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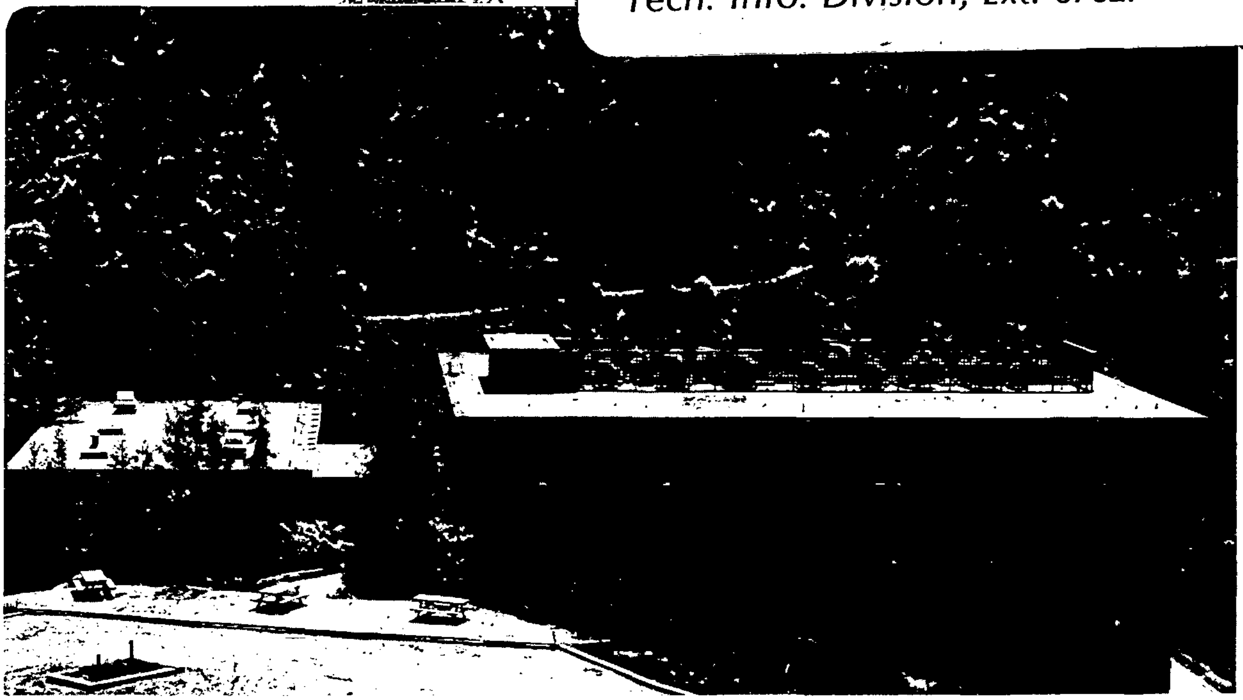

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THE SURFACE SCIENCE OF HETEROGENEOUS CATALYSIS

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I am grateful for the invitation to give this talk. I have always admired the Welch Foundation and Professor Milligan. As one of the Welch lecturers who visited with him at Arlington, El Paso and Prarie View, I was most impressed by the sense of quality and equilibrium with which the Welch funds are being utilized to improve education and research all through Texas in a most effective way. The high quality of research in surface science in Texas clearly shows the enormous beneficial impact of the Foundation. I have close contact, especially with Professor White's group at the University of Texas in Austin and with Professor Lunsford's group at Texas A & M, and they are certainly second to none. One of my best graduate students, Dr. Mark Davis, participated in undergraduate research with Professor Lunsford, and one of my recent postdoctoral associates, Dr. Bruce Koel who is a Miller Fellow at Berkeley, received his Ph.D. with Professor White.

I am also grateful to the Foundation for another reason. This is the first time I had one of my old graduate students (Dr. John Gland) in the same program as one of the speakers. This certainly proves that he was not irreversibly damaged by his graduate education at Berkeley.

It might be of value to this audience to place our studies of the surface science of heterogeneous catalysis into some historical perspective. When I came to this country I wanted to pursue graduate research in heterogeneous catalysis. I had the good fortune to go to Berkeley, but there was nobody on the chemistry faculty interested in catalysis. Fortunately, I managed to persuade Professor Richard Powell, an inorganic chemist, to give me a research topic in catalysis. Three years later I received a Ph.D for doing small angle x-ray scattering. Since Professor Powell got his Ph.D at Princeton with Professor Eyring I consider myself the academic grandson of this great man.

After receiving my Ph.D in 1959 I left the field of catalysis and surface chemistry for several years. I really wanted to study surfaces on the molecular scale. Perhaps the only technique for this purpose available at that time--field emission and field ion microscopy--had only limited applicability in my view. At IBM Research, where I had my first job, my research was in the field of solid state physics and chemistry. I had then learned about the great developments at the Bell Telephone Laboratory in the field of low energy electron diffraction (LEED) that were pioneered by L. Germer and J. Lander. LEED permitted one to view and study the structure of ordered surfaces of solids and of adsorbed ordered monolayers on the atomic scale and I was immediately anxious to return to the study of surfaces with the hope that catalytically active surfaces would also be excessible to atomic scale scrutiny in the near future.

When I returned to Berkeley as a junior faculty member in 1964 I started to work with LEED to scrutinize the structure of platinum crystal surfaces. These experiments needed only very small, ~ 1 cm^2 surface area single crystal surfaces. Figure 1 shows a typical crystal surface that we utilize, placed in the middle of an ultra high vacuum chamber.

We could structurally characterize such a surface readily, we could determene the surface composition and the oxidation state of surface atoms using electron diffraction and electron spectroscopies. It is very difficult to similarly characterize large surface area ($10-10^2$ m^2/gram) specimen that are used in most catalytic studies in the chemical technology.

Figure 2 shows the intensity of back-scattered electrons as a function of energy when a 2000 eV energy electron beam strikes a solid surface. The elastically scattered fraction is used for low energy electron diffraction (LEED).(1) The most useful energy range for surface structure studies by LEED is 10 eV to

200 eV. Those electrons that lost very little energy in the mev range due to vibrational excitation of surface atoms and molecules are utilized in high resolution electron energy loss spectroscopy (HREELS) for determination of surface structure.(1) HREELS uses incident electrons with energies in the range of 2-6 eV most frequently. This technique was not available in the 1960's but it is very popular and useful nowadays for studies of the structure of disordered adsorbates where LEED cannot be employed. Auger electron spectroscopy (AES), that was developed in 1968, that is based on the emission of electrons as a result of deexcitation of surface atoms provides us with the surface composition with about 1% of a monolayer sensitivity. X-ray photoelectron spectroscopy (XPS) yields the oxidation states of surface atoms at a similar level of sensitivity. Table 1 lists some of the most frequently used techniques for surface analysis at present. All these techniques are being utilized to determine the surface properties (structure, composition, valency) of small area samples.

The most important result that came out of the early studies of platinum and other metal surfaces is the discovery of surface reconstruction.(2) It was found that the first layer of atoms at the surface may have a different structure than the projection of the bulk structure to the surface. Figure 3a shows the diffraction pattern characteristic of the clean Pt(100) crystal face while Figure 3b exhibits the pattern that is expected based on the bulk structure of this fcc metal. The extra diffraction spots indicate the presence of a different surface unit cell as we discovered it in 1965. Similar reconstructed surface structures were exhibited by the gold and iridium(100) crystal faces as well. It took us 15 years to solve this surface structure that we could only do as a result of the development of dynamical surface structure analysis during this period.(3) In 1980 we published the complete surface structure analysis of the clean Pt(100) surface that exhibits the diffraction pattern displayed in Figure 3a. The square unit cell of this surface is buckled into a hexagonal arrangement. The periodic coincidence of atoms in the hexagonal layer with atoms in the underlying square layer produces the busy diffraction pattern and the complex unit cell that is shown in Figure 4. Of course the most famous surface structure that shows how different the surface is from the bulk structure is that of the (7 x 7) surface structure of the silicon (111) crystal face.(1) While this surface is commonly used to prepare silicon based integrated circuitry the location of surface atoms still has not been identified as yet by surface crystallography or by the use of other techniques. Surface structure analysis by LEED surface crystallography indicates that the surface atoms in many solid surfaces seek new equilibrium positions as a result of the anizotropy of the surface environment.

Not only the surface structure but also the composition of surfaces can be very different from the bulk composition. In Table 2 several binary metallic systems are listed for which there is surface segregation of one of the two bulk constituents.(1) There are good surface thermodynamic reasons for such surface segregation. By placing atoms of one type on the alloy surface the surface free energy (or surface tension) is markedly lowered. The surface segregation of one of the constituents in a multicomponent metal system can be utilized for the passivation of surfaces against chemical attack. We now have surface thermodynamic models based on regular solution theory that can predict the surface composition of multicomponent systems. For a two component system that behaves as an ideal or as a regular solution the atom fractions X_1^s and X_2^s at the surface are related to the atom fractions in the bulk, X_1^b and X_2^b as shown in Figure 5.

We can also predict how the changed surface composition in the surface monolayer approaches the bulk composition layer by layer. This is shown for the Au-Ag alloy that forms a regular solid solution by Figure 6. The first surface layer is rich in silver, the second layer is rich in gold, the third layer is again rich silver and by the fourth layer the bulk alloy composition is reestablished.(1) We can actually see the beginning of compound formation by the alternation of excess constituents for alloys with exothermic heat of mixing, layer by layer.

An interesting case is that of bimetallic monolayer systems. In this case there is no bulk, there is only surface and for these two-dimensional systems the bulk phase diagrams are no longer valid. These two-dimensional systems may have very different phase diagrams and miscibility gaps that are at a lower temperature. Two-dimensional binary alloy systems are of great importance in heterogeneous catalysis as shown by the studies of John Sinfelt. Using two-dimensional systems there is an opportunity to produce surface compounds that would not exist if the surface were in equilibrium with the bulk phase.

During the 1960's we have learned a great deal about the structure and composition of surface monolayers. However, we gained very little information about how these properties relate to heterogeneous catalysis. One promising technique for studies of elementary surface reactions was molecular beam surface scattering.(1) The scheme of the experiment is shown in Figure 7. By the use of molecular beams of reactants we could determine the reaction probability upon a single collision with the metal surface. We found that when beams of H_2 and O_2 were scattered from the (111) crystal face of clean platinum the reaction probability was so low that we could not detect the formation of water. In fact, the lack of reactivity of this surface at low temperatures (< 800 K) and pressures ($\sim 10^{-6}$ torr) was unlike the reactivity of platinum as reported when using platinum foils or sponges at higher pressures (atomspheres).

About this time in 1972, I attended the Welch Conference on Solid State Chemistry where I was one of the Discussion Leaders. I heard a talk by Professor Michel Boudart in which he discussed that by introducing defects into MgO that could be monitored by electron spin resonance, H_2-D_2 exchange activity appeared that could be correlated with the defect concentration. It occurred to me that we are missing defects from the Pt(111) crystal face that could account for the poor reactivity. In returning to Berkeley we started our studies of high Miller Index stepped and kinked crystal faces of platinum.

When we cut fcc metals at some small angle to the low Miller Index (111) or (100) crystal faces we obtain stepped or kinked surfaces that are shown in Figures 8 and 9. There are terraces of variable widths depending on the angle of cut, separated by periodic steps of one atom in height, usually.(4) The step periodicity as well as the step height can readily be determined by LEED studies.(1) These surfaces can be cut in such a manner that the steps also have a large concentration of kinks. Surfaces may have as much as 40% of their atoms in step sites and the kink concentration can reach 10%. As compared to these high concentrations of line defects, point defects such as adatoms or vacancies have very small surface concentrations (< 1%) when in equilibrium with the bulk and with other surface defects. These steps and kinks are stable under the conditions of most catalytic surface reactions.

When we carried out H_2-D_2 exchange on these stepped surfaces we immediately detected the formation of HD on a single scattering.(5) Unlike on the flat (111) crystal faces H_2, D_2 or O_2 dissociate on these low coordination number surface sites with near zero activation energy while there is a finite activation energy for dissociation of these diatomic molecules on the flat surface. Thus, it appeared that surface defects must play important roles in breaking large binding energy chemical bonds which is one important elementary reaction step in many catalyzed surface reactions.

Low pressure reaction studies are valuable for several reasons. They reveal the kinetics and mechanisms of elementary reaction steps: adsorption, bond breaking, surface diffusion and desorption. In addition they permit the simultaneous characterization of the surface structure and surface composition while the kinetic parameters (rates, selectivity, activation energy) are obtained.

I wanted to investigate the catalysis of hydrocarbon reactions by platinum surfaces at low pressures but the experiments did not work. Let me demonstrate the reasons for this by discussing a simple reaction, the dehydrogenation of cyclohexene to benzene. This reaction readily occurs on the stepped platinum crystal surfaces at low pressures ($\sim 10^{-6}$ torr) and its rate is shown in Figure 10. First the reaction rate increases then after about five minutes it declines rapidly. After ten minutes the surface is poisoned and the reactivity is almost undetectable. If we simultaneously monitor the surface composition by AES we find the build-up of a monolayer of carbon on the platinum surface. The explanation appears to be that the surface poisoned by the build-up of this carbonaceous monolayer, which is the result of a stoichiometric reaction between the incident cyclohexane molecules and the metal surface. Of course, there are low pressure reactions which do not poison--the oxidation of CO to CO_2 is one of these. Nevertheless, hydrocarbon reactions poison rapidly at low reactant pressures on transition metal surfaces.

The reason for the rapid poisoning of the transition metal surface during low pressure hydrocarbon reaction conditions is demonstrated in Figure 11. After chemisorbing several different alkenes on the Pt(111) crystal face at 300 K the sample was heated and the thermal desorption of various species was monitored.(6) We find that the chemisorbed hydrocarbons undergo sequential dehydrogenation with increasing temperature. The carbonaceous residue that is left behind is adsorbed irreversibly and above 800 K it is converted to graphite.

Thus, we had to go to high reactant pressures to study catalyzed hydrocarbon conversion reactions. We had to develop the technology to carry out high pressure reactions over small 1 cm^2 area crystal surfaces.

The high pressure-low pressure apparatus that premits us to study the rate and selectivity of hydrocarbon reactions at high pressures(7) (up to 100 atm) using small area (~ 1 cm^2) crystal surfaces is shown in Figure 12. The sample, after suitable surface characterization in ultra high vacuum by LEED, AES and other surface sensitive techniques, is enclosed in an isolation cell that can be pressurized with the reactants. The sample is then heated to the reaction temperature and the products that form are analyzed by a gas chromatograph that is connected to the high pressure loop. The high pressure reactor can be used in a batch or in a flow mode. The detection sensitivity of the gas chromatograph is high enough that a 1 cm^2 surface area is adequate to monitor the product distribution as long as the turnover rates over the catalyst are greater than 10^{-4} molecules/site/sec. Using this high pressure-low pressure apparatus we can carry out catalytic reactions under conditions that are virtually identical to those used in the chemical technology. We can then evacuate the high pressure cell, open it and analyze the surface properties of the working catalyst in ultra high vacuum using the various techniques of surface science. Then, the isolation cell may be closed again and the high pressure reaction may be continued and again interrupted for in situ surface analysis in vacuum.(7) We cannot, however, carry out surface analysis under the high pressure reaction conditions.

When working with model catalysts, like our small area single crystal surfaces, it is essential to compare its rates, product distributions, activation energy for a given reaction and other kinetic parameters with dispersed high surface area catalysts that are used in the technology. Table 3 displays the results of CO hydrogenation over dispersed rhodium catalysts as obtained by Vannice and the results obtained over rhodium foils in my laboratory under identical experimental conditions.(8) The agreement is excellent, the product distribution (mostly methane) and the activation energies for methanation are identical. Figure 13 compares the rates of hydrogenation of cyclohexene to cyclohexane obtained by Boudart et. al. using dispersed high surface area supported platinum catalysts with our data using platinum single crystal surfaces. Again the turnover rates are the same within the experimental error. Similar agreement was reached for several other structure insensitive reactions(9) as well that were carried out under identical experimental conditions to provide credibility to our model studies that utilize small area well characterized metal surfaces. Thus, we used this combination of model catalyst studies at high pressure to determine the reaction rates and product distribution and the surface analysis of their composition and structure to develop the surface science of heterogeneous catalysis.

We concentrated our studies on a few catalytic reactions. These included the catalysis of hydrocarbon conversion over metals, the hydrogenation of CO and the photodissociation of water to H_2 and O_2. Platinum is an excellent catalyst for dehydrocyclization reactions that produce aromatic molecules from alkanes, or for isomerization. Another metal we studied extensively 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/H_2 reaction was also the focus of our investigations. Finally the photodissociation of water to hydrogen and oxygen was one of the important reactions that we studied. These reactions were chosen for their importance in energy conversion processes. I believe that physical sciences must focus on understanding the energy related problems of our society, that includes energy conversion, production, transport and storage. Catalysis is of course at the heart of most energy problems.

Having a high pressure-low pressure apparatus permitted us to measure the rates of reactions over 10 orders of magnitude pressure range. This we have carried out for the hydrogenation and dehdyrogenation of cyclohexene to cyclohexane and to benzene respectively,(10) and the results are shown in Figure 14. The turnover rates increase with pressure as expected. It is possible, however, to replot the same information as reaction probabilities by dividing the rate of product molecule formation by the rate of molecular incidence on the surface that can be calculated from the total reactant pressure. The reaction probability is defined as the number of product molecules formed per incident reactant molecule. It can be seen from Figure 11 that the reaction probabilities are very low, in the range of 10^{-5} to 10^{-7} and it decreases with increasing pressure. This is due to the very long residence time (seconds) of the molecules on the surface that causes a traffic jam. Most surface sites are occupied by adsorbates and the catalyst cannot cope with the traffic because of the very long molecular residence times.

Out of our studies of model catalysts came the identification of three necessary ingredients of selective molecular scale catalysis. These are:

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

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

1) Structure Sensitivity Of Catalytic Reactions.

Figure 15 compares the rates of ammonia synthesis over the (111), (100) and (110) crystal faces of iron.(11) The (111) crystal face is 420 times as active and the (100) face is 32 times as active as the (110) iron surface. This reaction was studied by several outstanding researchers that include P. Emmett, M. Boudart and G. Ertl who worked for a long time on the mechanism of the ammonia synthesis.(12) The extreme structure sensitivity of this reaction was predicted by many. However, this data is the first clear demonstration of this structure sensitivity. Figure 16 shows the atomic surface structures of the studied iron crystal faces. Professor Boudart suggested that the so-called C_7 (seven-coordinated) sites are the most active sites for the dissociation of dinitrogen,(13) which appears to be the rate limiting step for the synthesis of ammonia. Since these sites are found in the (111) crystal face with the largest concentrations our results are certainly in support of his model.

The reactions of n-hexane or n-heptane over platinum surfaces are excellent probes of structure sensitivity.(14) The various reactions of n-hexane are displayed in Figure 17. The reactions leading to branched isomers (isomerization) and cyclic molecules (dehydrocyclization) are especially desirable for producing high octane gasoline from petroleum naphta. The third type, hydrogenolysis reactions that involves the scission of C-C bonds yields low molecular weight gaseous products that are undesirable when producing gasoline. The reactivity of the flat (111) and (100) sufaces for the dehydrocyclization of n-hexane and n-heptane are compared in Figure 18. The hexagonal (111) surface is 3 to 7 times more active than the platinum surface with the square unit cell.(14) In Figure 19 the selectivity of stepped platinum surfaces are compared with the flat surfaces under identical conditions for the same reaction. Maximum aromatization activity is obtained on stepped surfaces with terraces about 5 atoms wide with hexagonal orientations as indicated by reaction rate studies over more than 15 different crystal surfaces with varied terrace orientations and step and kink orientations.

The reactivity patterns displayed for alkane isomerization reactions is completely different to that for aromatization.(15) Our studies revealed that maximum rates and selectivity (rate of desired reactions/total rate) for butane isomerization reactions are obtained on flat crystal faces with square (100) unit cell. Isomerization rates for this surface are 4 to 7 times higher then those for hexagonal surfaces as shown in Figure 20.

For the undesirable hydrogenolysis reactions that require C-C bond scission we found that the two flat surfaces exhibit very similar reaction rates. However, the distribution of hdyrogenolysis products varies sharply over these two surfaces. The hexagonal surface displayes high selectivity for scission of the terminal C-C bond whereas the (100) square surface always prefers cleavage of C-C bonds located in the center of the reactant molecule.(16) The hydrogenolysis rates increase markedly (3-5 fold) when kinks are present in high concentrations on the platinum surfaces (Figure 20).

Since different reactions are sensitive to different structural features of the catalyst surface we must prepare the catalyst with appropriate structure to obtain maximum activity and selectivity. The terrace structure, the step or kink concentration or a combination of these structural features is needed to achieve optimum rates for a give reaction. Our studies indicate that H-H and C-H bond breaking processes are more facile on stepped surface then on flat crystal faces, while C-C bond breaking is aided by ledge or kink sites that appear to be most active for breaking any of the chemical bonds during hydrocarbon conversion reactions. Since molecular rearrangements must also occur in addition to bond breaking it is not surprising that the terrace structure exerts such an important influence on the reaction path that the adsorbed molecules are likely to take.

The differences in the chemical behavior of terrace, step and ledge atoms arises not only from their different structural environment but also from their different electronic charge densities that result from variation of the local coordination. Electron spectroscopy studies reveal altered density of electronic states at the surface irregularities; there is a higher probability of electron emission into vacuum at these sites (lower work function) indicating the redistribution of electrons.

These results, revealing the structure sensitivity of hydrocarbon conversion reactions over platinum surfaces can be used to interpret changes that occur on platinum catalysts used in the chemical technology. Figure 21 shows the changes of product distributions that occur as a function of time over Pt-Re catalysts that are often used in petroleum refining. With time the selectivity to produce aromatic molecules is increasing while the selectivity to produce isomerized products decreases. This can be interpreted as due to the slow restructuring of the catalyst surfaces from (100) to (111) type that facilitates dehydrocyclization.

While many reactions of organic molecules are structure sensitive there are some that show no structure sensitivity: the ring opening of cyclopropane and the hydrogenation of cyclohexene to cyclohexane are two structure insensitive reactions when carried out on various metal surfaces.

It should be noted that the metal surface structures that are stable in the presence of an adsorbed layer of hdyrocarbons may be unstable in an oxidizing environment.(4) In the presence of chemisorbed oxygen other crystal faces may be more stable. As a result, changing the reducing chemical environment into oxidizing or the other way around could cause a massive reorganization of the surface structure. One should not expect all the catalyst surfaces to remain stable under the varied conditions encountered during catalytic reaction studies. One of the reasons for the application of certain additives is to stabilize the surface structure of the catalyst as more extreme conditions for the catalytic chemistry and for its regeneration are used.

2) 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. 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. Figure 11 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,(17) thermal desorption and hydrogen-deuterium exchange 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 of hydrogen and AES studies indicate that the stoichiometry of this mobile layer is C_2H_3. Above 120°C with increasing temperature an increasingly larger fraction of the surface carbon becomes irreversibly adsorbed as it looses 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°C, to obtain reasonably high turnover numbers. Figure 22 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. The stoichiometry of this tenaceous 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.(18) In the temperature range of 300-400 K the adsorbed alkenes form alkylidyne molecules that are shown in Figure 23. The C-C bond closest to the metal is perpendicular to the surface plane and its length corresponds to a single bond 1.5Å. The carbon atom that bonds the molecule to the metal is located in a three-fold site equidistant 2.0Å from the nearest metallic neighbors. This bond is appreciably shorter than the covalent metal-carbon bond (2.2Å) and is indicative of multiple metal-carbon bonds of the carbene or carbyne type. While this layer is ordered, on heating to about 100°C it disorders and hydrogen evolution is detectable by a mass spectrometer that is attached to the system. As the molecules dehydrogenate the disordered layer is composed of CH_2, C_2H and CH type fragments that can be identified by HREELS. 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 looses 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 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.(15) Figure 24 shows a fraction of the clean platinum surface as a function of the carbon surface concentration. (Θ/Θ_{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 24. At about 400°C the carbonaceous overlayer that is irreversibly adsorbed gradually looses 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 of the working platinum catalyst can be proposed and is shown in Figure 25. 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.(15) 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 CH_2 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.

The surface structure of the bare platinum islands may be the same or may be different from the structure of the initially clean metal. In order to study this we carried out CO thermal desorption from the platinum crystal surface after various hydrocarbon conversion reactions and compared the TDS spectra with that obtained from the clean platinum surface.(15) We found that after the reactions with light alkanes the TDS spectrum was identical to that from the clean metal surface the term the peaks due to the desorption of CO from the terrace (lower temperature) and step sites (higher temperature) being attenuated uniformly. Thus, the bare platinum islands maintained the same surface structure as the initially clean platinum surface. After the reactions with heavier hydrocarbons, n-hexane or n-hexane, the TDS spectrum was altered as shown in Figure 26. CO could no longer adsorb on step sites only on terrace sites. Thus, the higher molecular weight alkanes produced a carbonaceous deposit during their catalyzed reaction that blocked off the step sites. As a result, all the catalytic activity could be attributed to the flat terrace, in this circumstance.

3) 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 when prepared under appropriate experimental conditions.(19) Our studies using unsupported polycrystalline rhodium foils 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 over supported rhodium catalyst along with the identical activation energies for methanation (about 24 kcal/mole) that we both found (Table 2).(20) 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. 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 adsorption of CO and D_2 as the oxidation state of the transition metal ion is varied. This is demonstrated in Figure 27. The CO adsorption energy is decreased upon oxidation while the heat of adsorption of D_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.(21) As shown in Figure 27, 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

(Figure 28). At low enough temperatures, below 250°C, the formation of methanol predominates.(21) 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 rsult 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 dehydrogenation characteristics of the material control the product distribution.(21)

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.(22) 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. Figure 29 shows the catalytic cycle that explains most of the experimental results found so far. 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.(24) 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. Thus the importance of the proper oxidation state of transition metal ions to carry out catalyzed reactions is again demonstrated.

4) 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 heterogenous catalysis have been uncovered. The model of the working platinum catalyst reveals not only how selective hydrocarbon catalysis ocurs 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,(25) and one of them is shown in Figure 30. Zeolites are aluminum silicates that can be prepared with variable pore sizes that have molecular dimensions. 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.(26) 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. Figure 31 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.

Very different results are obtained when gold was difused into platinum at elevated temperatures. The gold-platinum alloy that forms showed a much higher activity for isomerization than clean platinum. 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. However, this cannot completely 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 adsorption of adsorbates such as carbon monoxide. HREELS and TDS studies showed that the coadsorption of potassium and carbon monoxide on platinum surfaces has decreased the CO stretching frequency by about 300 wave numbers as compared to the stretching frequency on the clean platinum, in the absence of potassium.(27) This effect is shown in Figure 32. 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. 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 that when alkali hydroxides or carbonates are adsorbed on the surface of graphite they catalyse its reaction with water vapor.(28) At low temperature in the range 200-250°C methane and carbon dioxide are produced (Figure 33). 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 CH_4 and for its oxidation to CO_2 or CO. This reaction involves ionic intermediates, the formation of H^+ and OH^-, that are catalyzed by the alkali hydroxides.(28) 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.(28)

c) Strong metal-support interaction. A control of the oxidation state of the surface transition metal ions has been reported by Tauster and coworkers.(29) 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. We also need more high quality people who take a long range view in their research so necessary to successfully build new catalysts. I hope that funding that is essential to combine surface science based characterization of catalysts with catalytic reaction studies will remain excessible to researchers entering this exciting field.

ACKNOWLEDGMENT

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TABLE I: Table of surface characterization techniques that are used to determine the structure and compostion 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 adsorbe species

TABLE II: Surface Composition Of Alloys: Experimental Results And Predictions Of The Regular Solution And Unified Segregation Models

		Segregating Constituent	
		Predicted	
Alloy Systems	Phase Diagram	Regular Solution	Experimental
Ag-Pd	simple	Ag	Ag
Ag-Au	simple	Ag	Ag
Au-Pd	simple	Au	Au
Ni-Pd	simple	Pd	Pd
Fe-Cr	low-T phase	Cr	Cr
Au-Cu	low-T ordered phases	Cu	Au, none, or Cu, depending on composition
Cu-Ni	low-T miscibility gap	Cu	Cu
Au-Ni	miscibility gap	Au	Au
Au-Pt	miscibility gap	Au	Au
Pb-In	intermediate phase	Pb	Pb
Au-In	complex	In	In
Al-Cu	complex	Al	Al
Pt-Sn	complex	Sn	Sn
Fe-Sn	complex	Sn	Sn
Au-Sn	complex	Sn	Sn

TABLE III: Comparison Of Polycrystallin Rh Foil With a 1 Percent Rh/Al_2O_3 Catalyst In The CO-H_2 Reaction At Atmospheric Pressure

	Polycrystalline Rh[a] foil	Supported 1% Rh/Al_2O_3[b]
Reaction conditions	300°C, 3:1 H_2/CO, 700 torr	300°C, 3:1 H_2/CO, 760 torr
Type of reactor	Batch	flow
Conversion	<0.1%	<5%
Product distribution	90% CH_4 ± 3 5% C_2H_4 ± 1 2% C_2H_6 ± 1 3% C_3H_8 ± 1 <1% C_4^+	90% CH_4 8% C_2H_6 2% C_3 <1% C_4^+
Absolute methanation rate at 300°C (turnover no.)	0.13 ± 0.03 molecules/site/sec	0.034 molecules/site/sec
Activation energy (kcal)	24.0 ± 2	24.0

[a] The values in this column are from B.A. Sexton and G.A. Somorjai, J.Catal. 46, 167 (1977).

[b] The values in this column are from M.A. Vannice, J. Catal. 37, 462 (1975).

FIGURE CAPTIONS

Figure 1: Small surface area sample mounted in an ultra-high vacuum chamber prepared for surface studies.

Figure 2: Experimental number of scattered electrons n(E) of energy E versus electron energy E curve.

Figure 3:
a) Diffraction pattern from the Pt(100) 5 x 1 structure.
b) Schematic representation of the 100 surface with hexagonal overlayer.
c) Diffraction pattern from the Pt(100) 1 x 1 structure.
d) Schematic representation of the 100 surface.

Figure 4: Structure of the reconstructed Pt(100) crystal face as solved by surface crystallography.

Figure 5: The ideal and regular solid solution models that predict surface segregations of the constituents with lower surface free energy.

Figure 6: Surface excess of silver as a function of bulk composition in silver-gold alloys.

Figure 7: Scheme of the molecular beam surface scattering experiment.

Figure 8: Structure of several high Miller Index stepped surfaces with different terrace widths and step orientations.

Figure 9: Surface structures of several high Miller Index surfaces with differing kink concentrations in the steps.

Figure 10: The comparison at 150°C of the cyclohexane dehydrogenation rate over Pt(223) stepped surface at low pressures with the simultaneous buildup of the irreversibly chemisorbed carbonaceous overlayer C_{273}/Pt_{237} ratio of 2.8 corresponds to monolayer coverage.

Figure 11: Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of ethylene, propylene and cis-2-butene chemisorbed on the Pt(111) crystal surface at 120 K. The ratio of heating is 12 K/sec.

Figure 12: Schematic representation of the experimental apparatus to carry out catalytic reaction rate studies on single crystal or polycrystalline surfaces of low surface area at low and high pressures in the range of 10^{-7}-10^{4} torr.

Figure 13: Comparison of studies of cyclohexene hydrogenation to cyclohexane on platinum single crystal surfaces and on dispersed platinum catalysts.

Figure 14: Correlation of cyclohexene reaction rates and reaction probabilities over a pressure range of ten orders of magnitude. The reactions were performed at 150°C over the stepped Pt(223) crystal surface with a hydrogen to hydrocarbon ratio of ten.

Figure 15: Surface structure sensitivity of Fe-catalyzed NH_3 synthesis.

Figure 16: Idealized atomic surface structure for the low index planes of iron Fe(100), Fe(111) and Fe(110).

Figure 17: Skeletal rearrangement reactions of hydrocarbons are catalyzed by platinum with high activity and unique selectivity. Depicted here are the several reaction pathways which occur simultaneously during the catalyzed conversion of n-hexane, C_6H_{14}. The isomerization, cyclization and aromatization reactions that produced branched or cyclic products are important in the production of high octane gasoline from petroleum naptha. The hydrogenolysis reaction that involves a C-C bond yields undesirable gaseous products.

Figure 18: Dehydrocyclization of alkanes to aromatic hydrocarbons is one of the most important petroleum reforming reactions. The bar graphs shown here compare reaction rates for n-hexane and n-heptane aromatization catalyzed at 573 K and atmospheric pressure over the two flat platinum single crystal faces with different atomic structure. The platinum surface with the hexagonal atomic arrangement is several times more active than the surface with a square unit cell over a wide range of reaction conditions.

Figure 19: The selectivity of various platinum surfaces for the dehydrocyclization reaction. The stepped (557) surface with five atom wide terraces of (111) orientation appears to be the most active.

Figure 20: Reaction rates are shown as a function of surface structure for isobutane isomerization and hydrogenolysis catalyzed at 570 K and atmospheric pressure over the four platinum surfaces. The rates for both reaction pathways are very sensitive to structural features of the model single crystal catalyst surfaces. Isomerization is favored on the platinum surfaces that have a square (100) atomic arrangement. Hydrogenolysis rates are maximized when kink sites are present in high concentrations as in the Pt(10,8,7) platinum crystal surface.

Figure 21: Change of selectivity as a function of time over platinum-rhenium dispersed catalysts that are widely used in the chemical technology.

Figure 22: Carbon-14 labeled ethylene, C_2H_4, was chemisorbed as a function of temperature on a flat platinum surface with hexagonal orientation Pt(111). The H/C composition of the adsorbed species was determined from hydrogen thermal desorption studies. The amount of preadsorbed ethylene, which could not be removed by subsequent treatment in one atomosphere of hydrogen, represents the irreversibly adsorbed fraction. The adsorbtion reversibility decreases markedly with increasing adsorption temperature as the surface species become more hydrogen deficient. The irreversibly adsorbed species have very long surface residence times on the order of days.

Figure 23: Atomic surface structures for alkylidyne species chemisorbed on Pt(111).

Figure 24: 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 25: Model for the working platinum catalyst that was developed from our combination of surface studies using single crystal surfaces and hydrocarbon reaction rate studies on these same surfaces.

Figure 26: CO thermal desorption following reaction studies on a stepped platinum surface.

Figure 27: Heat of desorption (kcal/mole) of CO and D_2 from La_2O_3 fresh and used, $LaRhO_3$ used, Rh_2O_3 used and Rh metal. The spread of each value represents the variation with surface coverage rather than experimental uncertainty.

Figure 28: Variation of product distribution during dehydrogenation of carbon monoxide over $LaRhO_3$ surfaces as a function of temperature.

Figure 29: A proposed mechanism for the photodissociation of water over TiO_2 and $SrTiO_3$ surfaces.

Figure 30: One of the important zeolites, mordanite, $Na_8Al_8Si_{40}O_{96} \cdot 24\ H_2O$ viewed along the 001 axis.

Figure 31: The rate of formation of various products from n-hexane as a function of fractional gold surface coverage for gold-platinum alloys that were prepared by vaporizing and diffusing gold into Pt(111) crystal surfaces.

Figure 32: Vibrational spectra of the saturation CO coverage chemisorbed on Pt(111) at 300 K as a function of preadsorbed potassium coverage.

Figure 33: Number of CH_4 molecules produced during the LiOH, NaOH, KOH and CsOH catalyzed water graphite reactions as a function of reaction time at 522 K.

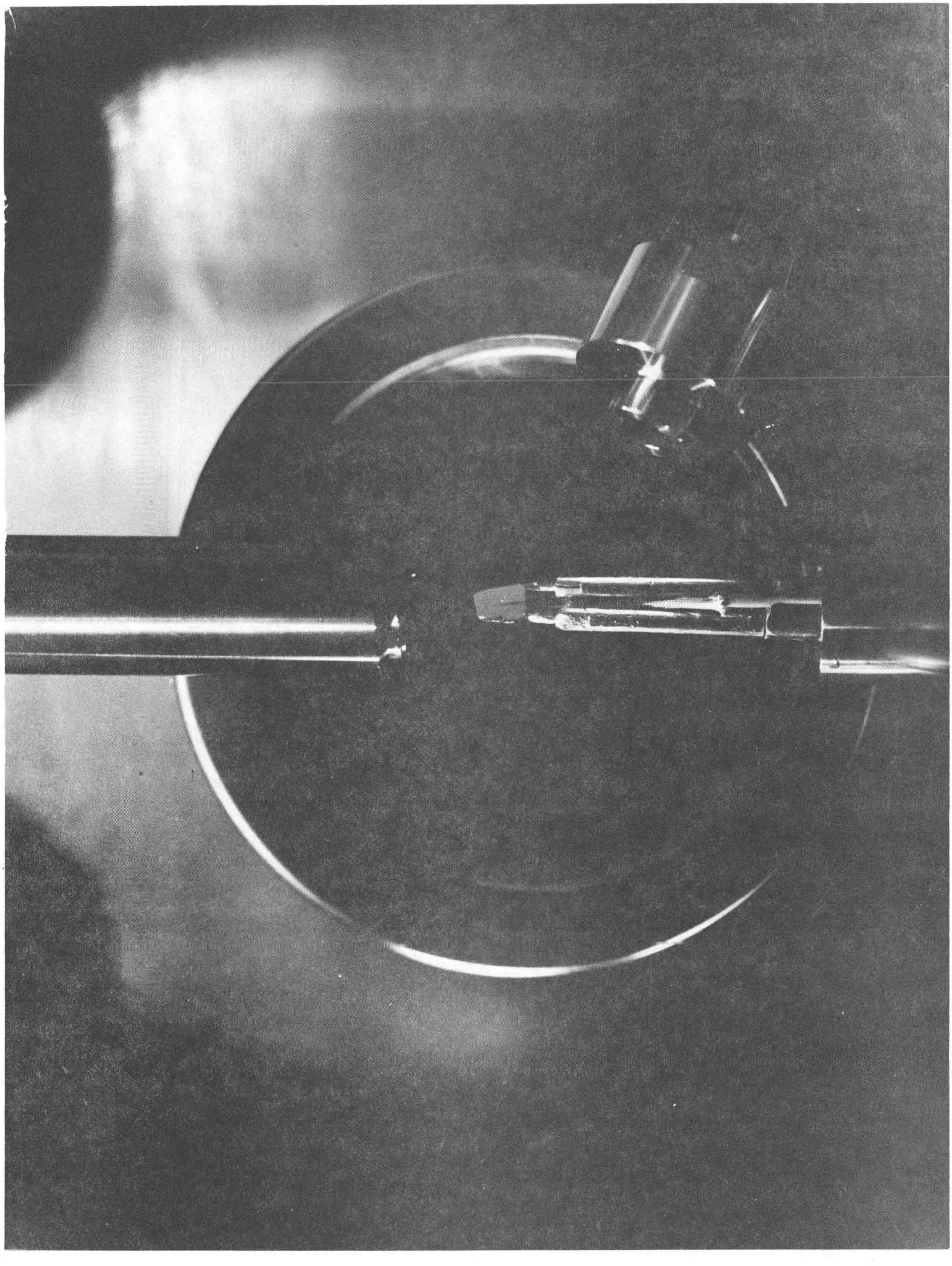
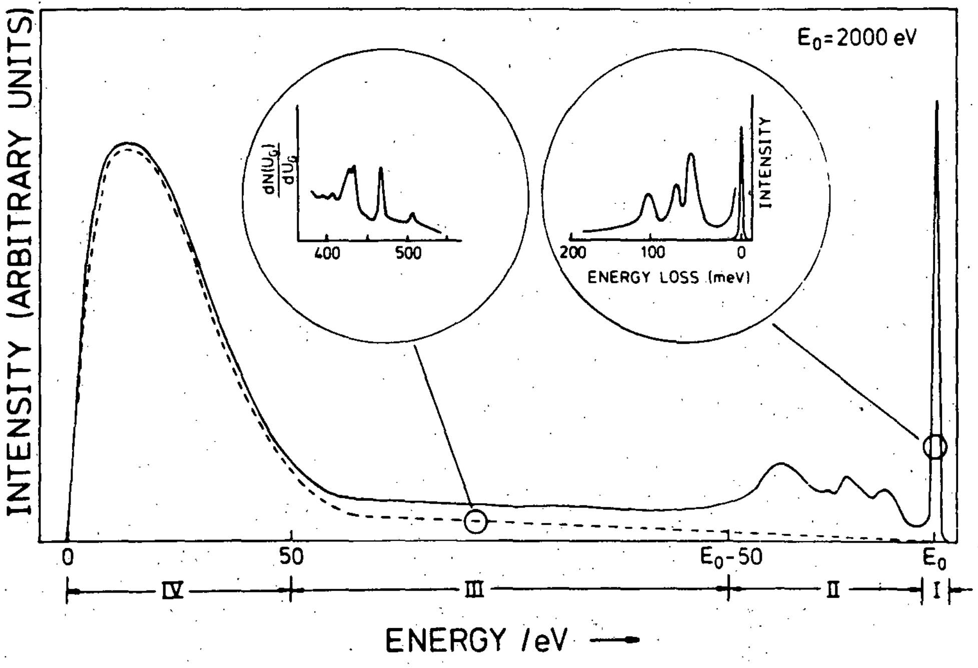


Fig. 1

CBB 819-9186



XBL 814-9177

Fig. 2

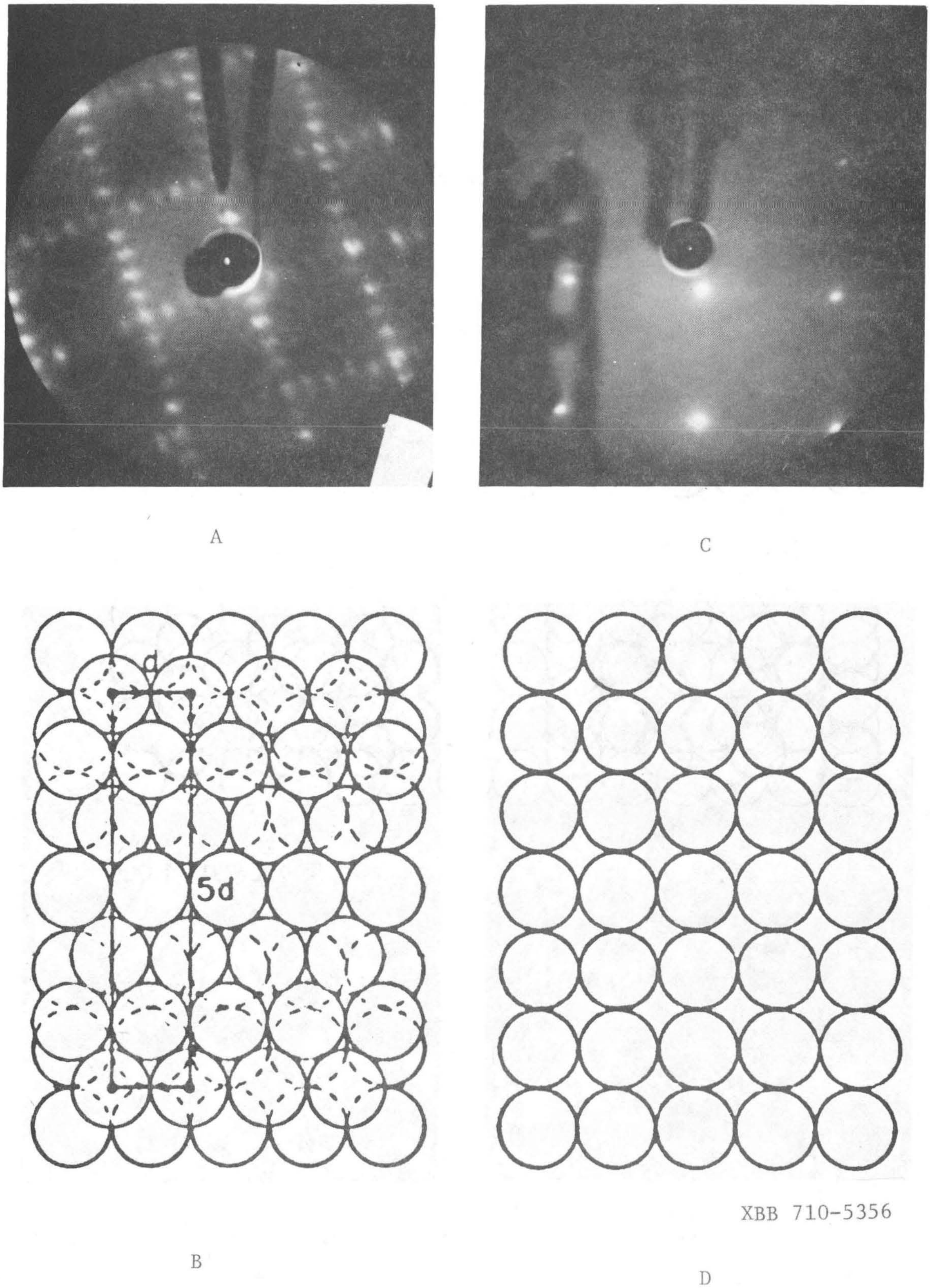


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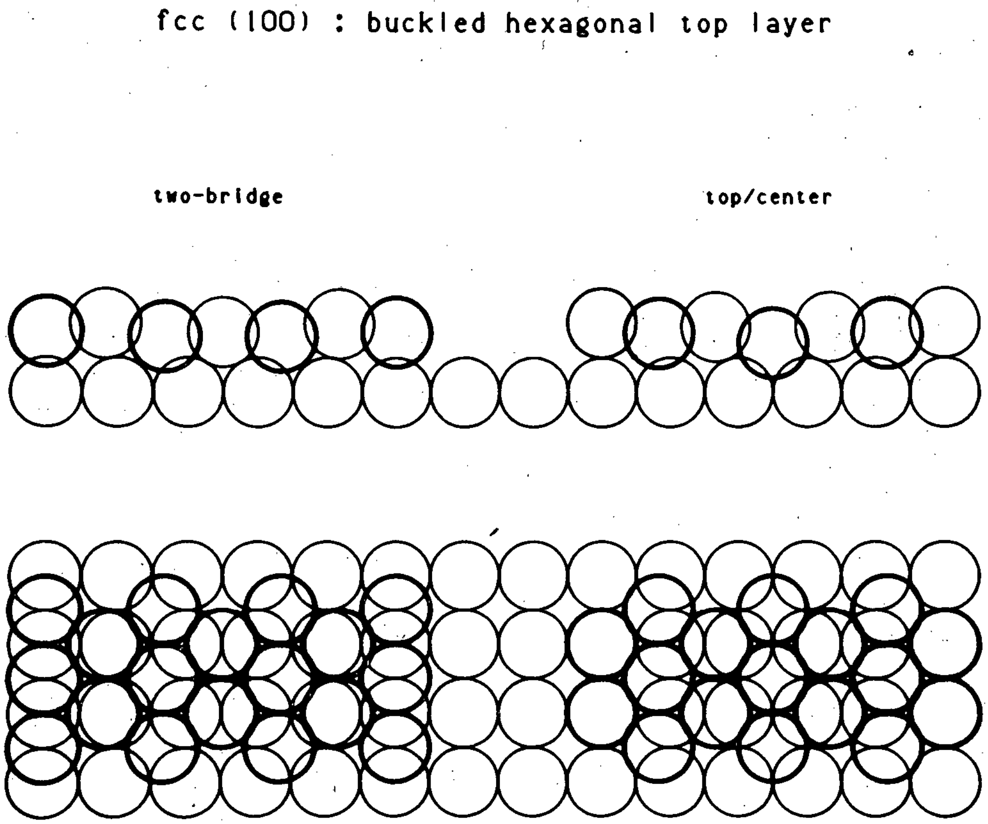
Fig. 3



XBL 7912-13739

Fig. 4

For an ideal solid solution:

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \exp\left[\frac{(\sigma_1 - \sigma_2)a}{RT}\right]$$

For a regular solid solution:

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \exp\left[\frac{(\sigma_1 - \sigma_2)a}{RT}\right] \exp\left\{\frac{\Omega(\ell + m)}{RT}\left[(x_1^b)^2 - (x_2^b)^2\right] \frac{\Omega\ell}{RT}\left[(x_2^s)^2 - (x_1^s)^2\right]\right\}$$

where Ω = regular solution parameter = $\dfrac{\Delta H_{\text{mixing}}}{x_1^b \cdot x_2^b}$

ℓ = fraction of nearest neighbors in surface layer.

m = fraction of nearest neighbors in adjacent layer.

XBL 741-234

Fig. 5

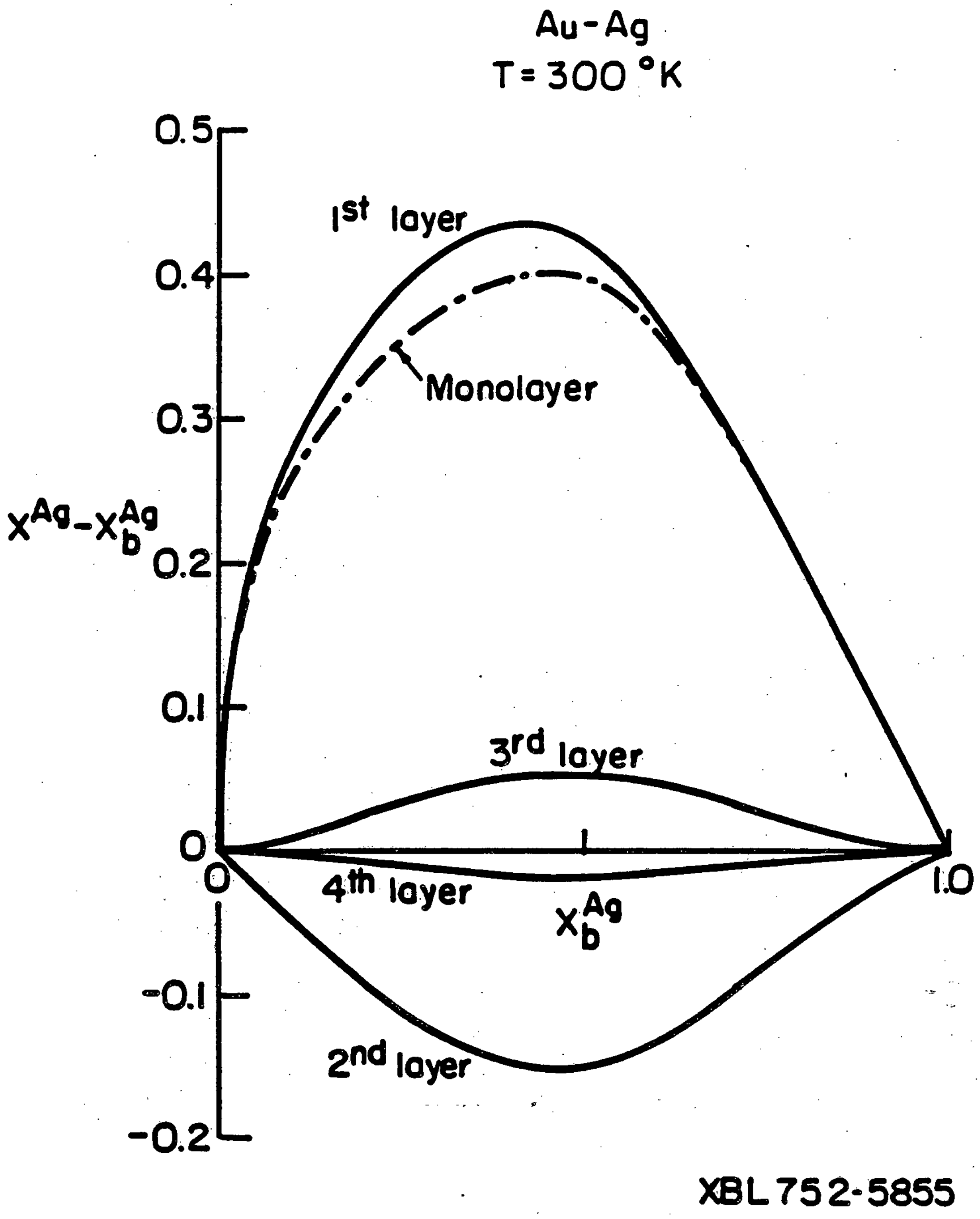

Au-Ag
T=300 °K
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
$X^{Ag}-X_b^{Ag}$
1st layer
Monolayer
3rd layer
4th layer
2nd layer
0
1.0
X_b^{Ag}
XBL 752-5855

Fig. 6

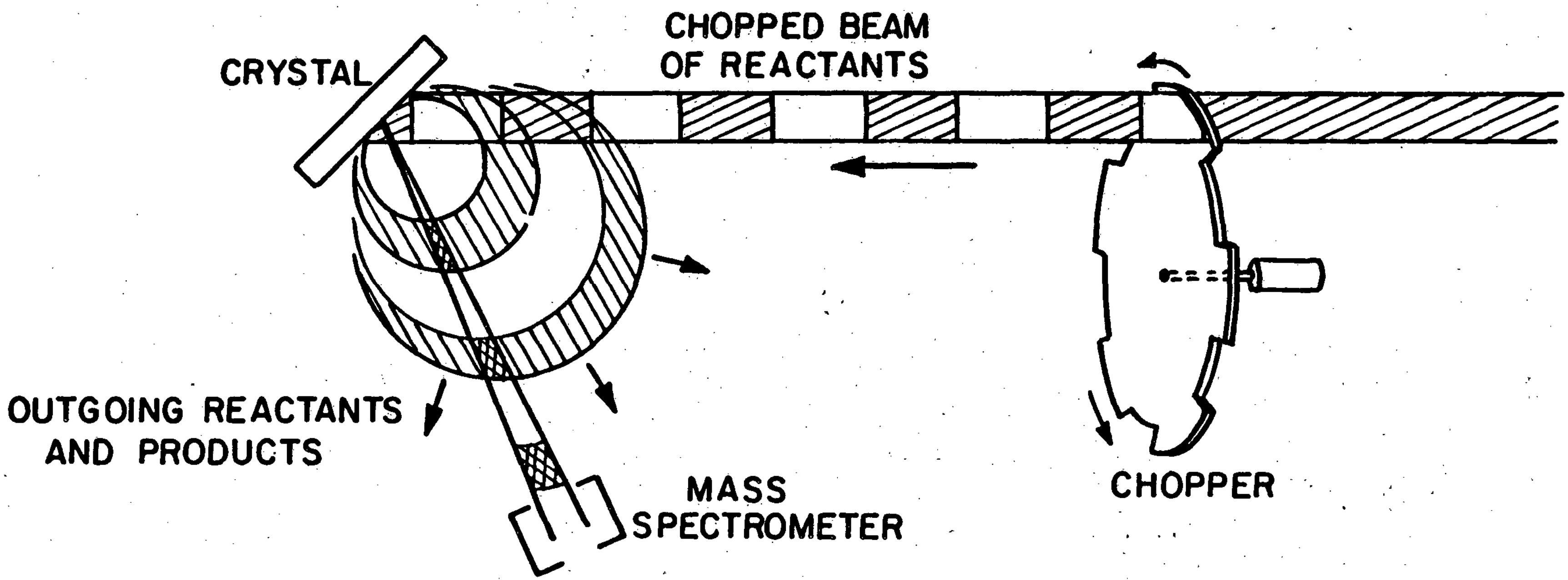
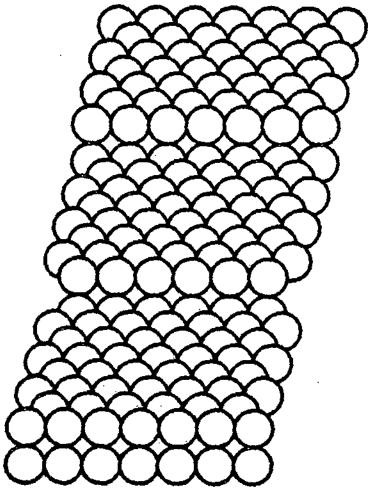
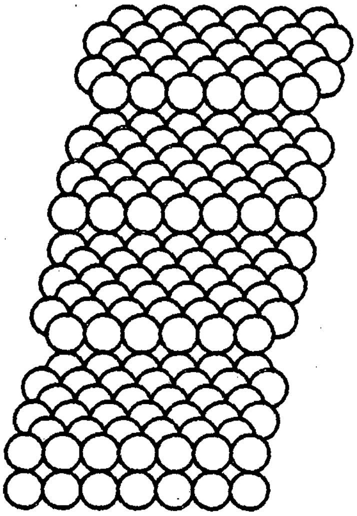


Fig. 7

XBL 772-5082



fcc (977)



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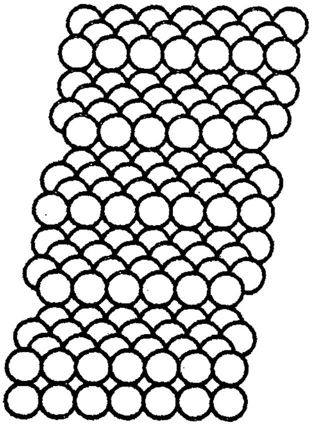

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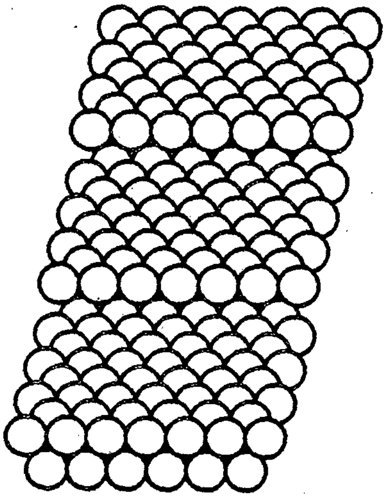

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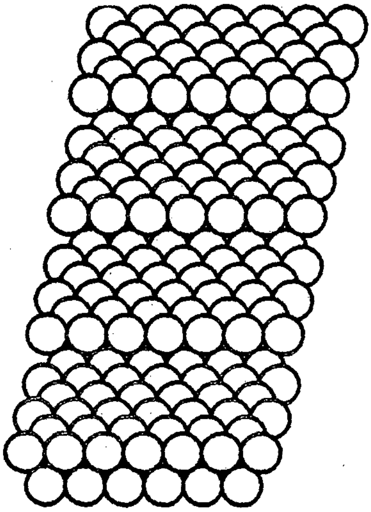

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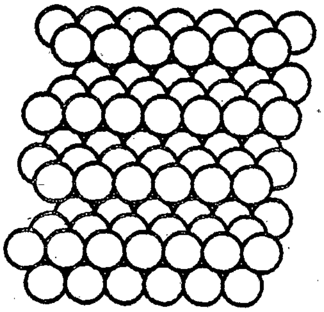
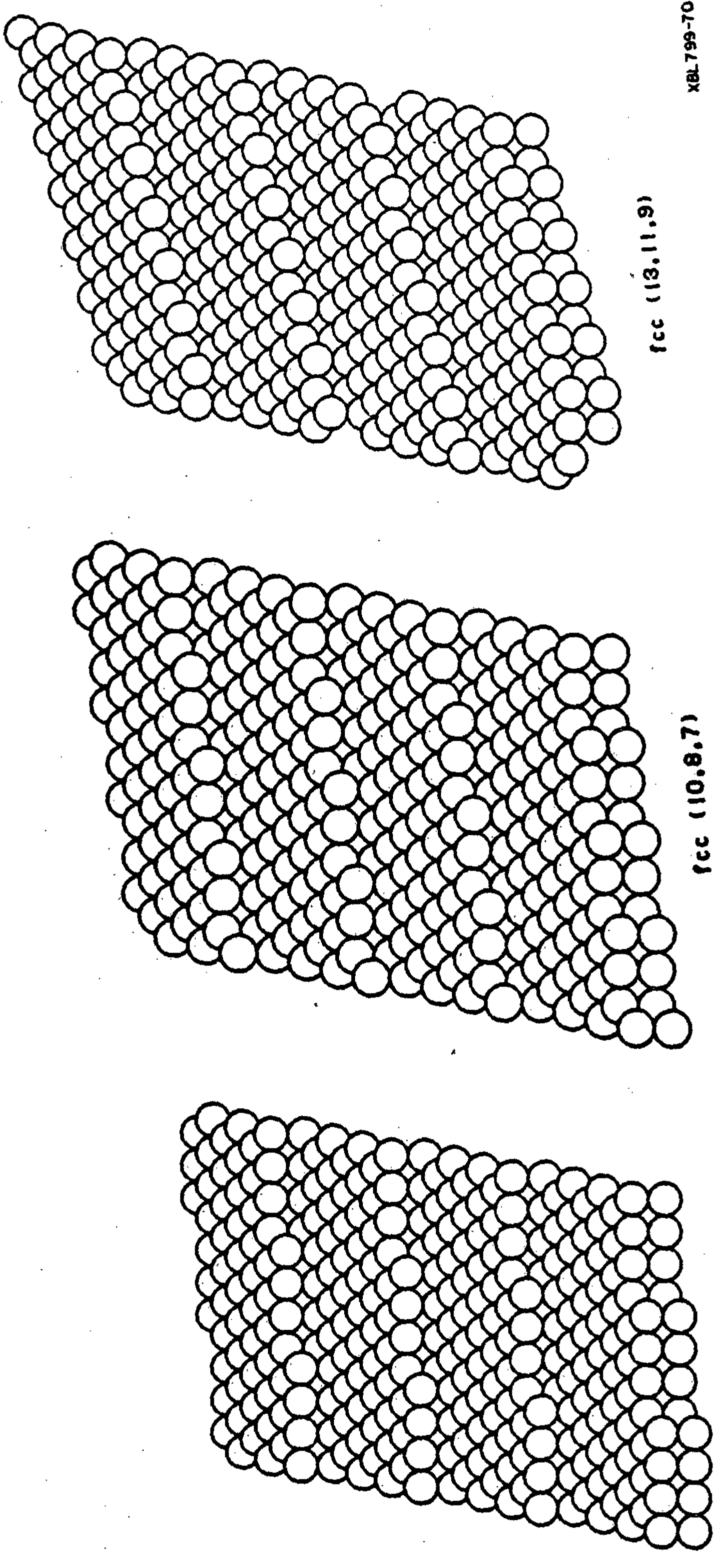


fcc (331)

XBL799-7019

Fig. 8



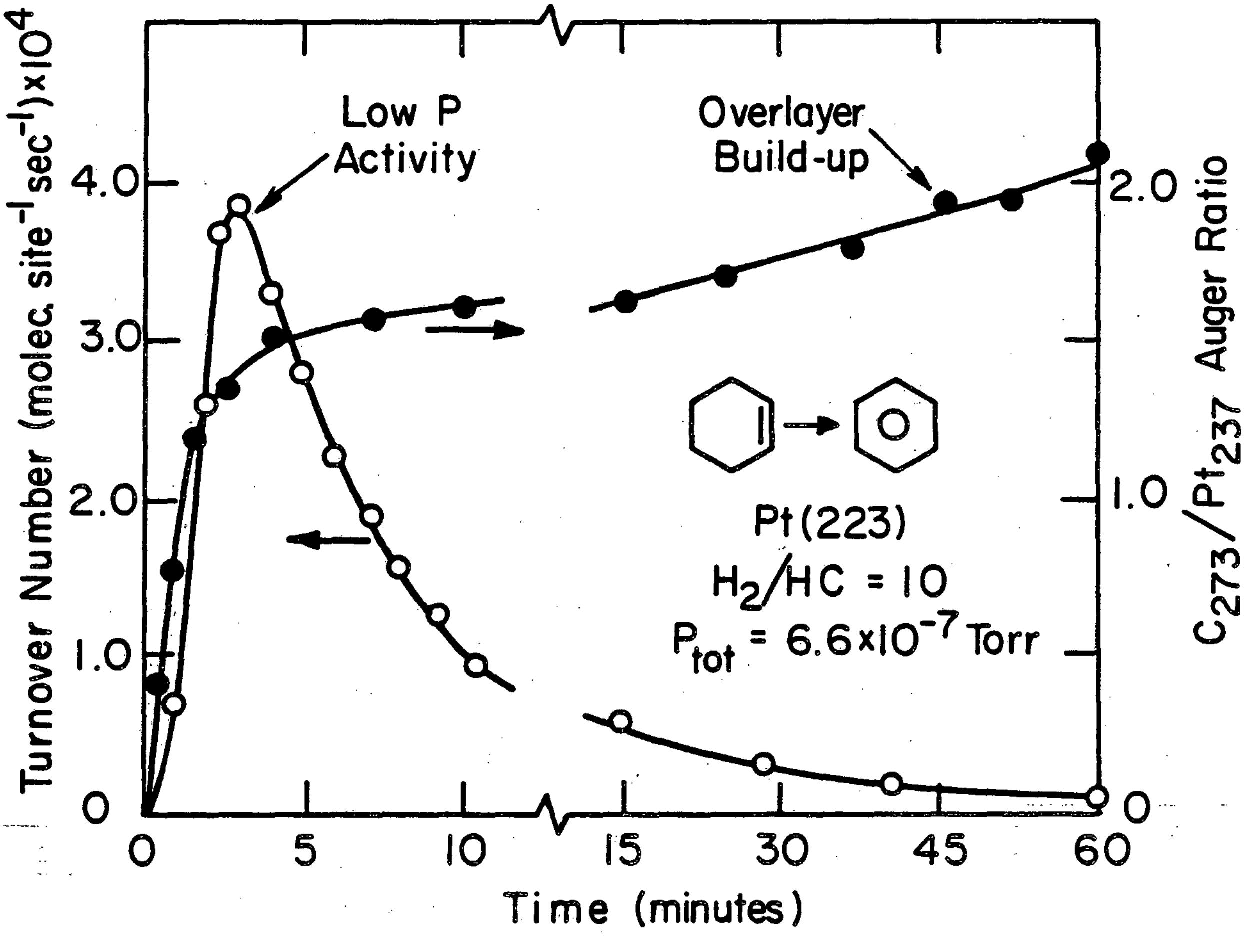
fcc (13,11,9)

fcc (10,8,7)

fcc (14,11,10)

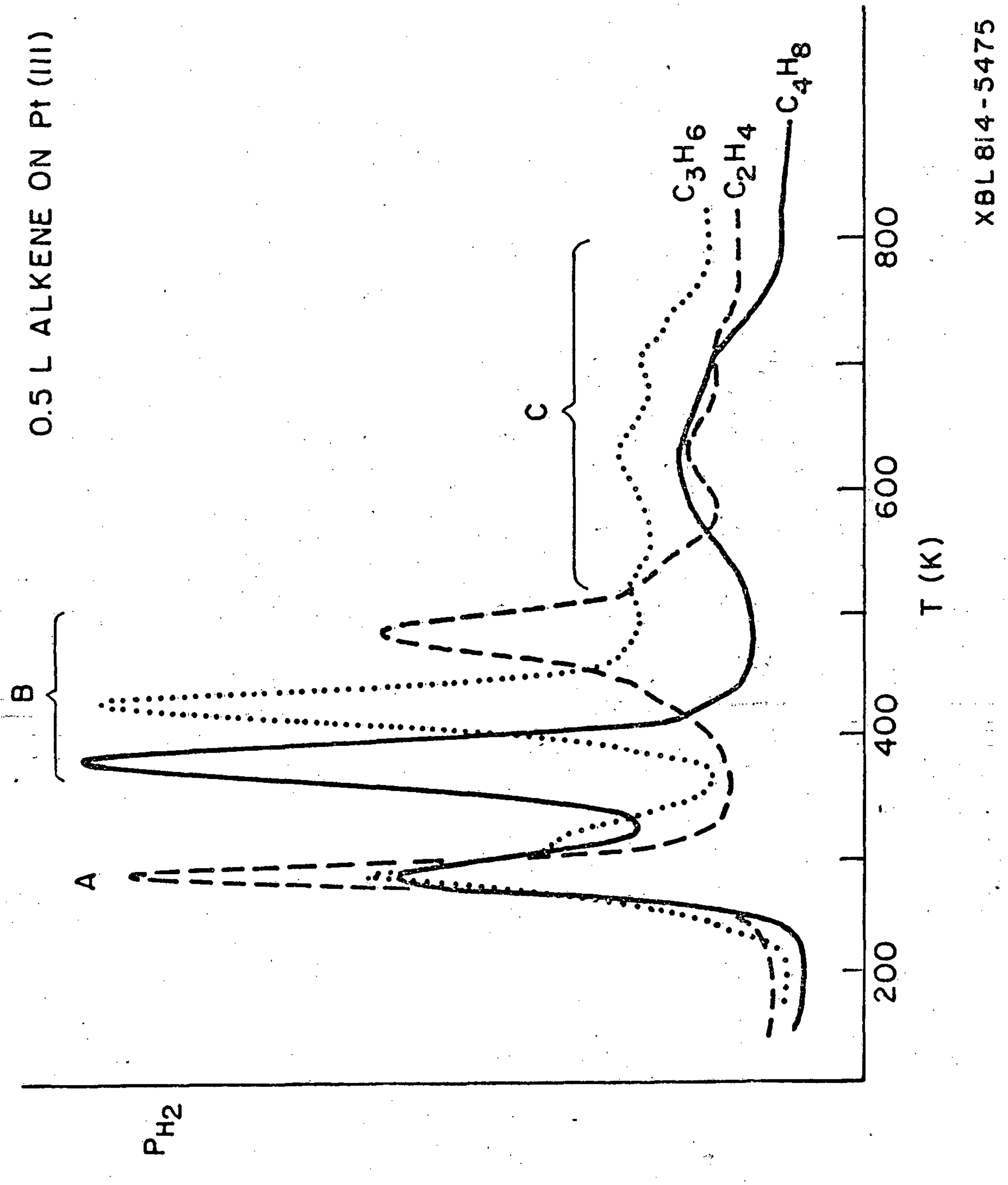
XBL 799-7018

Fig. 9



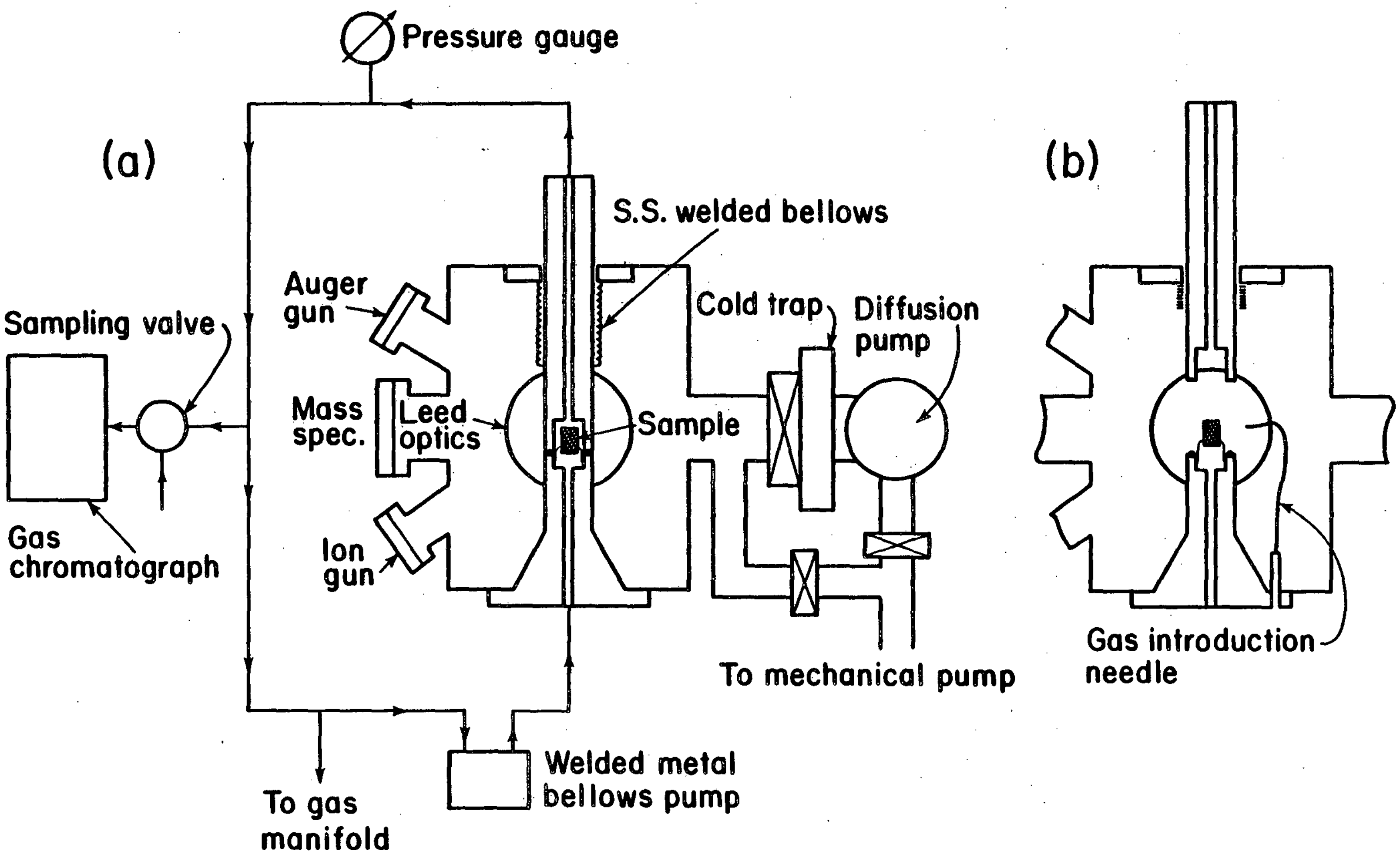
XBL 798-6750

Fig. 10



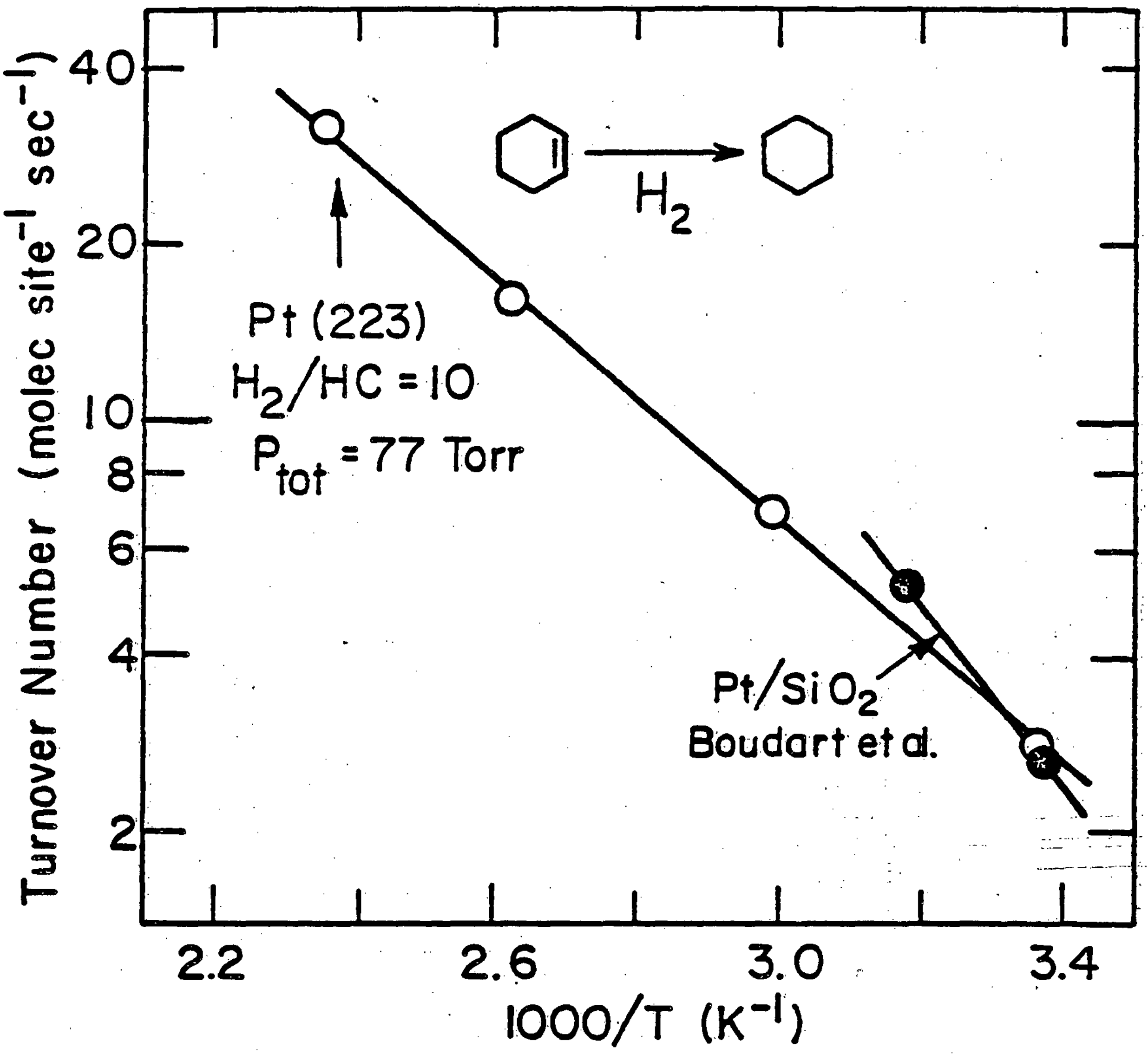
XBL 814-5475

Fig. 11



XBL 756-3160

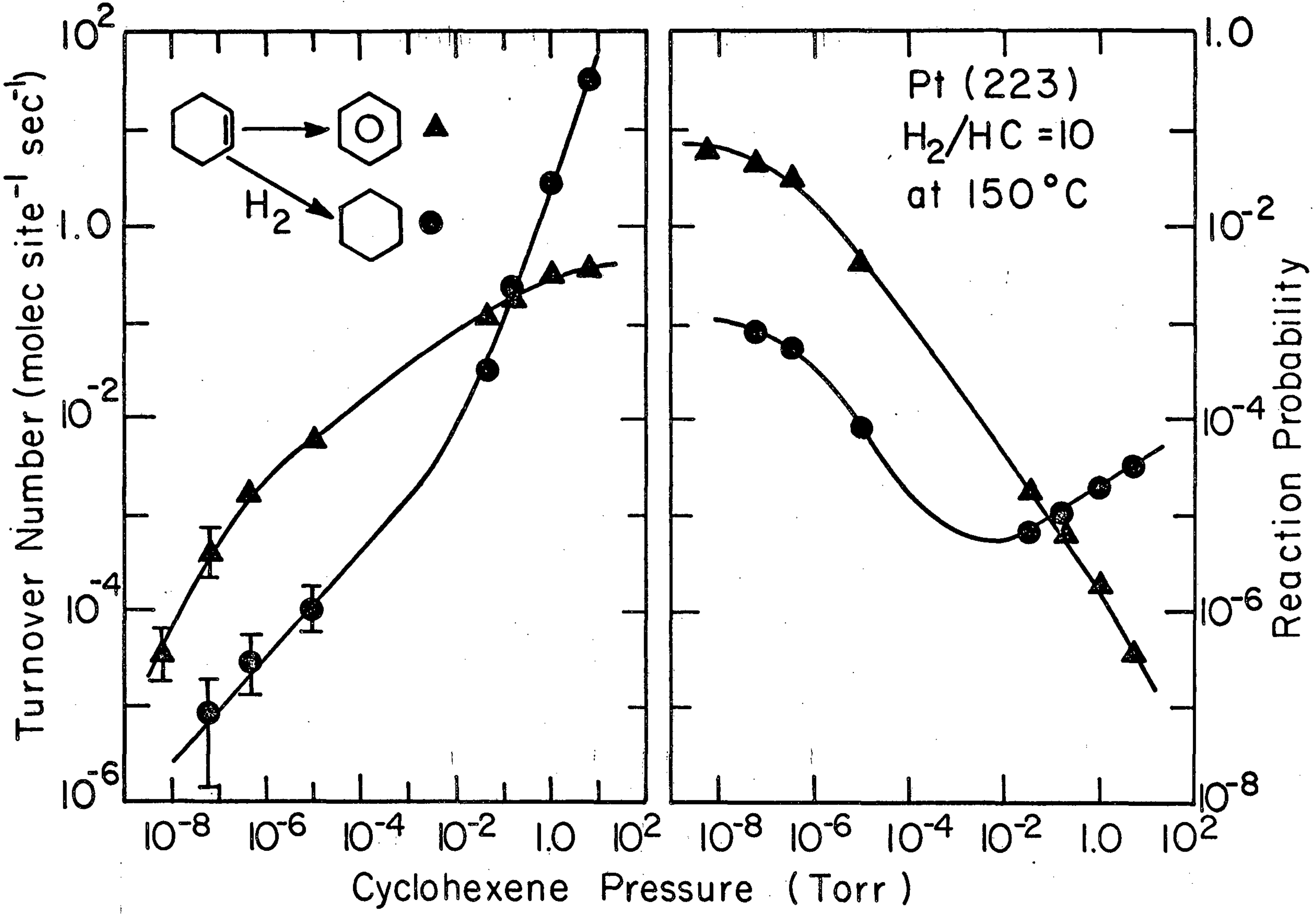
Fig. 12



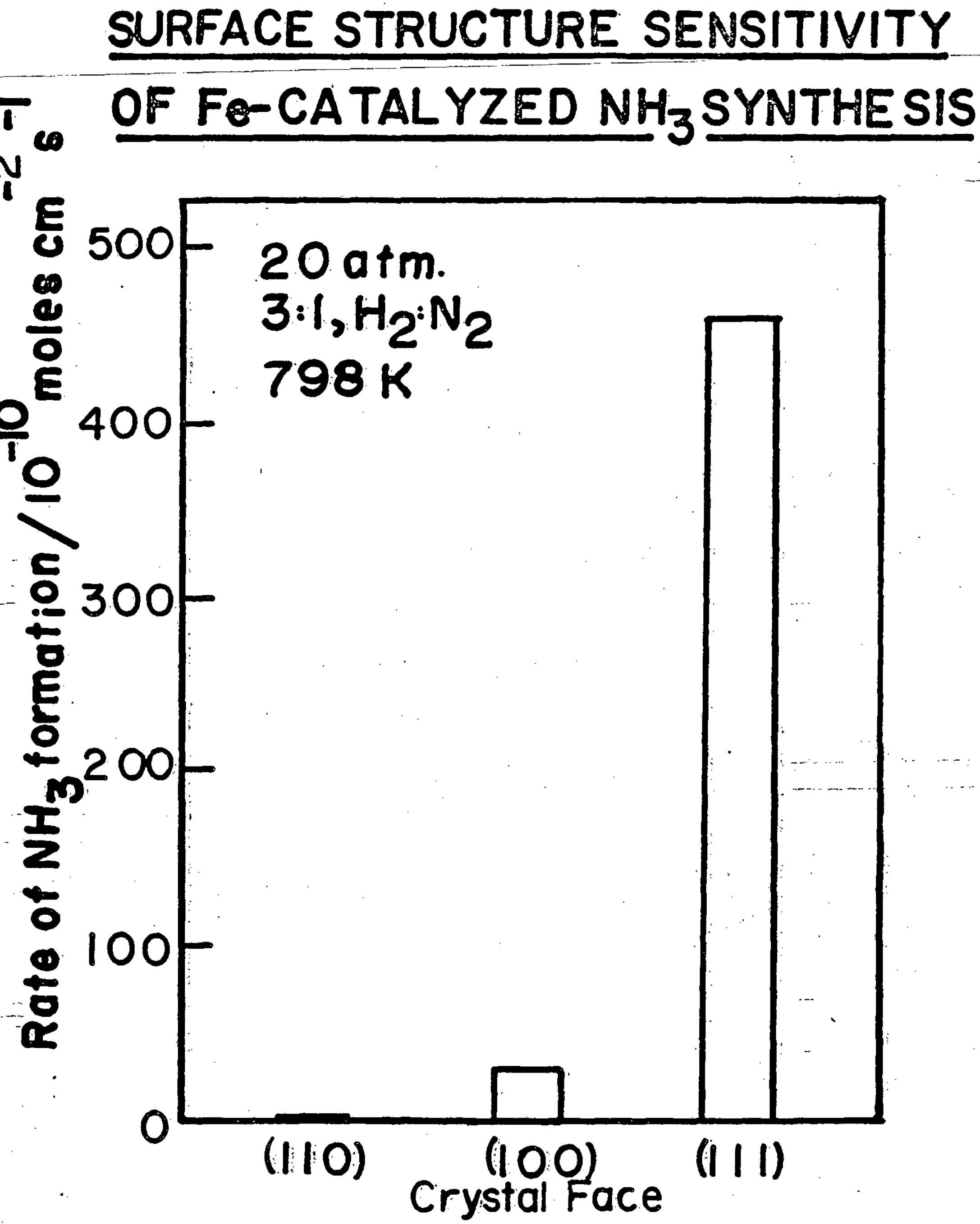
XBL797-6699

Fig. 13

Fig. 14



XBL 797-6698

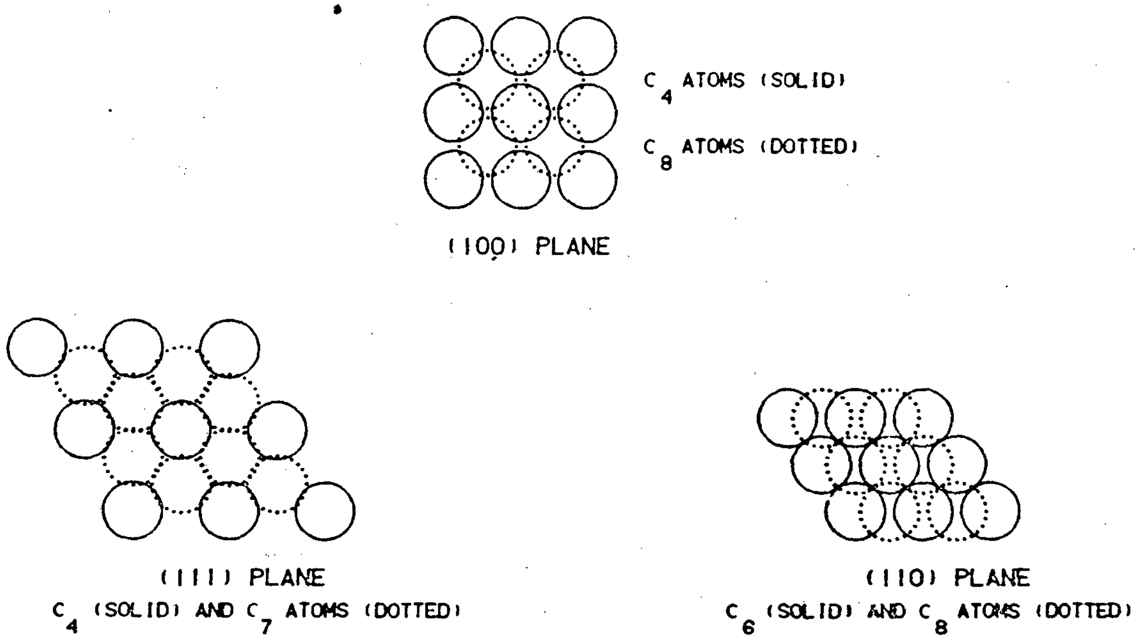


SURFACE STRUCTURE SENSITIVITY OF Fe-CATALYZED NH_3 SYNTHESIS

XBL 8110-7163

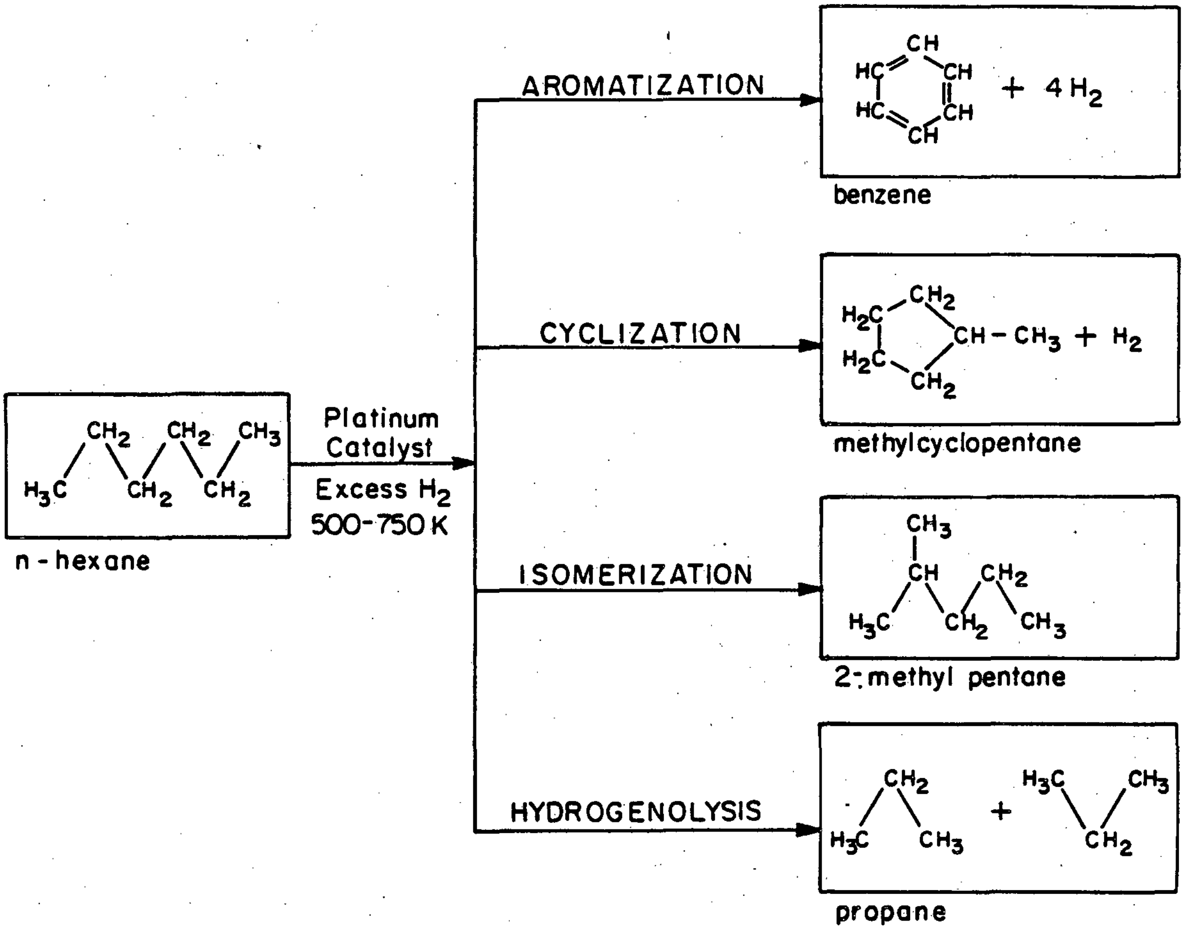
Fig. 15

LOW-INDEX PLANES OF IRON



XBL 819-1842

Fig. 16



XBL 822-5139

Fig. 17

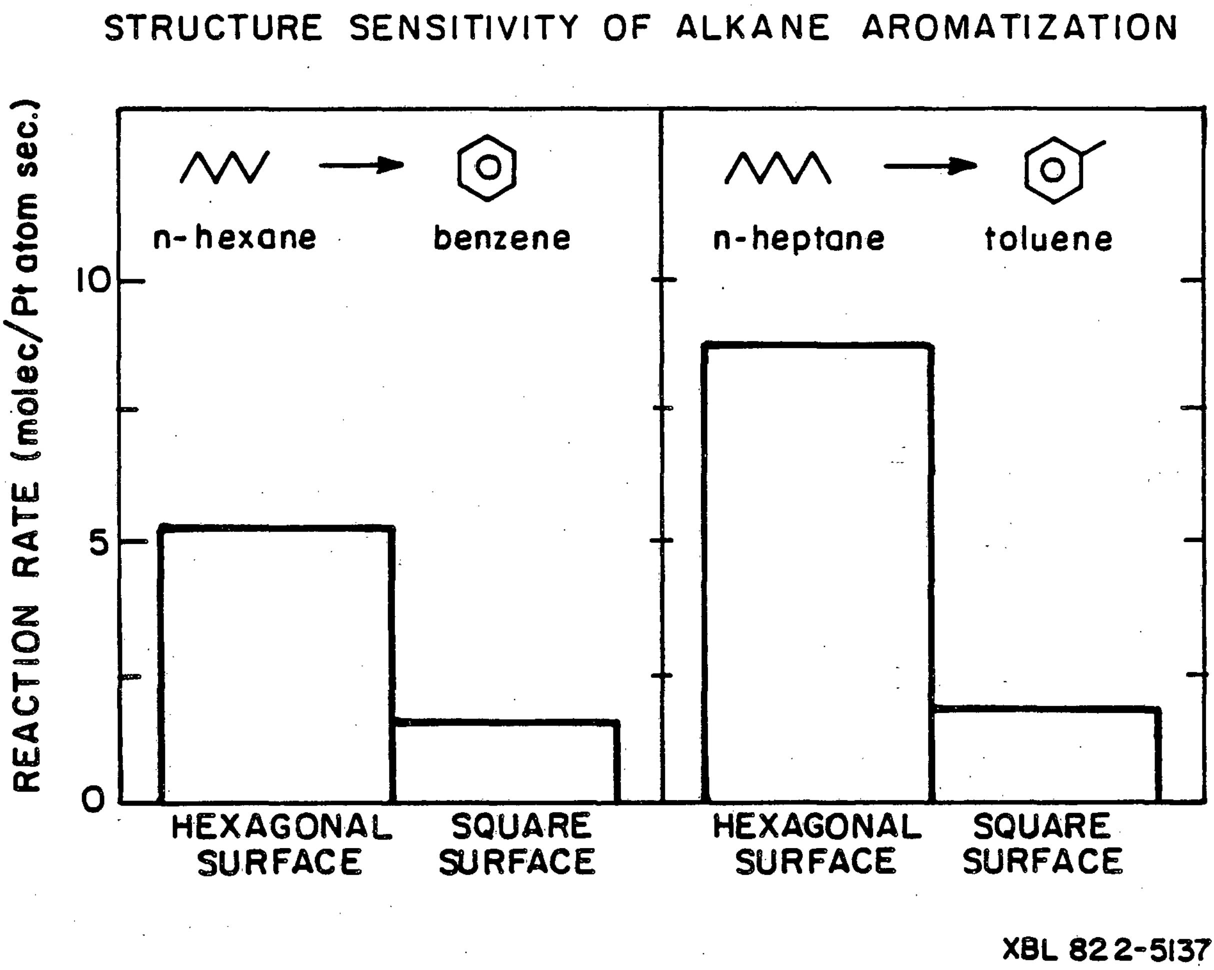
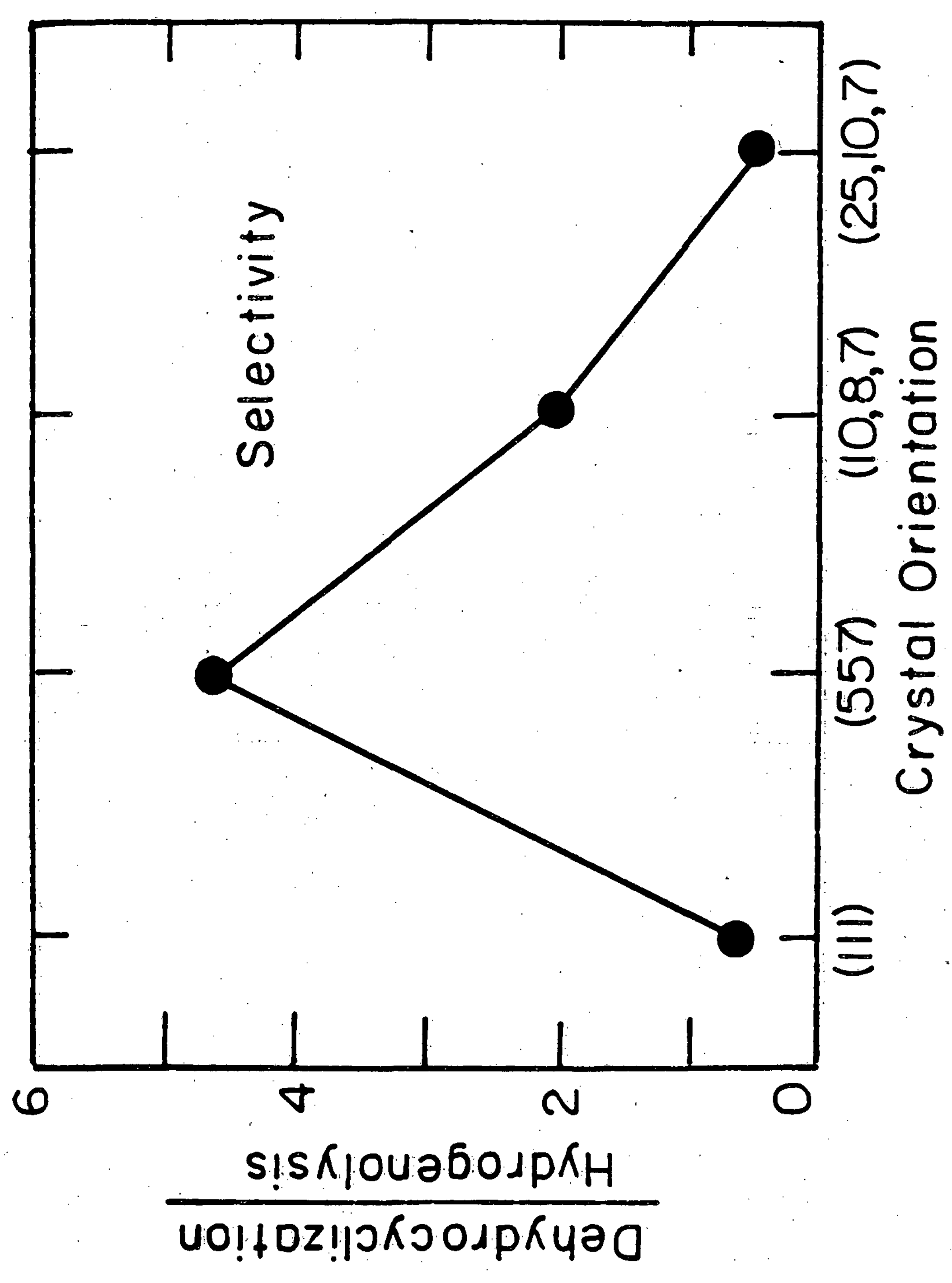

STRUCTURE SENSITIVITY OF ALKANE AROMATIZATION
REACTION RATE (molec/Pt atom sec.)
0
5
10
n-hexane
benzene
n-heptane
toluene
HEXAGONAL SURFACE
SQUARE SURFACE
HEXAGONAL SURFACE
SQUARE SURFACE
XBL 822-5137

Fig. 18



XBL 807 5520A

Fig. 19

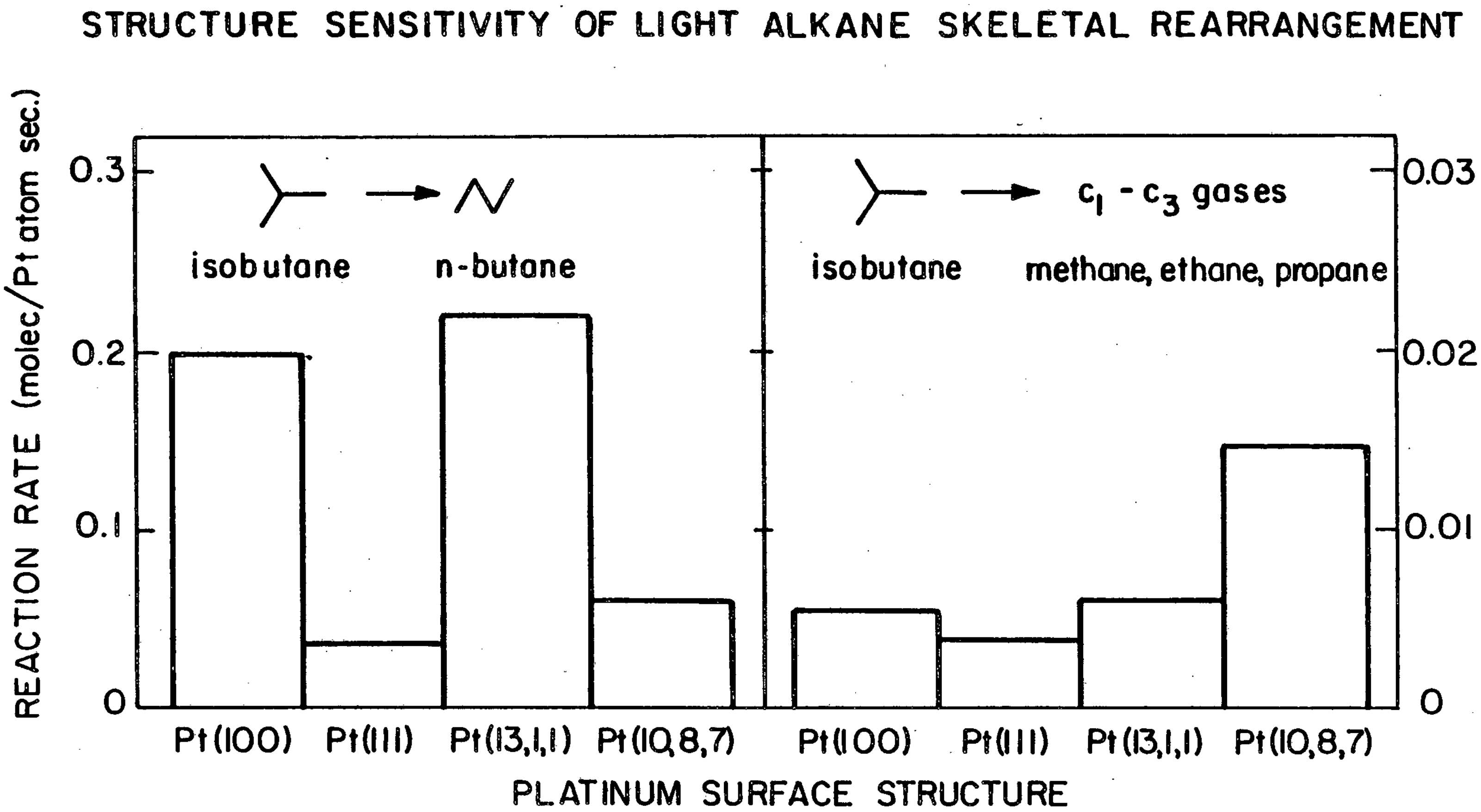


Fig. 20

XBL 822-5136

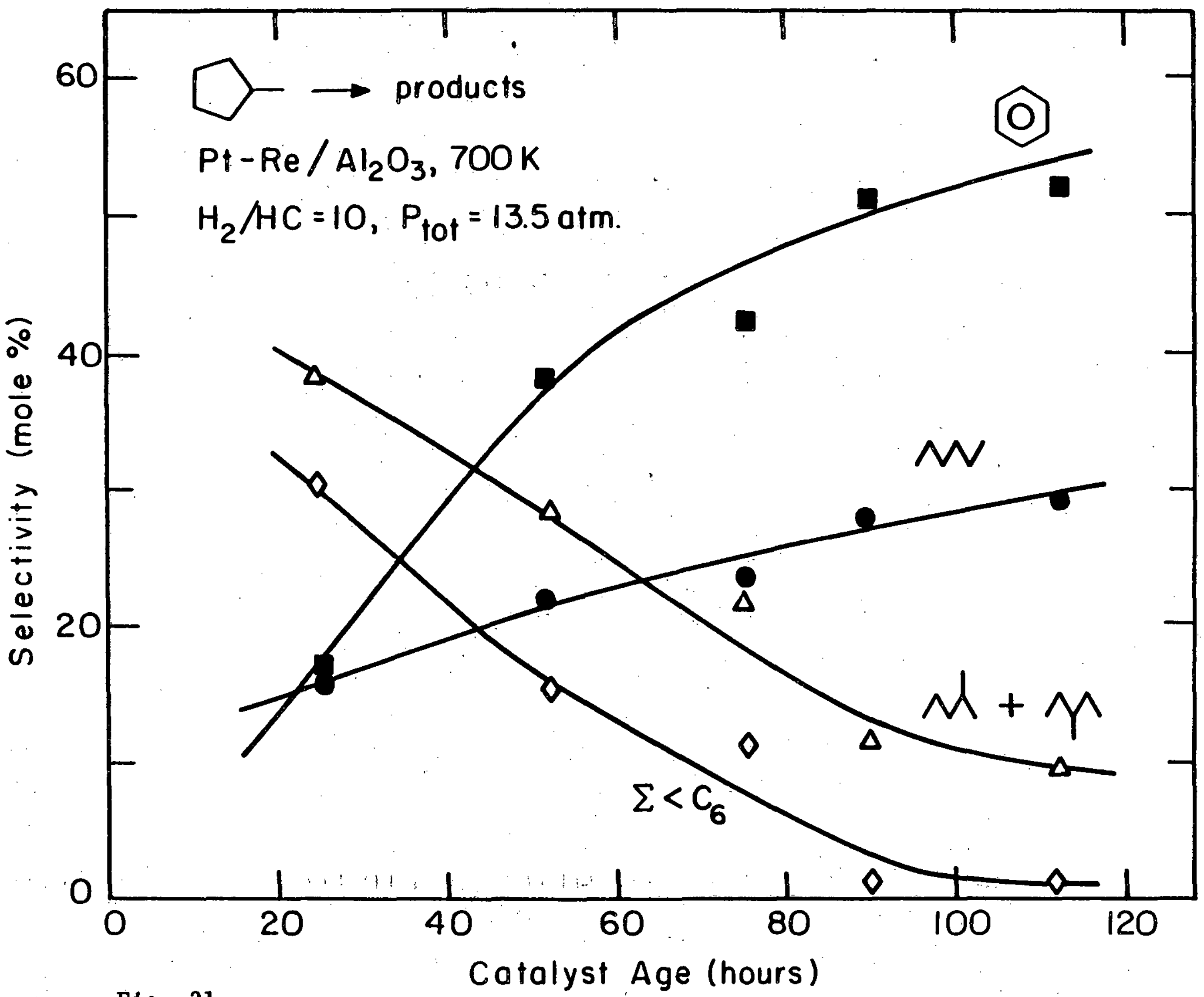


Fig. 21

XBL805-5218

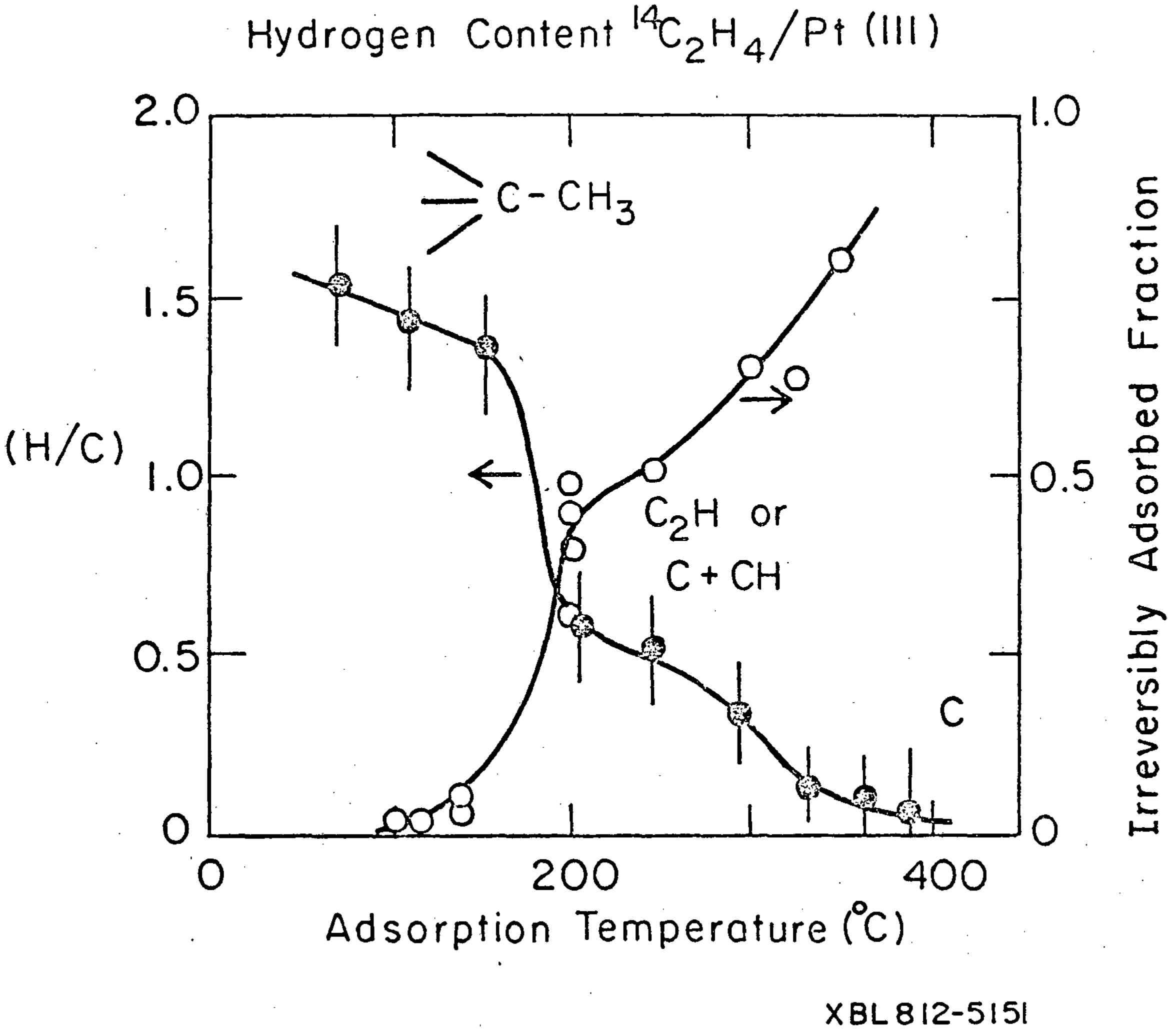
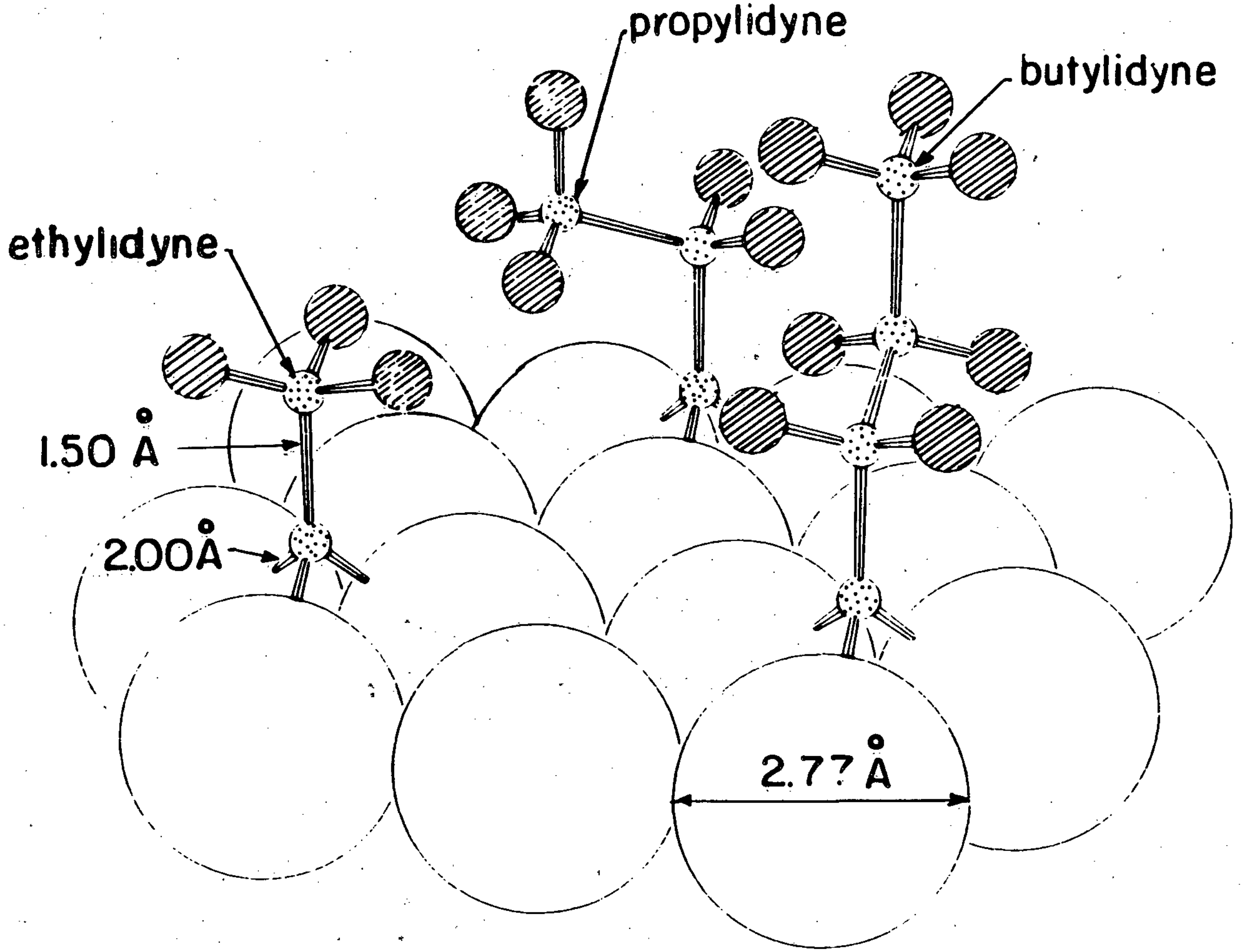

Hydrogen Content $^{14}C_2H_4$/Pt (111)
2.0
1.5
1.0
0.5
0
(H/C)
1.0
0.5
0
Irreversibly Adsorbed Fraction
C-CH_3
C_2H or
C + CH
C
0
200
400
Adsorption Temperature (°C)
XBL 812-5151

Fig. 22



Pt(111) + ethylidyne, propylidyne and butylidyne

Fig. 23

XBL 8110-6882

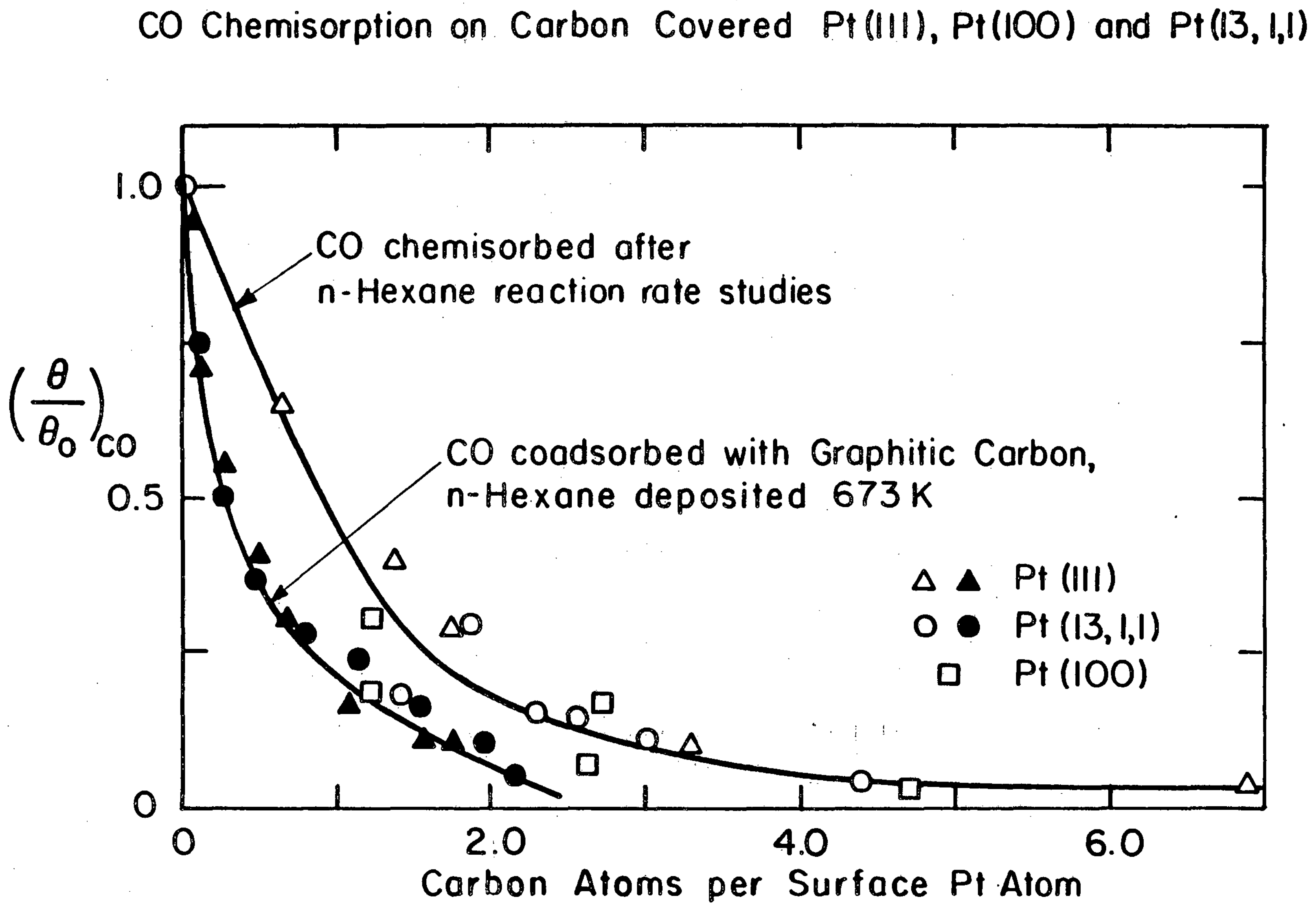
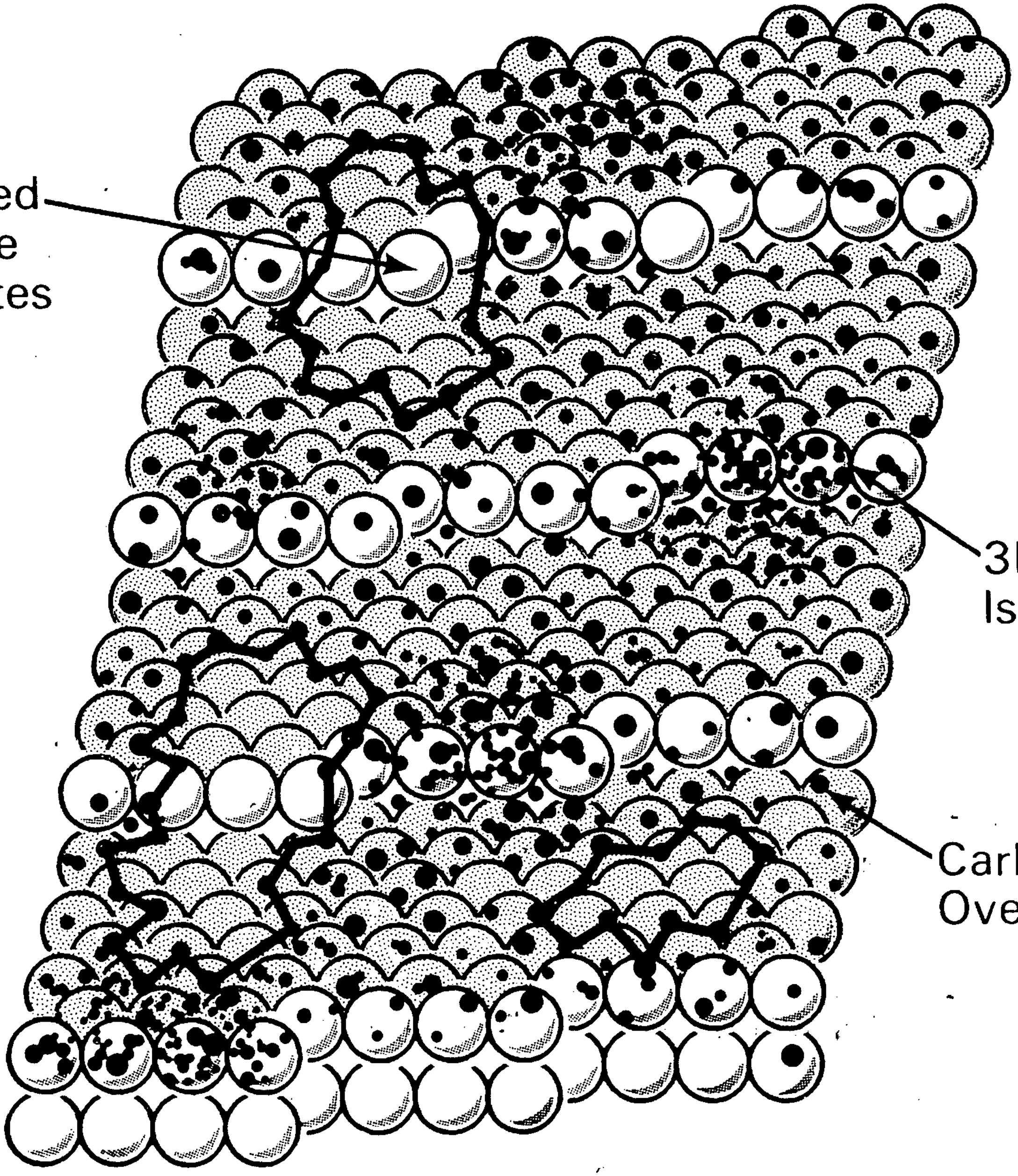


Fig. 24

XBL 816-5851

MODEL FOR THE WORKING PLATINUM CATALYST



CBB 816-5430

Fig. 25

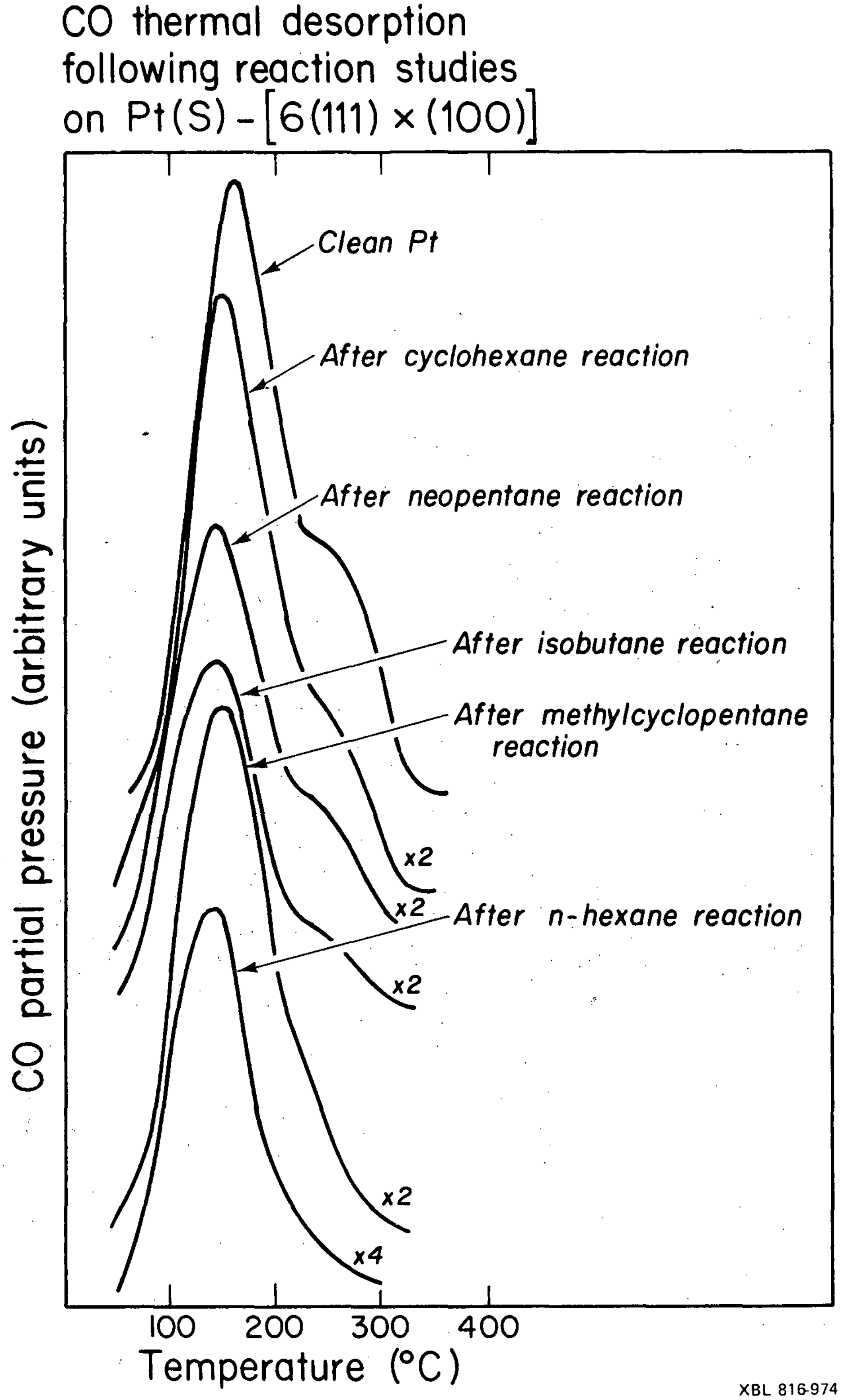

CO thermal desorption
following reaction studies
on Pt(S)-[6(111) × (100)]
Clean Pt
After cyclohexane reaction
After neopentane reaction
After isobutane reaction
After methylcyclopentane reaction
After n-hexane reaction
x2
x2
x2
x2
x4
CO partial pressure (arbitrary units)
100
200
300
400
Temperature (°C)
XBL 816-974

Fig. 26

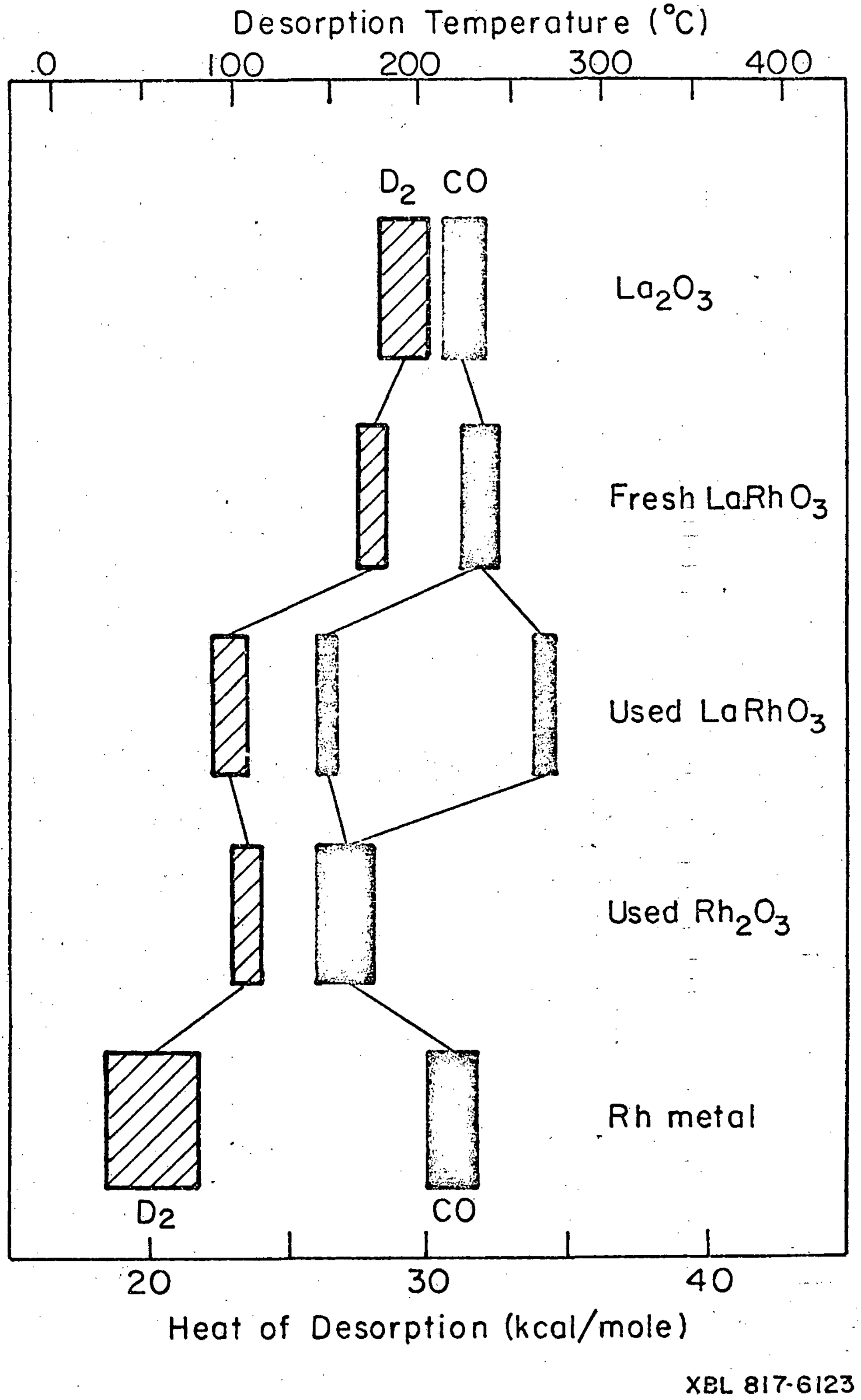
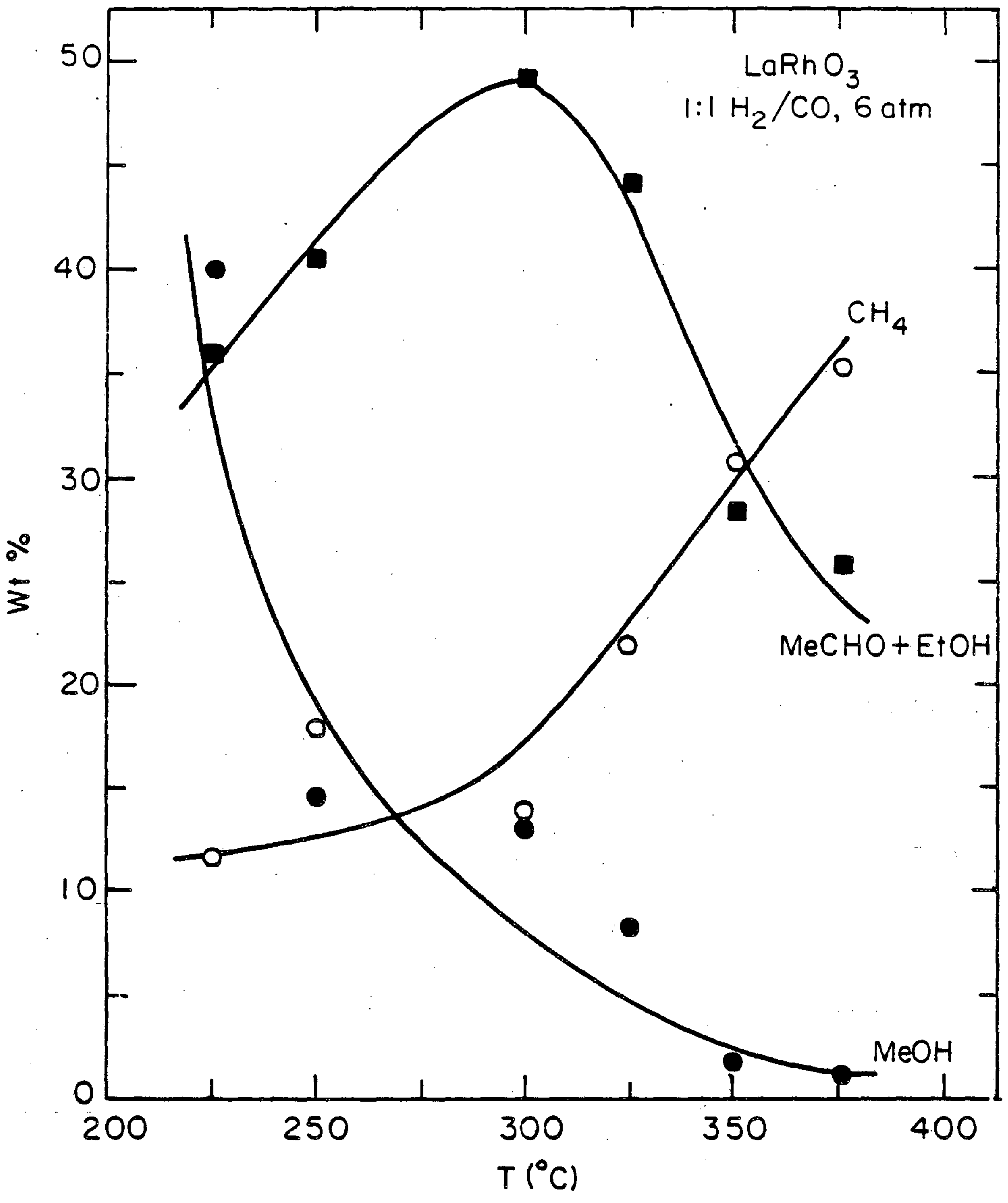
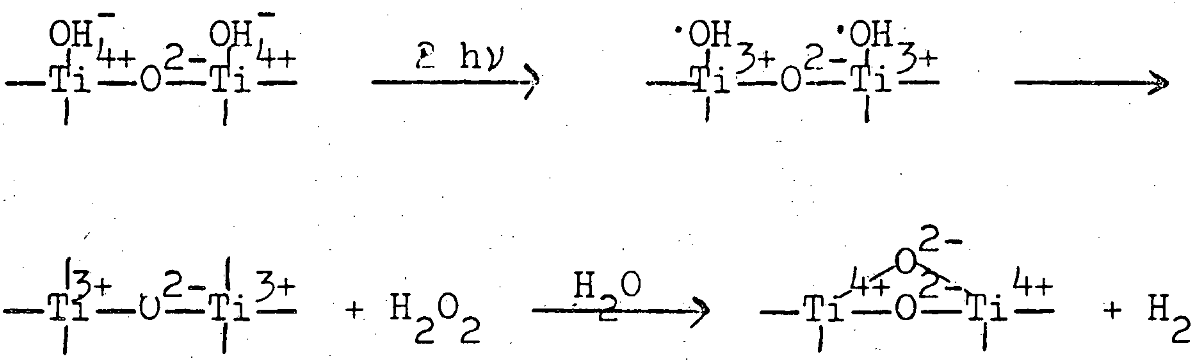

Desorption Temperature (°C)
0
100
200
300
400
D₂
CO
La₂O₃
Fresh LaRhO₃
Used LaRhO₃
Used Rh₂O₃
Rh metal
D₂
CO
20
30
40
Heat of Desorption (kcal/mole)
XBL 817-6123

Fig. 27



XBL 816-5965

Fig. 28



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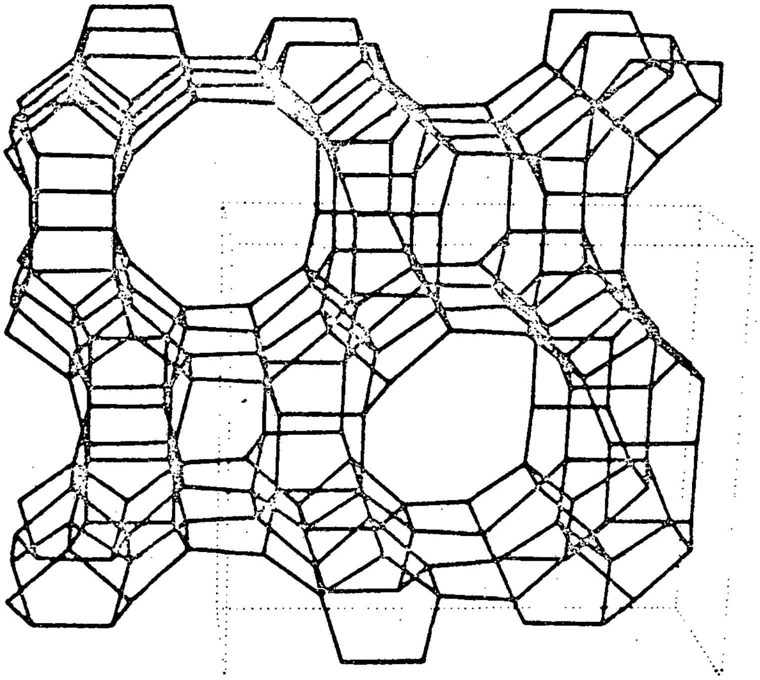
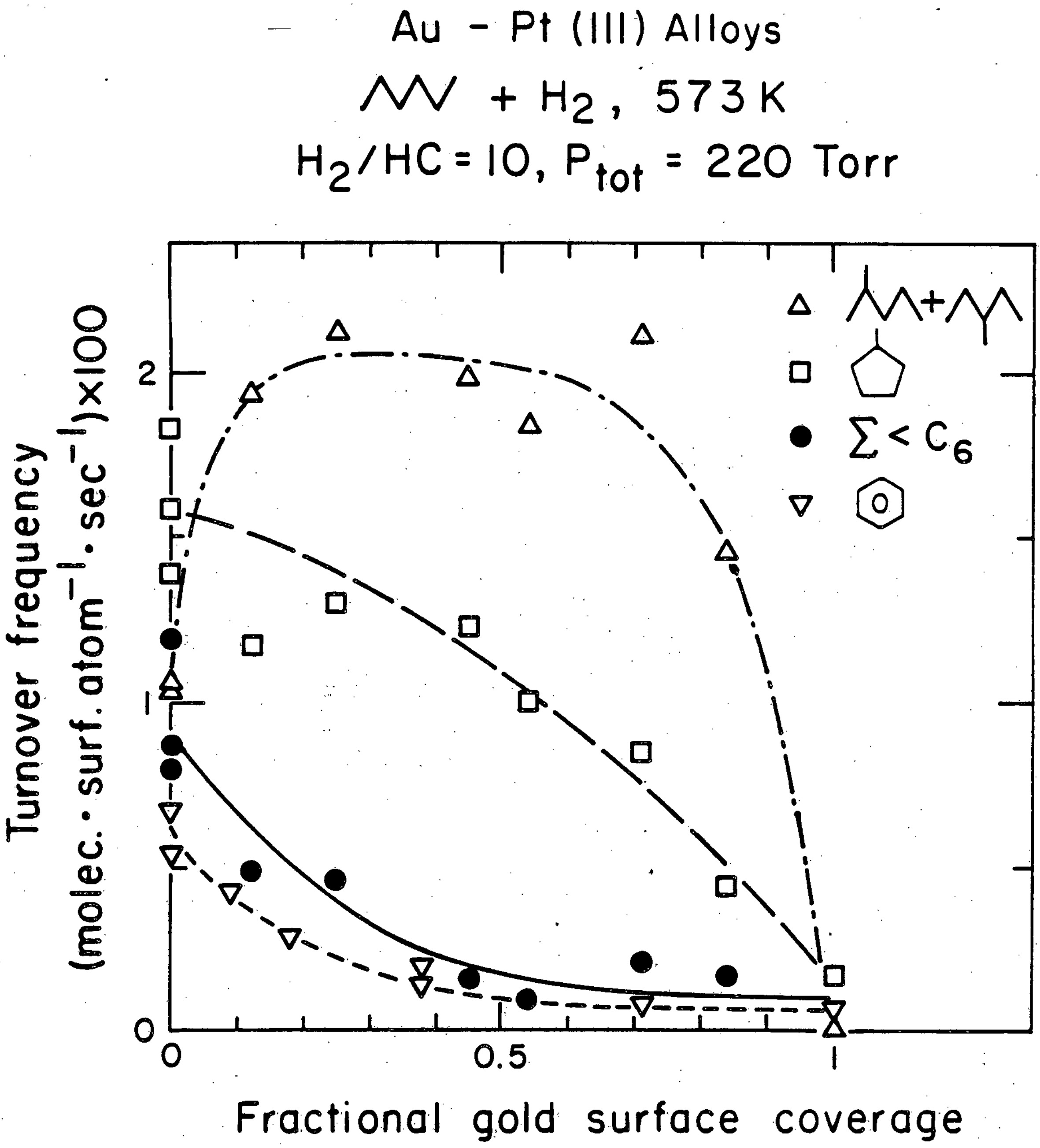
XBL 822-7816

Fig. 29



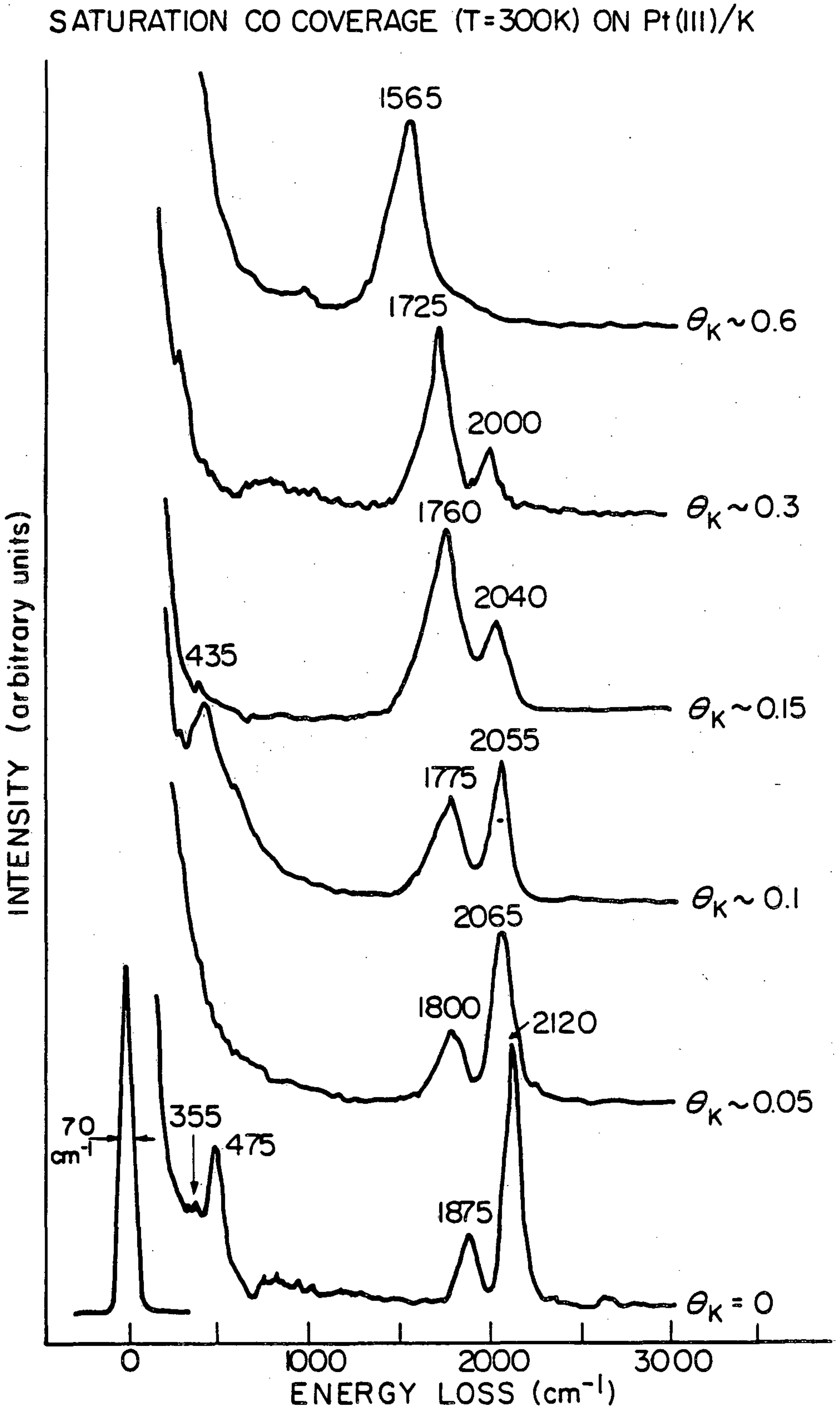
XBL 7911-12828

Fig. 30



XBL 819-2495

Fig. 31



XBL819-6628

Fig. 32

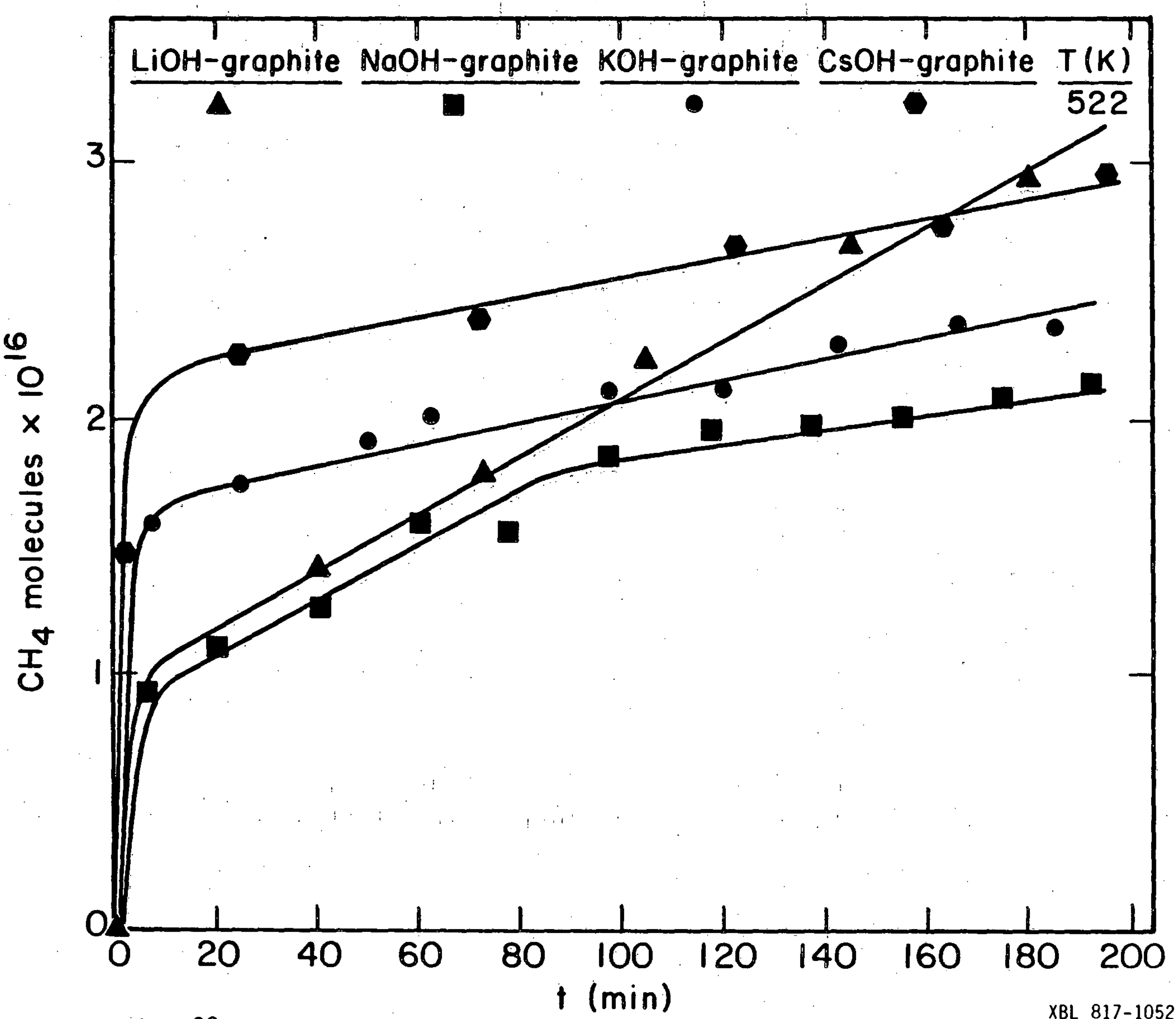


Fig. 33

XBL 817-10520

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