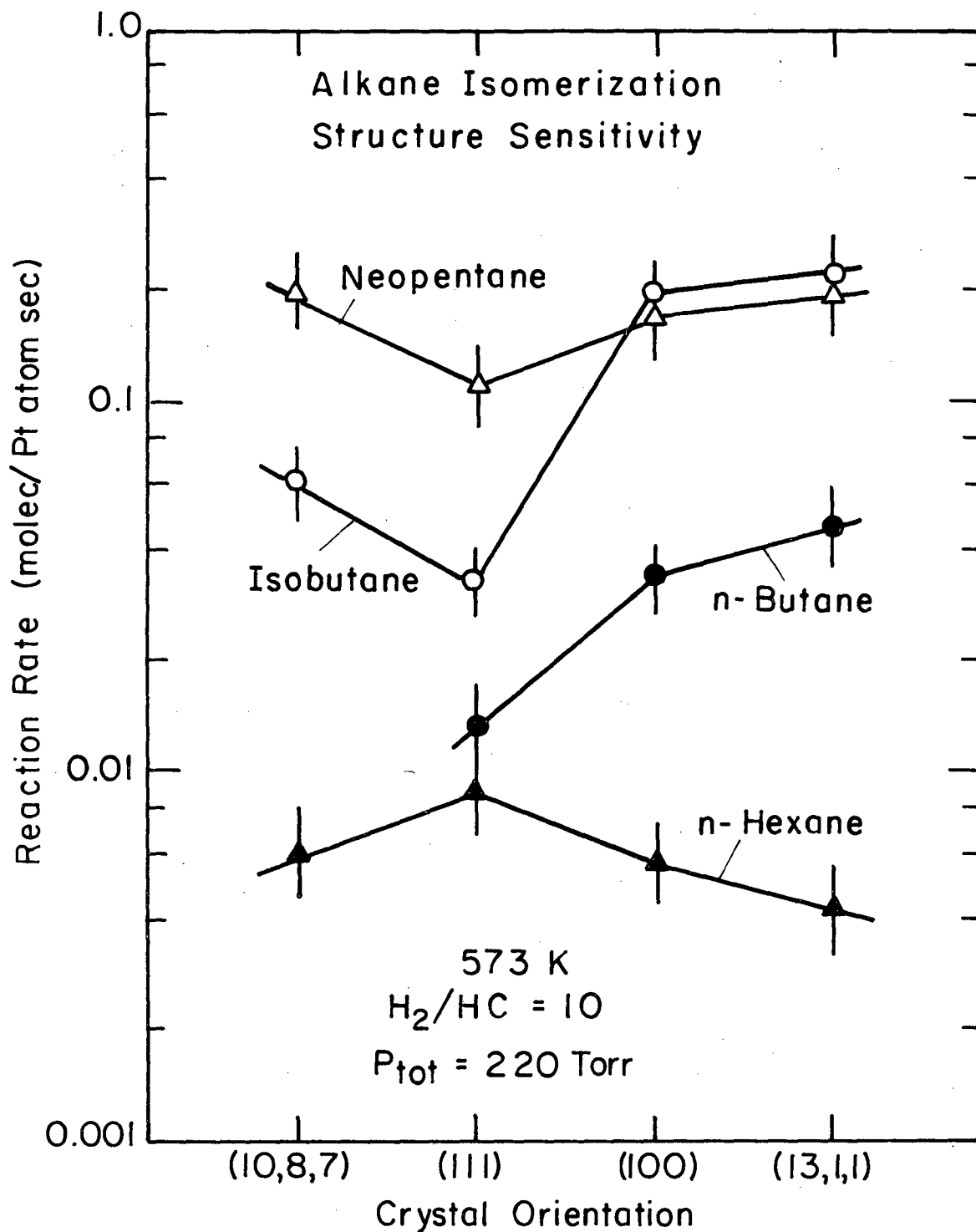


Fig. 5

XBL816-5915

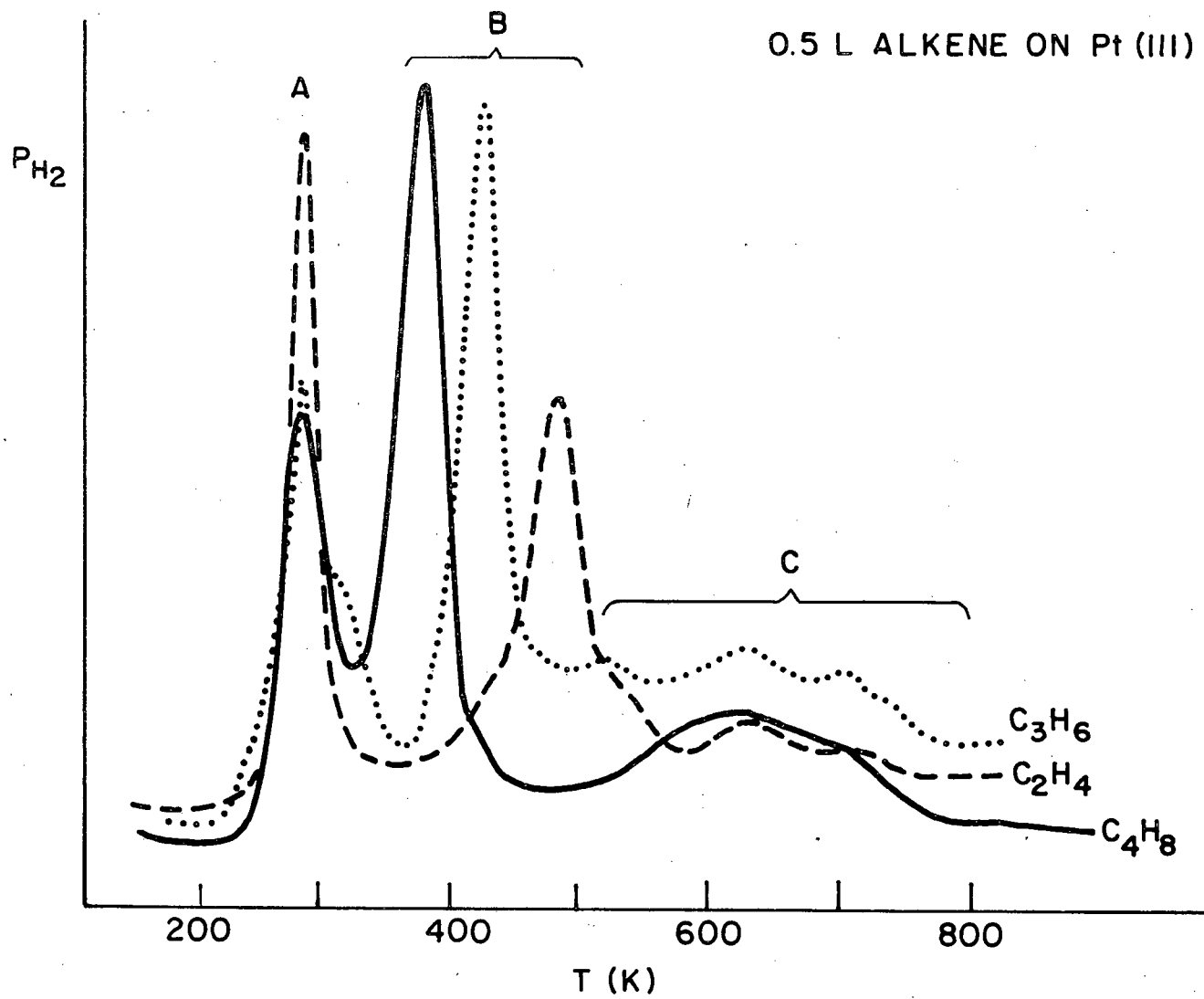


Fig. 6

XBL 814-5475

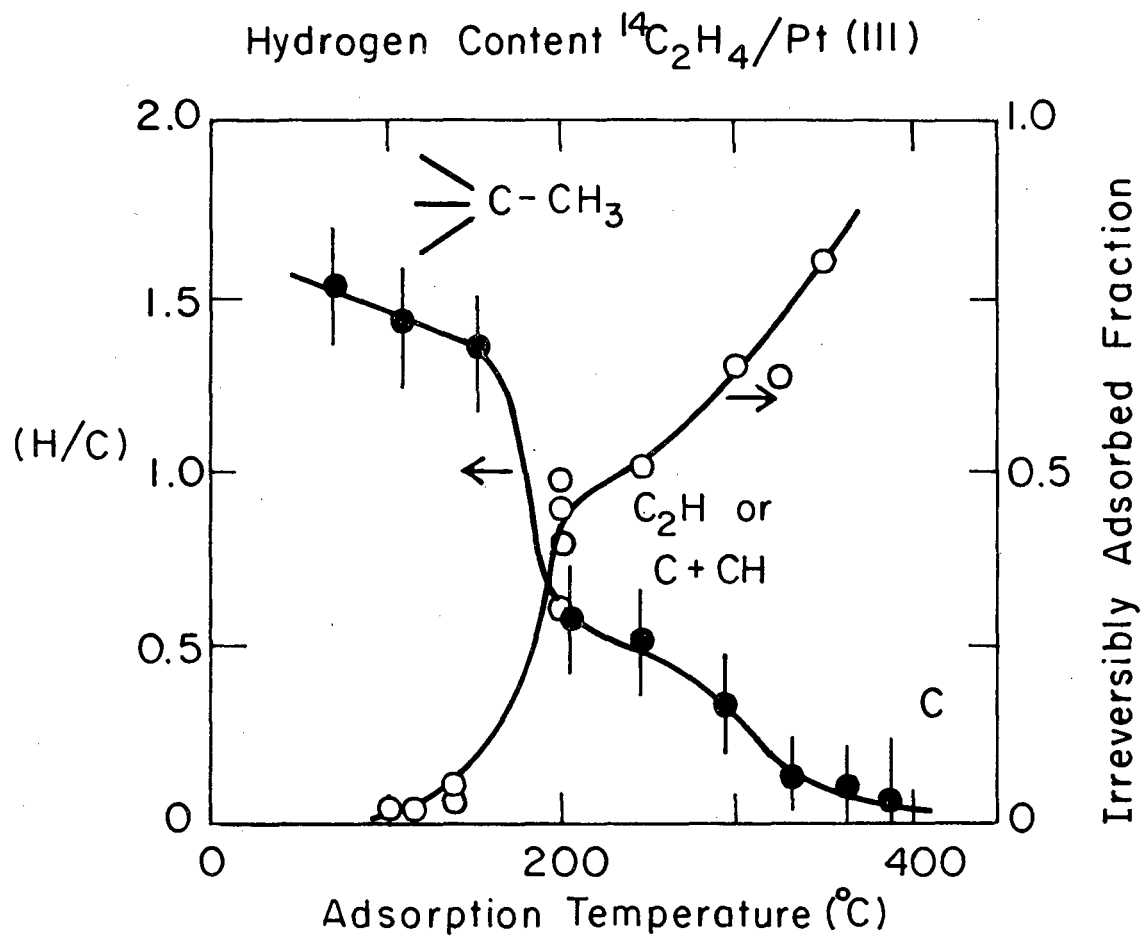
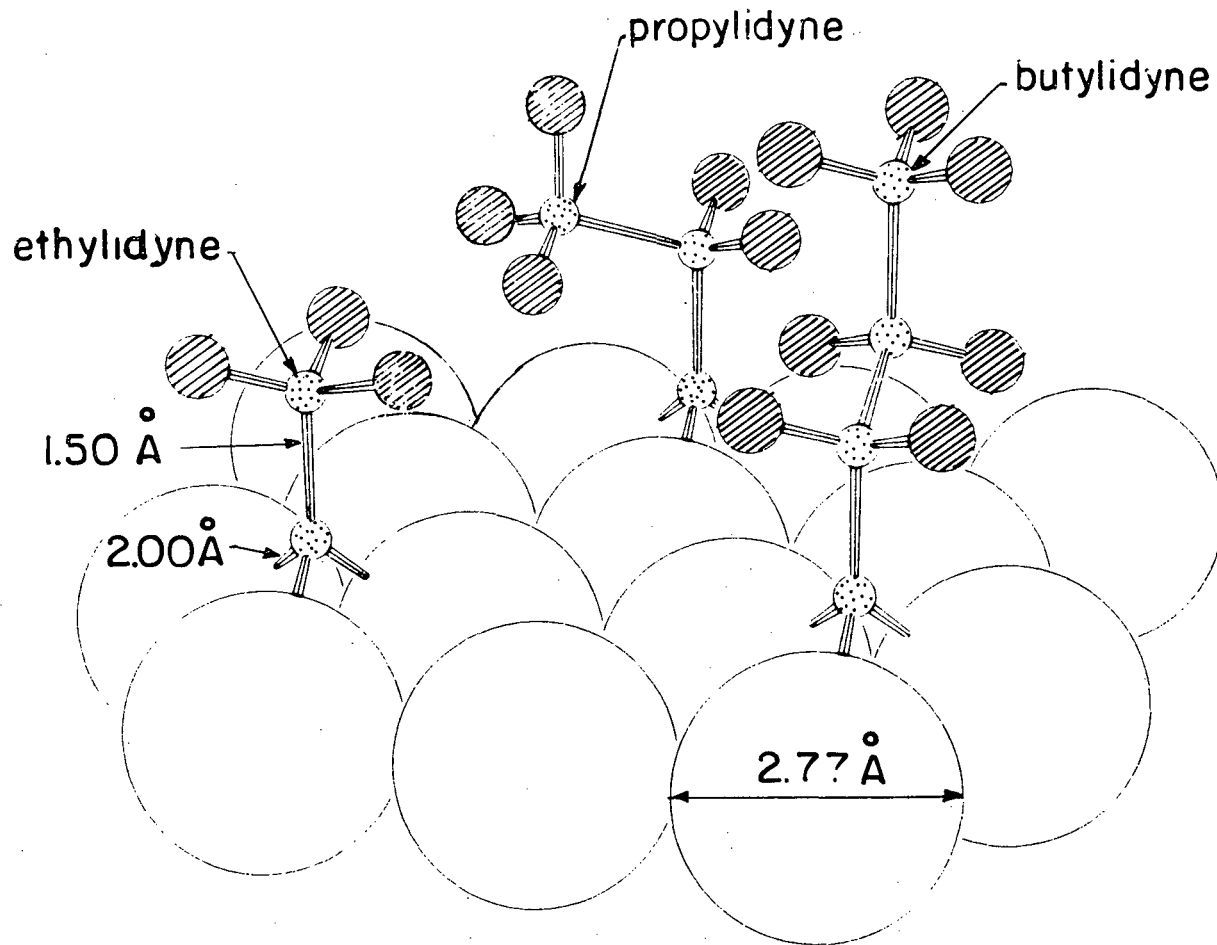


Fig. 7

XBL 812-5151



Pt(III) + ethylidyne, propylidyne and butylidyne

Fig. 8

XBL 8110-6882

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

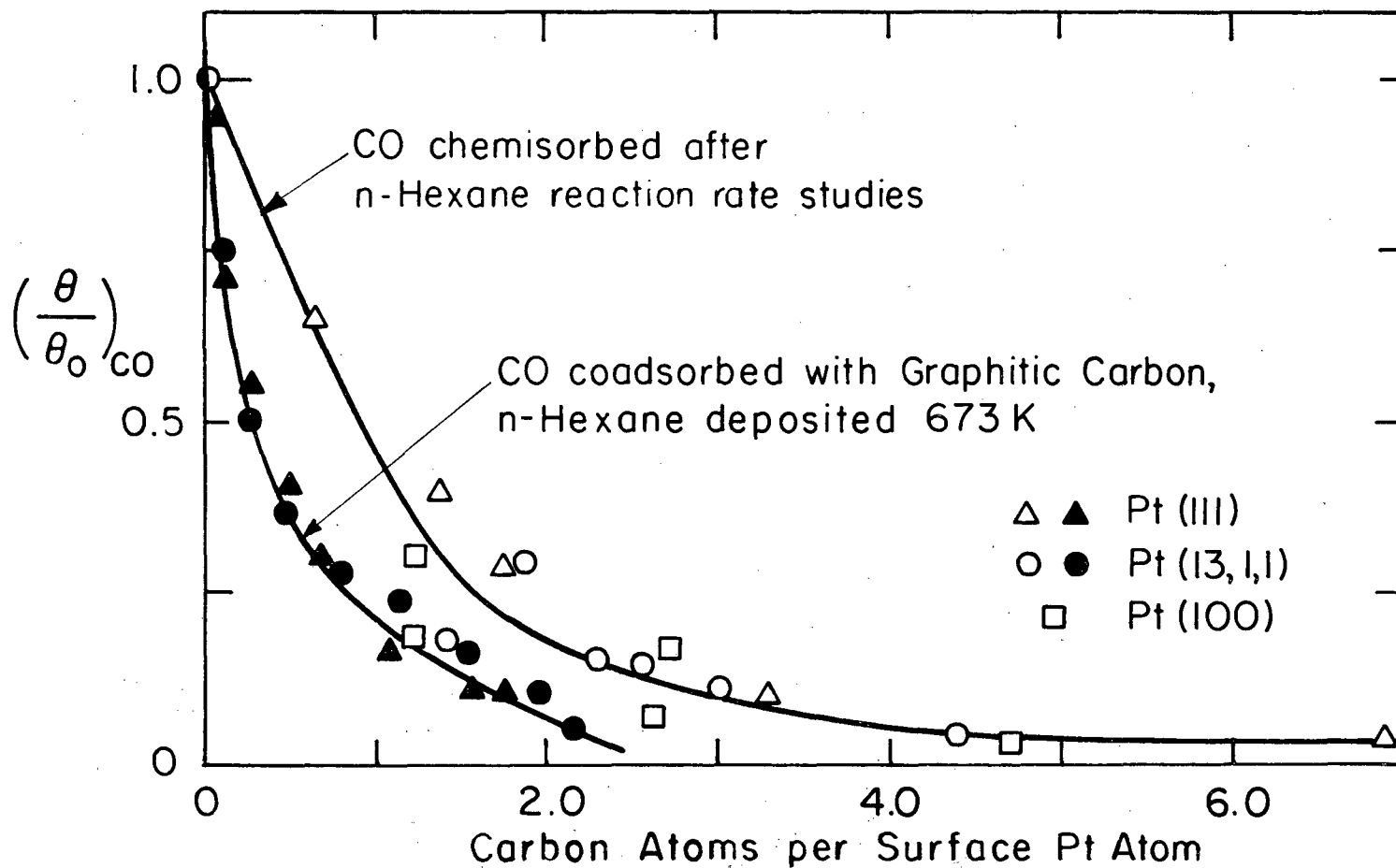


Fig. 9

XBL 816-5851

MODEL FOR THE WORKING PLATINUM CATALYST

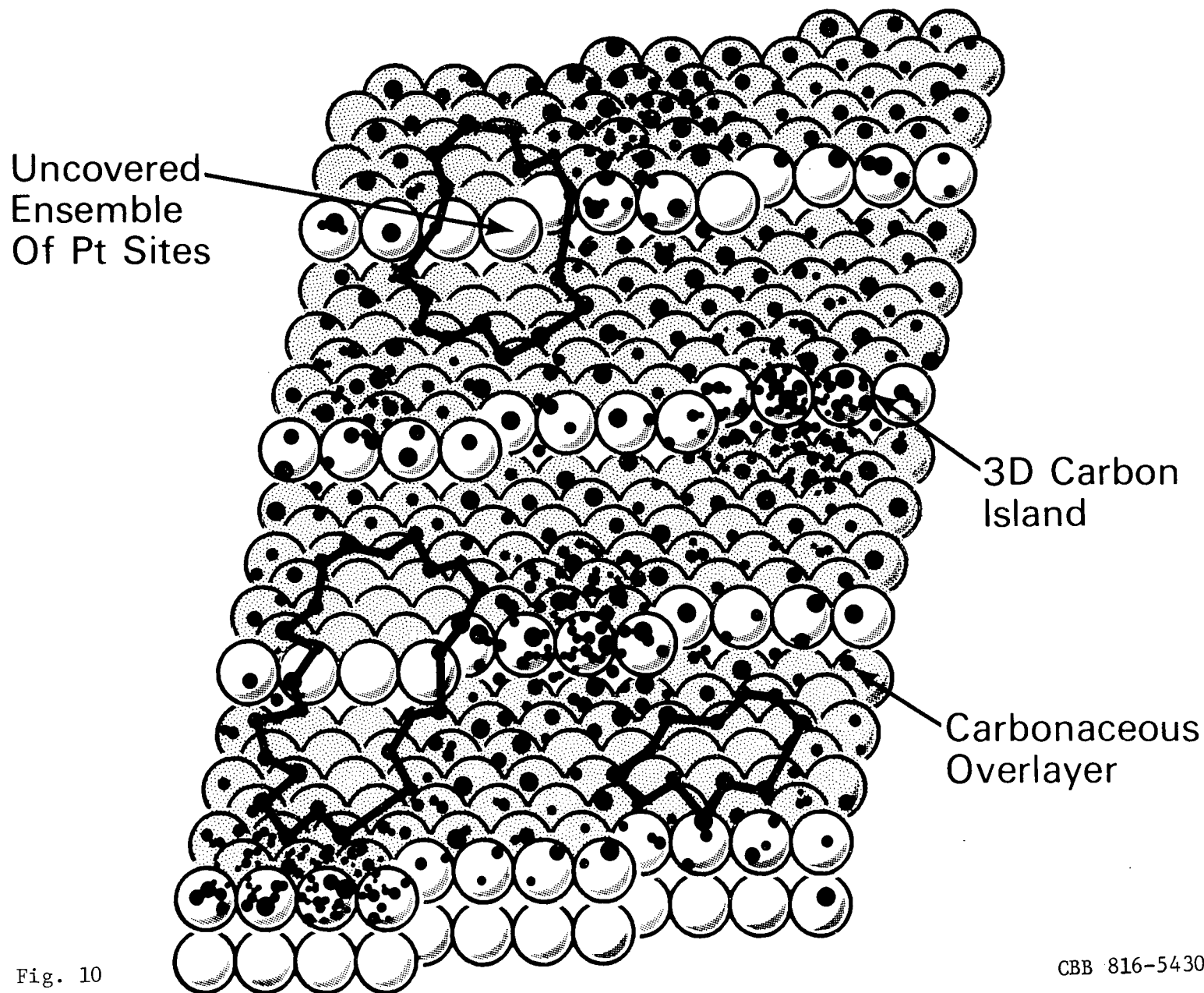


Fig. 10

CBB 816-5430

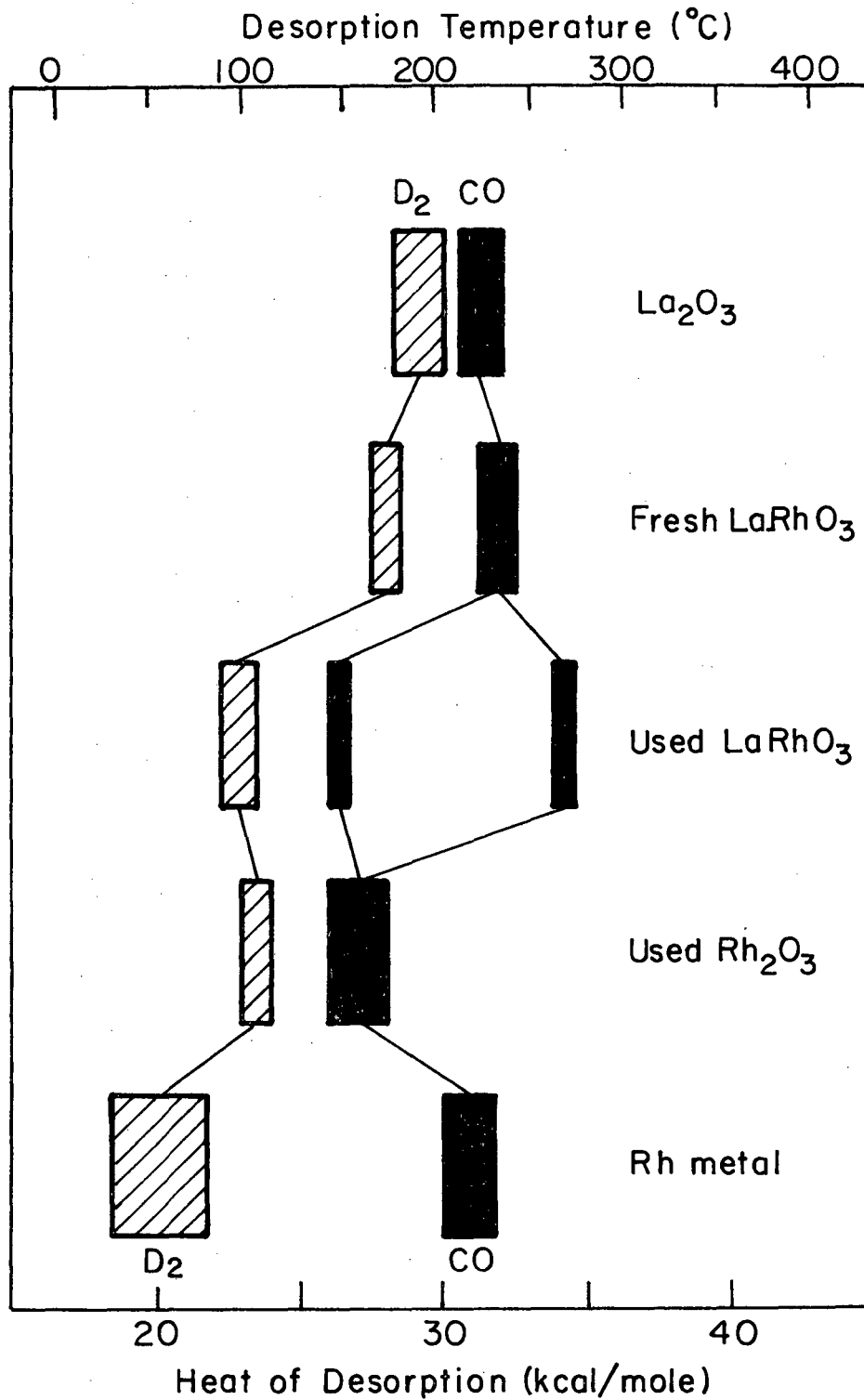
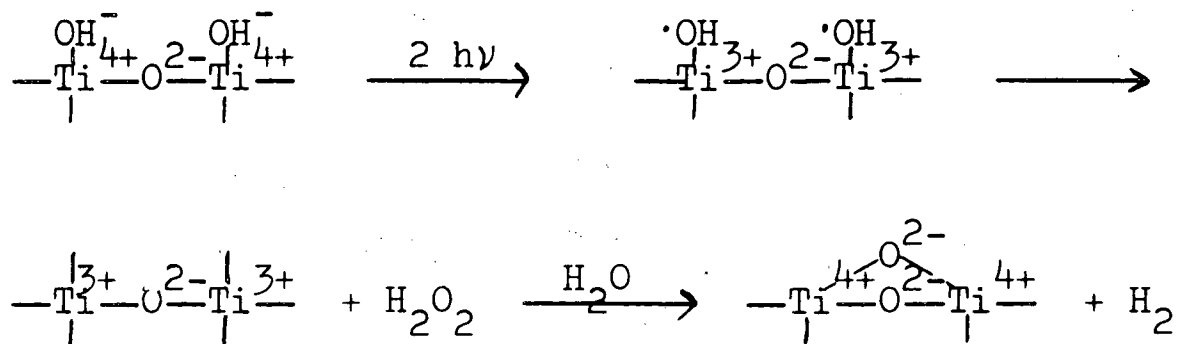


Fig. 11

XBL 817-6123



Van Damme and Hall, JACS 101 4373

XBL 822-7816

Fig. 12

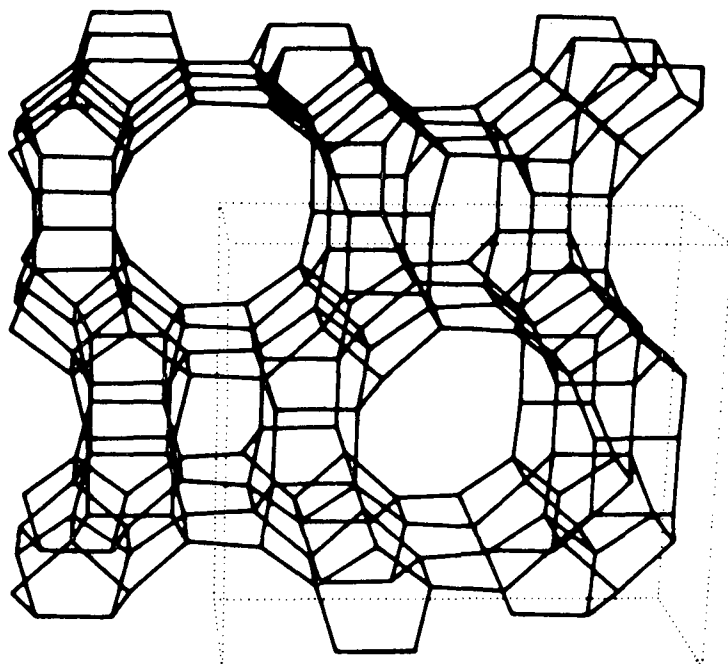


Fig. 13

XBL 7911-12828

Au-Pt(III)
W + H₂, 573K
H₂/HC=10, P_{tot}=220 Torr

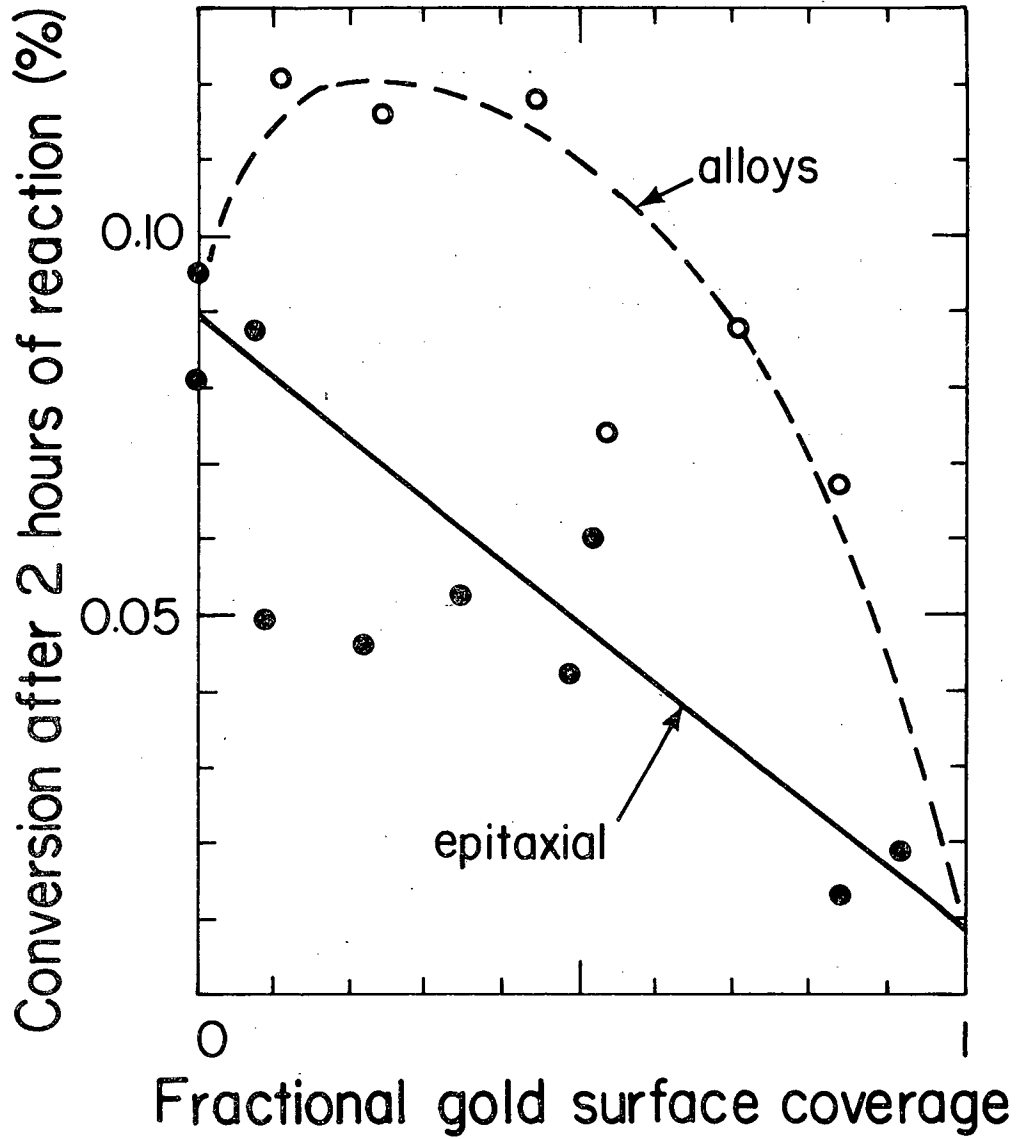


Fig. 14

XBL 819-1309

SATURATION CO COVERAGE (T=300K) ON Pt(111)/K

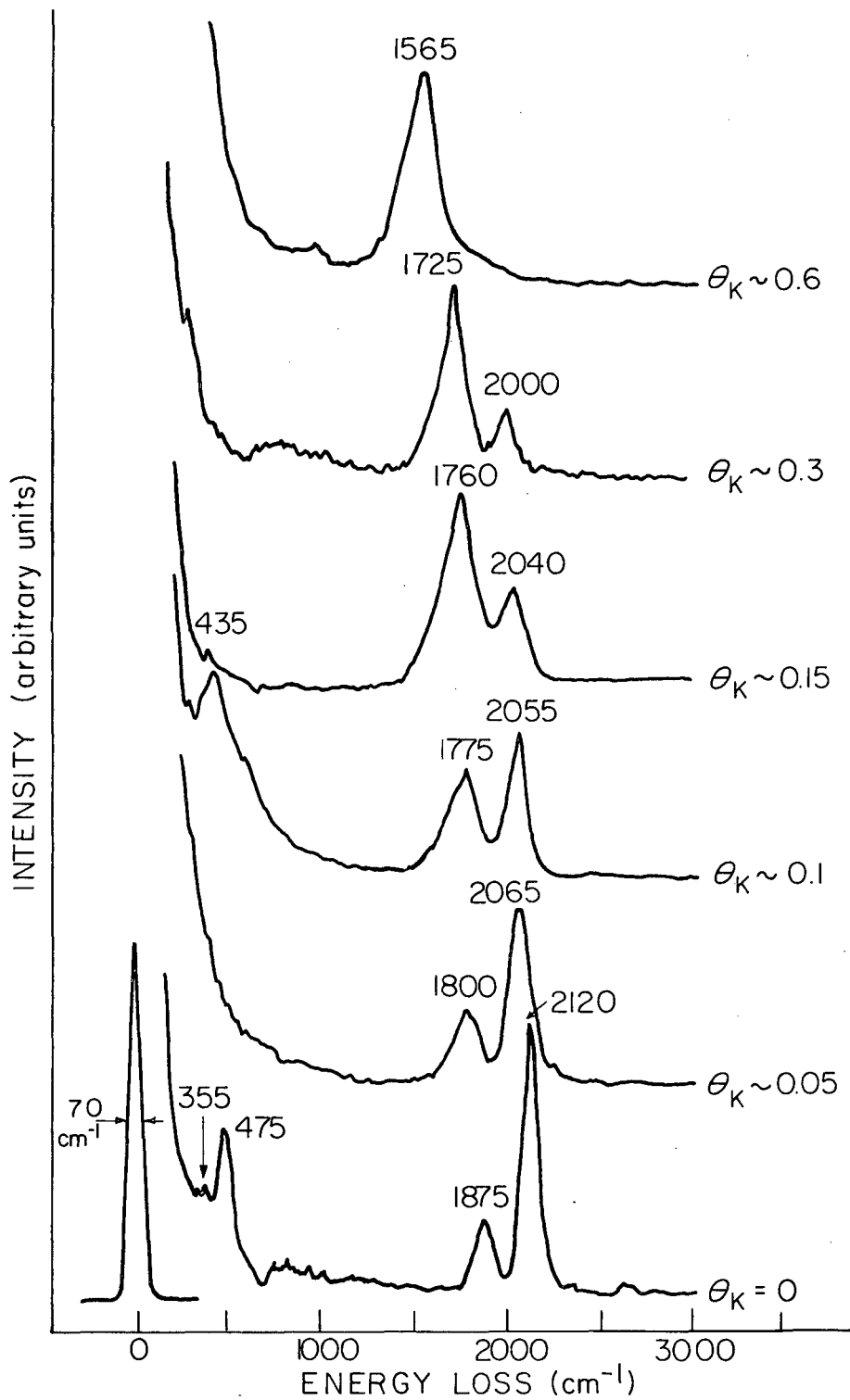


Fig. 15

XBL819-6628

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