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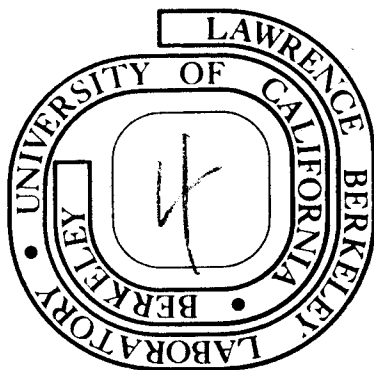
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CATALYSIS ON THE ATOMIC SCALE

(Emmett Award Lecture of 1977)

by

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I am deeply honored to receive this award, named after one of the great surface chemists of this century, Paul Emmett. I have the good fortune to know him personally and to have interacted with him on many occasions. He is a personal and scientific inspiration to me as well as to several generations of surface and catalytic scientists who can call themselves his students. His broad knowledge of so many fields of chemical sciences and his constant evaluation of the boundaries of surface processes imposed by thermodynamics have led to his successful elucidation of the kinetics and mechanism of important catalytic processes. These include the ammonia synthesis and the hydrogenation of carbon monoxide over promoted iron catalysts, just to mention two of the important studies from his laboratory. Paul Emmett has instilled the love and respect of research in surface chemistry and in heterogeneous catalysis into all his students and associates by demonstrating through his own work that major innovations in technology are the result of persistent and creative research in the laboratory.

Research in surface chemistry and in heterogeneous catalysis has been intertwined throughout his lifelong work and he pursued research in a period when techniques were not available to investigate surface properties on the atomic scale. Yet, by careful determinations of macro-parameters that included the surface area and the reaction rates, several atomic scale features that control the catalytic activity (the presence of active sites, the importance of surface diffusion or certain reaction intermediates) could be postulated.

I shall now attempt to demonstrate in this lecture how recent advances made by modern surface chemistry influence the science of heterogeneous catalysis.

Now, even though the field of heterogeneous catalysis has undergone many changes over the past 30 years, it is in the midst of yet another transition that has far-reaching consequences. This is due to the very rapid development of modern surface science that provided techniques to scrutinize the solid surface on the atomic scale. When applied properly, these techniques reveal the atomic structure, the electronic structure, the chemical composition, and the oxidation states of surface atoms.

Selected Techniques for Surface Studies on the Atomic Scale

Table 1 gives a partial list of the various surface diagnostic techniques that are employed most frequently. They can be employed to study small surface area ($\sim 1 \text{ cm}^2$) samples with the sensitivity of a fraction of a monolayer, and most of them are nondestructive probes of the surface properties. In addition, new methods have been developed

for studies of the dynamics of gas-surface interactions and the kinetics of surface reactions, using small area ($\sim 1 \text{ cm}^2$) well-characterized catalyst surfaces. One of them, the molecular beam-surface scattering experiment,¹ is schematically depicted in Fig. 1. A well-collimated beam of molecules of known velocity impinge on the surface at variable angles of incidence. The surface may be one face of a single crystal, with known atomic surface structure and composition, located in the center of an ultrahigh vacuum chamber to maintain surface cleanliness during the experiment. The exiting molecules, after scattering, are detected in a mass spectrometer that is rotatable, to detect the angular distribution by suitable chopping of the incident and of the exiting molecular beams. The surface residence time and the velocity are determined by time-of-flight analysis. The reaction probability upon a single collision with the surface is readily determined from the experimental data.

While low-pressure, single-scattering reaction conditions are of great value in deciphering the elementary surface processes, the experimental conditions are far removed from those utilized in practical surface reaction studies, where instead of reactant pressures of 10^{-8} to 10^{-5} Torr, pressures of 10^3 to 10^5 Torr are employed. The reaction mechanisms are expected to change significantly with pressure as the surface coverage as well as the surface residence times of adsorbates vary. In order to bridge the pressure gap, new instruments have been developed in my laboratory that enclose the small-area catalyst sample in a cup situated in the middle of an ultrahigh vacuum chamber. This is shown in Fig. 2. Once enclosed, the sample can be pressurized to 10^{-}

100 atm and the surface reactions can be carried out using a gas chromatograph as a detector.² The surface structure and composition can be characterized before and after the high pressure study without removing the sample from the controlled-atmosphere enclosure. The kinetics of high pressure catalyzed reactions that are obtained from well-characterized surfaces can be correlated with the kinetics of catalyzed reactions carried out on large-surface-area dispersed systems on the one hand, and with the kinetics of surface reactions studied at low pressure on the other. The unique application of the low pressure-high pressure apparatus is demonstrated in Fig. 3a and 3b, where the turnover number and the reaction probabilities for the dehydrogenation of cyclohexane to benzene are plotted, respectively, from studies over platinum crystal surfaces that range over 10 orders of magnitude reactant pressures. Figure 3a shows a steady increase in the rate of this reaction, and the straight-line pressure dependence could indicate that the reaction mechanism remains unchanged throughout the whole pressure range. The reaction probability, however, decreases rapidly with increasing pressure, as shown in Fig. 3b. Thus, the surface becomes a less efficient catalyst for this reaction at high pressures. Other important applications of this type of apparatus will be discussed later. A new application of thermal desorption to monitor the kinetics of elementary surface reactions has been pioneered by Madix.³ This method has been used to determine the kinetics of formic acid decomposition that depends on the surface structure and composition of nickel and to infer the nature of surface intermediates from the results.

Our Approach to Studies of Heterogeneous Catalysis and the Findings of Research on the Atomic Scale.

We utilize all available and appropriate surface diagnostic techniques to characterize the electronic, atomic, and defect structures of heterogeneous catalysts on the atomic scale and to determine the surface composition and oxidation states of surface atoms. For this purpose we have used small-area, often single-crystal, surfaces that could be prepared with uniform structure and composition. Then we carry out catalytic reactions on these well-characterized surfaces and study the kinetic parameters of elementary surface reactions, the rates of macroscopic catalytic reactions and the product distribution at low and at high pressures.⁴ The surface structure or surface composition is systematically changed and the effects of these changes on the reactivity and selectivity are studied. In this way we have developed, for several transition metal catalyst systems, correlations between the surface structure and composition and the catalytic activity.

Having this impressive array of surface diagnostic techniques at our disposal that permit surface characterization by static and dynamic measurements on the atomic scale, one may reasonably ask what we have really learned about heterogeneous catalysis that was not known before the advent of these techniques. Below, I would like to review four important surface phenomena, all of them major ingredients of heterogeneous catalysis that have been placed on firmer foundation by the modern atomic scale studies. The experimental findings, in turn, point to new directions of catalyst developments that were, in the past, not contemplated.

I. The Catalyst Surface is Heterogeneous

Figure 4 shown, schematically, the surface depicting the various surface sites that are identified by experiments. There are atoms on terraces surrounded by the largest number of neighbors. Atoms in steps have fewer nearest neighbors and atoms at kink sites have even fewer. Kink, step, and terrace atoms on any real surface have large equilibrium concentrations. Point defects such as adatoms and vacancies are also present and are important participants in the atomic transport along the surface, although their equilibrium concentration is less than 1% of a monolayer even at the melting point.

There is a great deal of experimental evidence from studies of transition metal and oxide surfaces indicating that each type of surface site may have different chemistry. This is exhibited in the large differences in the heats of adsorption of molecules on the various sites⁵ and in their differing ability to break large binding energy chemical bonds. These effects will be demonstrated below. There are theories that have been proposed to explain these phenomena that involve large variation in the localized charge density distribution⁶ as a result of the structural differences (crystal field splitting) and the appearance of large surface dipoles due to the redistribution of the free electrons at these various sites in metals.⁷ Herein lies one of the important reasons for the diversity of surface chemistry. The macroscopic rate and product distribution obtained in a catalytic reaction is the sum over rates and products formed at each surface site. Not only does the preparation of the surface establish the relative concentrations of each

site and thus determine the chemistry, but it is very difficult to distinguish elementary chemical processes associated with each site from macroscopic studies of dispersed, high-surface-area catalyst systems.

In order to identify the chemical processes associated with each surface site, single-crystal surfaces are utilized. Crystals can be cut to expose a surface in which one type of surface site predominates.⁸ The three types of surfaces that are most readily distinguishable by their chemical activity are shown in Fig. 5. The atomic structure of a (111) crystal face of a face centered cubic solid that can be deduced from the low energy electron diffraction pattern is shown in Fig. 5a. Such a surface may exhibit macroscopic irregularities when seen by an optical or scanning electron microscope. On the atomic scale, however, there are large ordered domains, with most of the surface atoms occupying their sixfold equilibrium positions. By cutting crystals along planes of lower atomic density (higher Miller Index), crystal faces that exhibit ordered steps and kink structures, as shown in Fig. 5b and 5c, can be prepared.⁹ By changing the cutting angle, the terrace width and simultaneously the step density can be altered. Surfaces with step densities as high as 33% of the total number of surface sites can be prepared.

The heats of adsorption of several small molecules, H_2 , O_2 , and CO , that were obtained by using single-crystal and polycrystalline surfaces have been compiled recently and are shown in Figs. 6, 7 and 8. Unlike the smooth curves obtained for the polycrystalline surfaces that yield an "average" heat of adsorption, there are many heats of adsorption

for a given single-crystal surface and an even larger variation from crystal face to crystal face. Heats of adsorption for a given molecule that vary by more than 20 - 30 kcal for a given transition metal are fairly common. Thus, there is no such thing as a unique heat of adsorption value for a given adsorbate-surface system. The surface exhibits many binding sites with different concentrations and binding energies for various adsorbates.

Another striking confirmation of the importance of surface structure in chemical activity comes from molecular beam-surface scattering studies.¹⁰ A molecular beam containing a mixture of H_2 and D_2 is directed to a stepped surface of a platinum crystal. The reaction probability to form HD exhibits a marked dependence on the orientation of the steps with respect to the incident beam. This is shown in Fig. 9. As the angle of incidence varied by rotation of the crystal, the rate of HD production dropped by 50% under a wide variety of reaction conditions (Curve a). The reaction probability is the highest when the beam strikes the open edge of the step and the lowest when the bottom of the step is shadowed.¹⁰ When the H_2 - D_2 mixed beam is incident parallel to the steps at all angles of crystal rotation, the rate of HD production is independent of the angle of incidence (Curve b). These results and a simple calculation indicate that the area between the platinum step and the terrace is about seven times more active for the dissociative adsorption of the hydrogen molecules than the platinum terrace atoms.

Similar structure-sensitive C-H and C-C bond breaking processes have been reported for the catalytic dehydrogenation and hydrogenolysis

of cyclohexane and cyclohexene.¹¹ Atomic steps and kinks can be responsible for selective bond breaking of hydrocarbon molecules. Conversely, by blocking the active sites (kinks for example) the selectivity of the catalysts may be markedly altered.

2. Reconstruction of the Catalyst Surface Structure Under the Reaction Conditions

The atomic surface structure of the freshly prepared catalyst is drastically changed under the reaction conditions and may be changed again with the presence of hydrocarbons or upon cleaning in oxygen or heating in hydrogen. This was revealed during studies of 22 single-crystal surfaces of platinum that were studied in ultrahigh vacuum when clean and in the presence of a monolayer of chemisorbed oxygen or carbon by low energy electron diffraction.⁹ Most crystal surfaces restructure as the surface composition is changed. Some of the surface structures that are stable in ultrahigh vacuum and in the presence of oxygen reconstruct in the presence of carbon, while others are stable when clean and when carbon covered but restructure when covered with oxygen. The type of changes of surface structure that occur most commonly are depicted schematically in Fig. 10. A surface that exhibits the one-atom-height, step-terrace configuration reconstructs into a multiple-height step structure with wider terraces as the surface composition is changed. Other surfaces develop a "hill and valley" configuration, consisting of large facet planes detectable by low energy electron diffraction. Interestingly, most of these restructuring processes are reversible. Once the adsorbate, oxygen or carbon, is removed, the surface returns to its original clean surface structure.

There are a few stable surfaces that do not restructure at all under any conditions of the experiments.⁹ Besides the low Miller Index surfaces (111), (001), and (011), these are the (112), (133), (122), and (012) orientation crystal faces. These crystal planes are characterized by a very high density of periodic steps one atom in height or a complete lack of steps. Because of their structural stability it is expected that they play important roles in the catalytic chemistry of transition metal surfaces.

Restructuring in the presence of adsorbates serves as a mechanism for redispersion. Chlorine is a known adsorbate that aids redispersion of transition metal catalyst particles. The structural changes that must accompany redispersion are described in detail elsewhere. Poisoning of catalytic activity is often due to the reconstruction of the active catalyst structure upon adsorption of impurities. Sulfur is known to cause gross restructuring of metal surfaces.¹²

There is another type of reconstruction that has been uncovered by modern surface science studies. The surface of most semiconductors and some of the metals exhibit structures with unit cells that are very different from the projection of the bulk x-ray unit cell to that crystal plane.¹³ The unusual structure of the clean surface is generally due to the periodic buckling of the surface as atoms in the topmost layer seek new equilibrium positions. The driving force for this type of reconstruction is the optimization of bonding among the surface atoms that are placed in very anisotropic environments compared to the location of atoms in the bulk. Many of these rearrangements are removed in the presence of a monolayer of adsorbates that provides a more bulk-like

environment for the surface atoms. The importance of this type of surface reconstruction in heterogeneous catalysis is yet to be studied and assessed.

3. The Catalyst Surface is Covered with a Near-Monolayer Deposit Under Most Reaction Conditions

Whether the catalyst is used in reducing or under oxidizing conditions, the active surface is covered with a monolayer or near monolayer deposit.^{4, 11} During hydrocarbon reactions this is a "carbonaceous" deposit, while it is an oxide during oxidation. The nature of this carbon-containing deposit has been subjected to experimental scrutiny by surface crystallography and by high resolution electron energy loss spectroscopy, as well as by recent reaction studies on transition metal surface. A carbene-like metal-carbon bonding was uncovered by low energy electron diffraction studies of C_2H_4 and C_2H_2 adsorbed on platinum surfaces.¹⁴ These molecules form ordered surface structures on the Pt(111) surface. Intensity analysis of the diffraction beams and the electron energy loss spectrum at various surface temperatures revealed that the nature of their bonding changes markedly with increasing temperature. Above 75°C the molecules assume a stable surface structure that is depicted in Fig. 11. This is the ethylidene molecule with the C-C internuclear axis perpendicular to the platinum surface. The carbon atom closer to the metal is bonded to three platinum atoms at a Pt-C bond distance of 2 Å. This short metal-carbon bond is characteristic of carbene-like molecules that exhibit unique chemical activity in many displacement reactions. The C-C bond is single bond (1.5 Å) in character

and is perpendicular to the surface plane. This structure resembles the structure of several trinuclear metal-acetylene complexes.

In order to place the carbon atoms of such symmetric molecules as C_2H_2 or C_2H_4 into asymmetric positions on the surface as shown in Fig. 11, a very strong metal-carbon bond is needed. The carbene-like Pt-C bond can be estimated to be stronger than 68 kcal from thermodynamic arguments.¹⁴ However, on platinum the Pt-C bond is not strong enough to cause breaking of the C-C bond under our experimental circumstances (although this is likely to happen at or above 400°C, as a precursor to graphitization in the carbon layer).

There is evidence from ultraviolet photoelectron spectroscopy studies that C_2H_4 breaks its C-C bond on iron surfaces at 25°C and CH_2 units remain on the surface.¹⁵ The presence of a chemically active form of carbon is also reported¹⁶ on nickel surfaces that form as a result of the disproportionation of carbon monoxide in the temperature range of 200°-400°C. This active form of carbon, that may well form carbene-like bonds similar to the bonding of carbon on platinum, yields methane by direct hydrogenation. This appears to be the predominant mechanism of methane formation over nickel during the hydrogenation of CO.

The "active" surface carbon with its carbene-like bonding appears to play an important role during hydrocarbon catalysis on transition metal surface. It is not clear whether the surface reaction takes place over the "active" carbon-covered surface that plays only the role of the catalyst or whether the active carbon builds into the reaction products and is being constantly regenerated from the reactant. Isotope

exchange studies will be of help in elucidating the nature of participation of the active carbon deposit in heterogeneous catalysis.

The changes of bonding of acetylene with small variations of temperature and the sequential bond breaking of the molecules with increasing temperature demonstrate one of the most important properties of the surface chemical bond: its temperature dependence. The behavior of CO adsorbed on nickel may be used to describe this striking effect. CO adsorbs as a molecule onto Ni at 25°C. Although it may undergo several changes of chemical bonding with increasing temperature that are not well documented, it is known to dissociate at around 200°C. The active metal-carbon bond that forms participates in important chemical reactions, one of which (the hydrogenation reaction to methane) has been mentioned above. Near 400°C, or above, the active carbon graphitizes and the graphitic overlayer exhibits little or no chemical activity of any kind (it is resistant to hydrogenation for example).¹⁶

Investigation of the surface chemistry of the active carbon or other active deposits appears to be a rich new field of catalytic chemistry. It is likely that the exploration of the surface chemistry of the deposit will help to build a bridge between metal-organic and heterogeneous catalytic chemistry.

4. Additives or Promoters are Partly Responsible for the Surface Chemistry of the Catalytic System

When catalytic reactions are claimed to take place on platinum or iron surfaces, they actually take place on a complex catalyst system that frequently includes an oxide support as well as a "promoter" such

as potassium, chlorine, calcium, or manganese, etc. I would like to show two examples that clearly indicate the important roles these additives play in the catalytic chemistry. In fact, in several instances catalysis would not take place without the support of the "promoter."

a) The effect of oxygen on the hydrocarbon catalysis by Pt

We have found that small amounts of chemisorbed oxygen present on platinum surfaces in concentrations of 10-30% of a monolayer can markedly change the rate and the product distribution in hydrocarbon reactions.¹⁷ In Fig. 12, the turnover number for the dehydrogenation of cyclohexene is plotted as a function of the oxygen/platinum ratio. The surface composition was obtained by Auger electron spectroscopy and the rate studies were carried out at low pressures. The rate is increased by an order of magnitude at an oxygen surface concentration that corresponds to about 25% of a monolayer on the kinked Pt surface that was studied. The oxygen may be introduced by heating the platinum in oxygen before the reaction or by adding small amounts of oxygen to the reaction mixture. As soon as the platinum is oxidized, the catalytic activity is poisoned.¹⁷ Our studies indicate that the active oxygen species are not those of the oxide but must be chemisorbed oxygen.

In the presence of oxygen, the kinked platinum surface exhibits hydrogenation activity as well; this was never observed in the absence of oxygen.¹⁷ This is also shown in Fig. 12. Interestingly, the optimum activity for hydrogenation of cyclohexene to cyclohexane occurs at a somewhat different oxygen surface concentration than the optimum activity for dehydrogenation of cyclohexene to benzene. Similar large changes in

the rate of the catalytic reaction with changing surface concentrations of chemisorbed oxygen were found for the dehydrogenation of cyclohexane as well.

Table 2 summarizes the effects of oxygen on the reactivity of the (111) stepped and kinked surfaces of platinum. It is apparent that not only surface irregularities play important roles, but also oxygen surface concentrations are needed to control the activity and selectivity of platinum.¹⁷ Since hydrocarbon catalysis on platinum takes place in the presence of excess hydrogen, the reactants cannot possibly be the source of chemisorbed oxygen that is necessary for optimum activity. The support appears to be the only source of oxygen through its solid state chemical interaction with the transition metal. Ternary compounds involving transition metals and oxides of aluminum, silicon, magnesium, and calcium have been reported recently.¹⁸ The oxygen activity on the platinum surface can be secured by solid state reactions between the metal and the support during the catalyst preparation.

b) The effect of potassium during the hydrogenation of carbon monoxide on iron surfaces

When the hydrogenation of carbon monoxide is carried out on the clean Fe(111) crystal face or on polycrystalline iron foils, the reaction poisons rapidly, as shown in Fig. 13. The main product of the reaction is CH_4 at 6 atm, using a H_2/CO ratio of 3:1 at 300°C . A build-up of a carbon multilayer is the cause of the drastic reduction of the reaction rate.¹⁹ Similar poisoning occurs when the reaction is carried out in a mixture of CO_2 and H_2 , or when the surface is preoxidized by oxygen heat treatment. Although the oxidized iron surface has a much higher initial

methanation rate, the surface oxygen is rapidly substituted by carbon that forms a multilayer deposit leading to poisoning similar to that for the initially clean iron surface.¹⁹

The resistance to poisoning and the catalytic activity can be altered, however, by the addition of about 0.5-1.0 monolayer of potassium.²⁰ Potassium is vaporized onto the metal surface and its concentration is monitored by Auger electron spectroscopy. The effect of a near-monolayer of potassium on the catalytic activity of clean and oxidized iron surfaces is shown in Fig. 14. The clean iron is completely poisoned by the presence of potassium.²⁰ This is readily seen by comparing the methanation rate obtained for the clean iron that is included in the figure for reference. When the oxidized iron surface is coated with potassium, however, the catalytic activity and the resistance to poisoning is markedly improved.²⁰ The initial high rate of methanation may be maintained for days without any apparent deterioration of activity. It should be noted that the product distribution does not appear to be affected by the presence of potassium.

Additives clearly play significant roles in controlling the chemistry of catalytic reactions. There is an intimate interplay between bonding of the reaction intermediates on the catalyst and the promoter that shifts the equilibrium among the surface species. Additives may also stabilize unusual oxidation states for surface atoms that would otherwise be unstable under the reaction conditions in the reaction mixture. Promoters may also play a role in keeping the active surface sites clean by reacting with the stable reaction byproducts that would otherwise rapidly poison the catalytic reaction.

The surface chemistry of promoters is another exciting field of modern heterogeneous catalysis that will, no doubt, lead to a better understanding of how to build and stabilize selective new catalyst systems.

Directions for the Near Future

In the past, much of the research in heterogeneous catalysis was directed toward optimization of the working catalytic system. The physical-chemical characterization of the catalyst that include the surface and solid state chemistry of its preparation, atomic scale scrutiny of its structure and composition, and atomic scale studies of the role of additives and support interactions has not received the attention it deserves. Most of the improvement of the performance of existing catalyst systems will come, I believe, from the application of modern surface diagnostic techniques of surface science that characterize the catalyst on the atomic scale. Often model systems such as single-crystal surfaces are useful for catalyst studies, as I have hoped to demonstrate in this lecture. It is just as important to find out what is missing from a model system that impedes its reactivity as it is to characterize the active and complex catalytic system in order to understand the nature of its catalytic activity.

Once the active catalyst is characterized on the atomic scale, ways of improving its selectivity or optimizing its activity can be found. Recently, improvements of metal catalysts, by alloying, have been made and alloy catalysis appears to be one of the more promising areas that will lead to the synthesis of new catalyst systems.²¹

Experimental studies of the surface composition of regular solution and

complex phase diagram alloy systems yielded the thermodynamic guidelines necessary to predict the surface composition (which is likely to be very different from the alloy bulk composition). The existence of surface compounds with unique bonding and phase diagrams has been uncovered by studies of bimetallic clusters; that is, systems where all of the atoms are located on the surface.²² This area of catalytic chemistry holds great promise for the synthesis and preparation of new catalyst systems with unique surface chemistry.

Another area of research that may yield new synthetic catalytic systems is the study of monolayers of metals on oxides or on metals of other types and the investigation of monolayers of oxides on metals. The substrate is likely to exert a profound influence in the control of the electronic and atomic surface structure of the catalytically active monolayer, which in turn influences the surface chemistry. Changes in chemical properties of monolayers as the result of substrate interactions have not yet been systematically explored. These monolayer systems may have high enough surface area and interesting catalytic activity to be promising candidates for the synthesis of new heterogeneous catalysts.

Acknowledgement

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Table 1. Partial listing of techniques most frequently utilized presently for studies of surfaces in vacuum.

Technique		Atomic Process	Main Information	Sensitivity (monolayer)	Depth Sampled
LEED	Low-Energy Electron Diffraction	Elastic back-scattering of electrons in 10-200 eV range	Surface structure	$\sim 10^{-2}$ - 10^{-1}	1-7 layers
XPS	X-Ray Photoelectron Spectroscopy	Electron emission from atoms at the surface	Oxidation state, composition, electronic structure	$\sim 10^{-2}$ - 10^{-1}	1-7 layers
AES	Auger Electron Spectroscopy	Electron emission induced by the de-excitation of atoms. Initial excitation by electron or ion impact	Surface composition, qualitative and quantitative	$\sim 10^{-3}$ - 10^{-2}	1-7 layers
HRELS	High Resolution Electron Loss Spectroscopy	Inelastic back-scattering of electrons in the 1-30 eV range	Vibrational spectrum of adsorbed atoms and molecules	$\sim 10^{-3}$ - 10^{-2}	1 layer
ISS	Ion Scattering Spectroscopy	Inelastic back-scattering of ions in the 1 keV range	Surface composition	$\sim 10^{-3}$ - 10^{-2}	1 layer
SIMS	Secondary Ion Mass Spectroscopy	Mass analysis of ionized surface atoms ejected by ion impact in the 1 keV range	Surface composition	$\approx 10^{-6}$	1 layer

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TABLE II

REACTANT	C_6H_{10}						C_6H_{12}		
PRODUCT	C_6H_{12}			C_6H_6			C_6H_6		
SURFACE	8(111)x(310)	6(111)x(100)	(111)	8(111)x(310)	6(111)x(100)	(111)	8(111)x(310)	6(111)x(100)	(111)
TURNOVER NUMBER FOR $O_{515}/Pt_{237}=0$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	2×10^{-4}	2×10^{-4}	3×10^{-5}	3×10^{-5}	3×10^{-5}	4×10^{-6}
OXYGEN EFFECT	Yes	Yes	No	Yes	Yes	Yes	No	No	?
TURNOVER NUMBER AT O_{515}/Pt_{237}	6×10^{-5} at .13	3×10^{-5} at .15	$<10^{-6}$	1.5×10^{-3} at .3	4×10^{-4} at .13	5×10^{-5} at .13	8×10^{-5} at .15	2.5×10^{-5}	?

The effect of chemisorbed oxygen on the turnover numbers for low pressure dehydrogenation and hydrogenation reactions of C_6H_{10} and C_6H_{12} on the (111), stepped and kinked platinum crystal surfaces.

Figure Captions

- Fig. 1 Scheme of the molecular beam-surface scattering experiment.
- Fig. 2 Apparatus for carrying out surface reactions at high and low pressures (10^{-8} Torr - 10^5 Torr) using small-area ($\sim 1 \text{ cm}^2$) samples that are characterized with the various surface diagnostic techniques.
- Fig. 3 a) Turnover number and b) reaction probability for the dehydrogenation of cyclohexane as a function of pressure.
- Fig. 4 Schematic representation of the heterogeneous surface on the atomic scale. Terrace, step, and kink atoms as well as point defects (adatoms and vacancies) have been identified by experiments.
- Fig. 5 LEED patterns and schematic representations of three types of fcc crystal surfaces: a) $(\bar{1}11)$ orientation containing less than 10^{12} defects/ cm^2 , b) $(\bar{5}57)$ with 2.5×10^{14} step atoms/ cm^2 and 6-atom-wide terraces between steps, and c) $(\bar{6}79)$ surface with 2.3×10^{14} step atoms/ cm^2 and 7×10^{13} kink atoms/ cm^2 . The average spacing between steps is 7 atoms and 3 atoms between kinks.
- Fig. 6 Heats of chemisorption of oxygen for a) various crystal faces, and b) polycrystalline surfaces of elements in the periodic table.
- Fig. 7 Heats of chemisorption of hydrogen for a) various crystal faces, and b) polycrystalline surfaces of elements in the periodic table.
- Fig. 8 Heats of chemisorption of carbon monoxide for a) various crystal faces, and b) polycrystalline surfaces of elements in the periodic table.

Fig. 9 The reaction probability to produce HD upon single scattering of a mixed $\text{H}_2\text{-D}_2$ molecular beam on a stepped platinum surface as a function of the angle of incidence.

Fig. 10 Schematic representation of surfaces exhibiting one-atom-height step-terrace configuration, multiple-height step structure, and "hill and valley" configuration consisting of large facet planes. Reconstruction from one type to another type occurs upon adsorption.

Fig. 11 Ethylidyne molecule that forms upon the adsorption of ethylene or acetylene on the Pt(111) crystal face.

Fig. 12 Turnover number for the dehydrogenation and hydrogenation of cyclohexene as a function of the oxygen/platinum ratio.

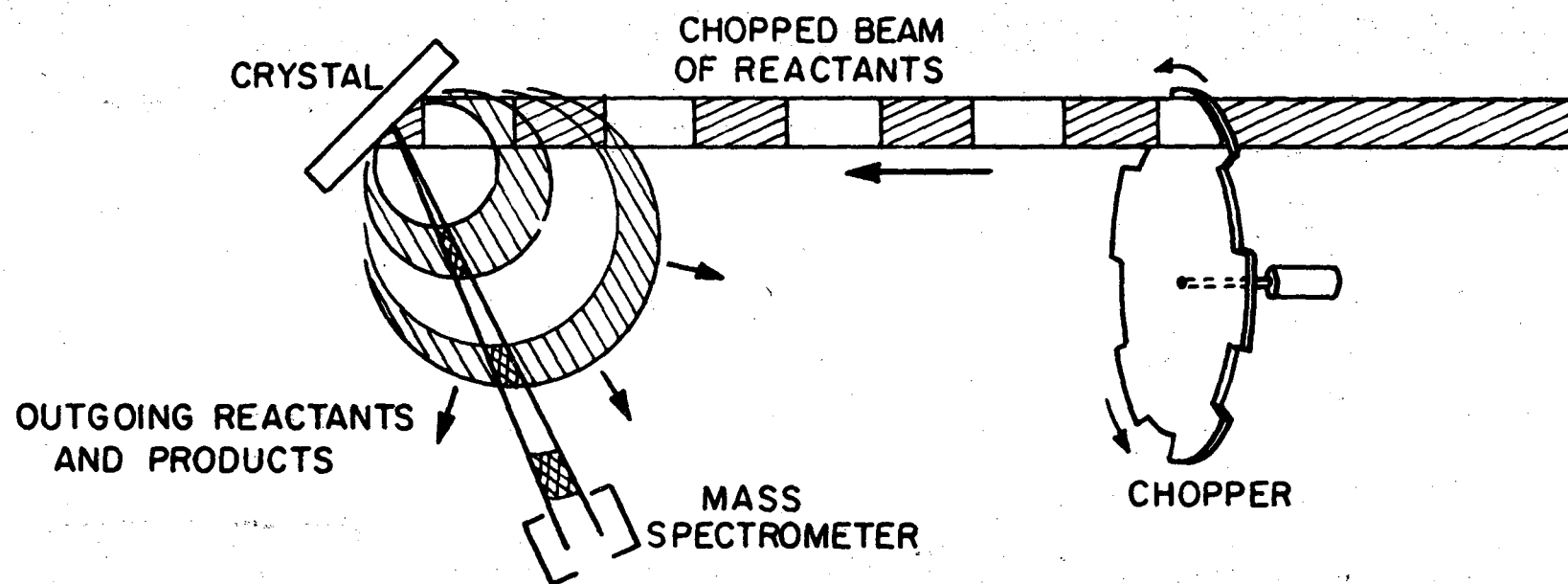
Fig. 13 Methane production from CO/H_2 and CO_2/H_2 mixtures, using clean iron and oxidized iron surface.

Fig. 14 Methane production from CO/H_2 mixtures, using potassium-covered iron and oxidized iron surfaces.

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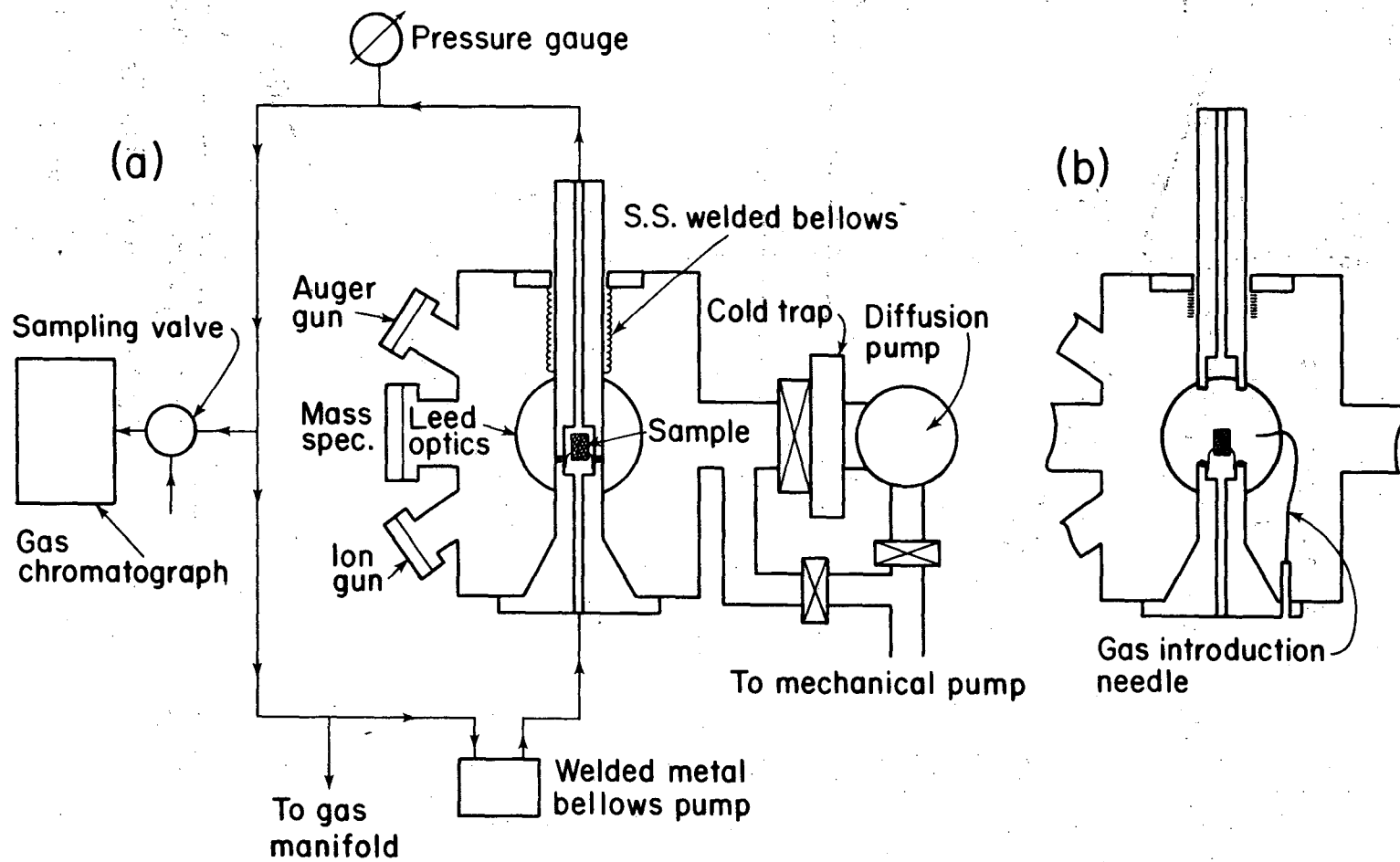
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XBL 772-5082

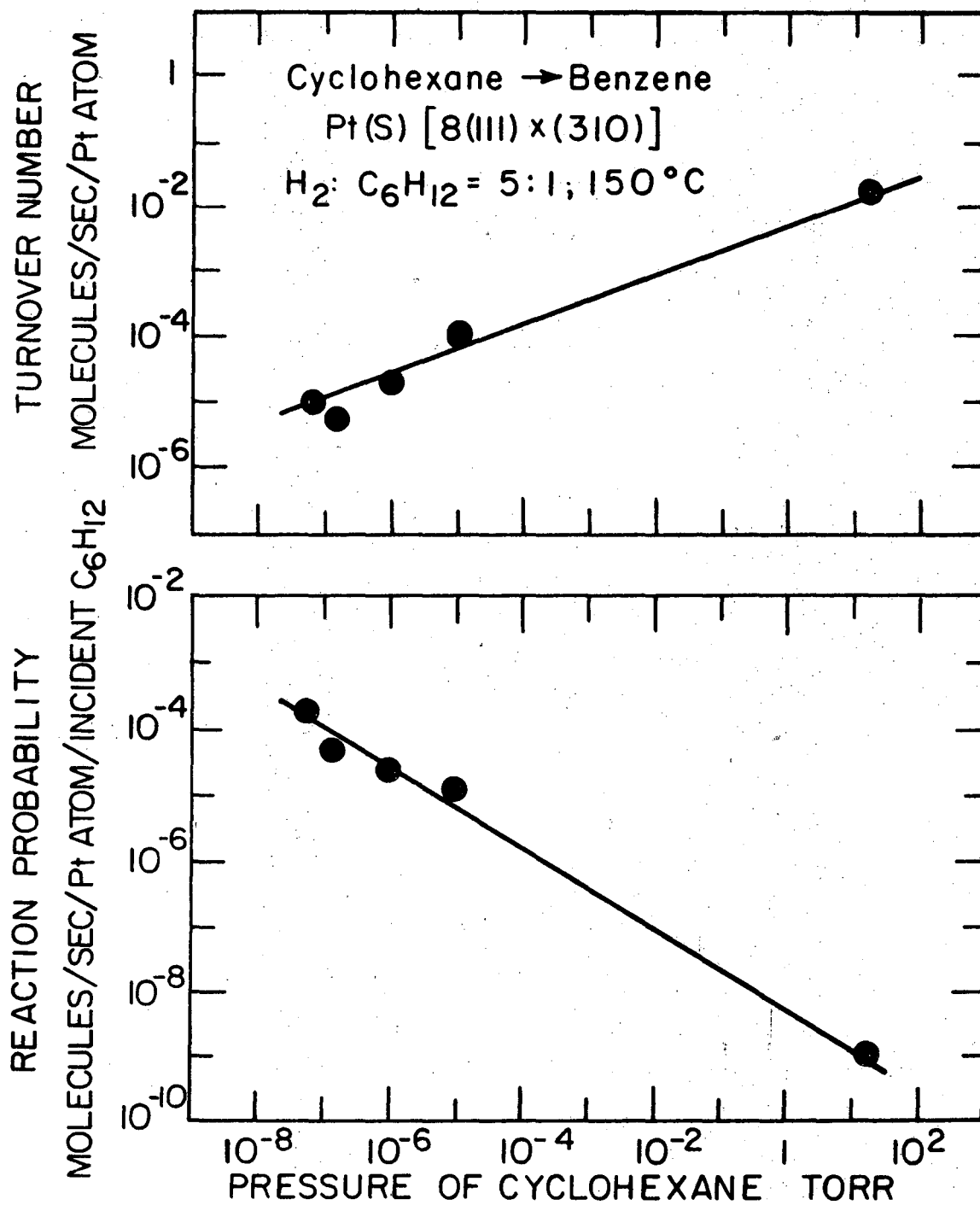
Fig. 1

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XBL 756-3160

Fig. 2



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Fig. 3

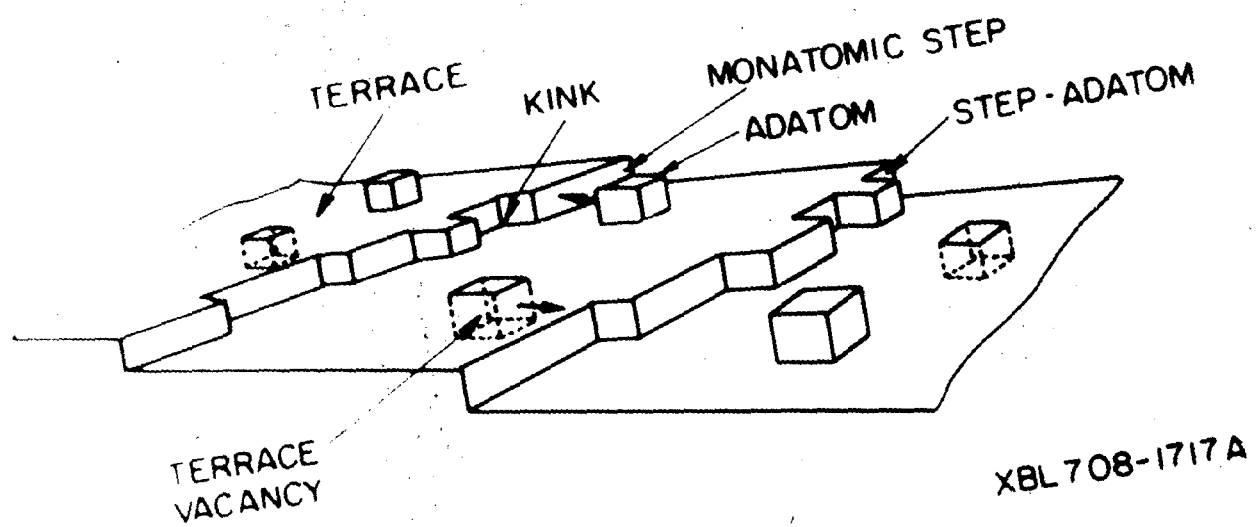
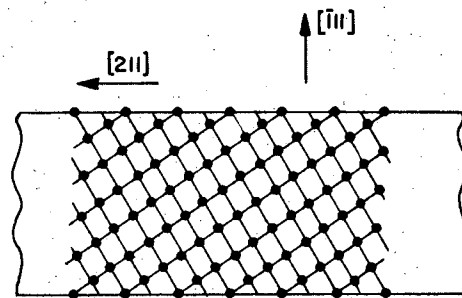
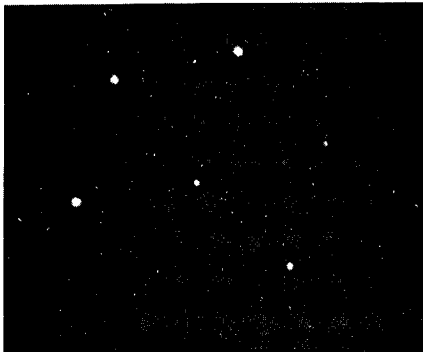
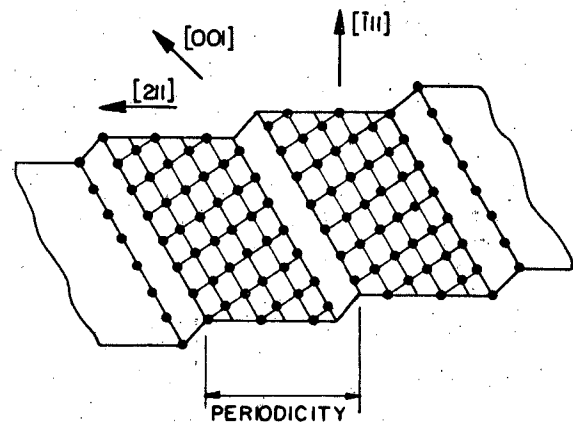
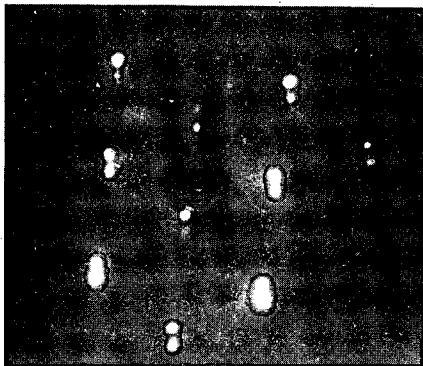
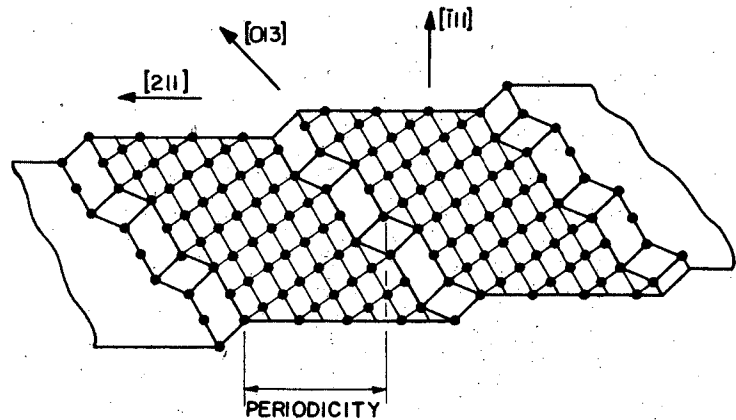
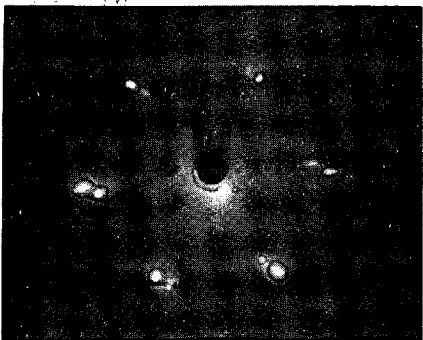


Fig. 4

a) Pt - ($\bar{1}11$)b) Pt - ($\bar{5}57$)c) Pt - ($\bar{6}79$)

XBB 758-5903

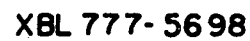
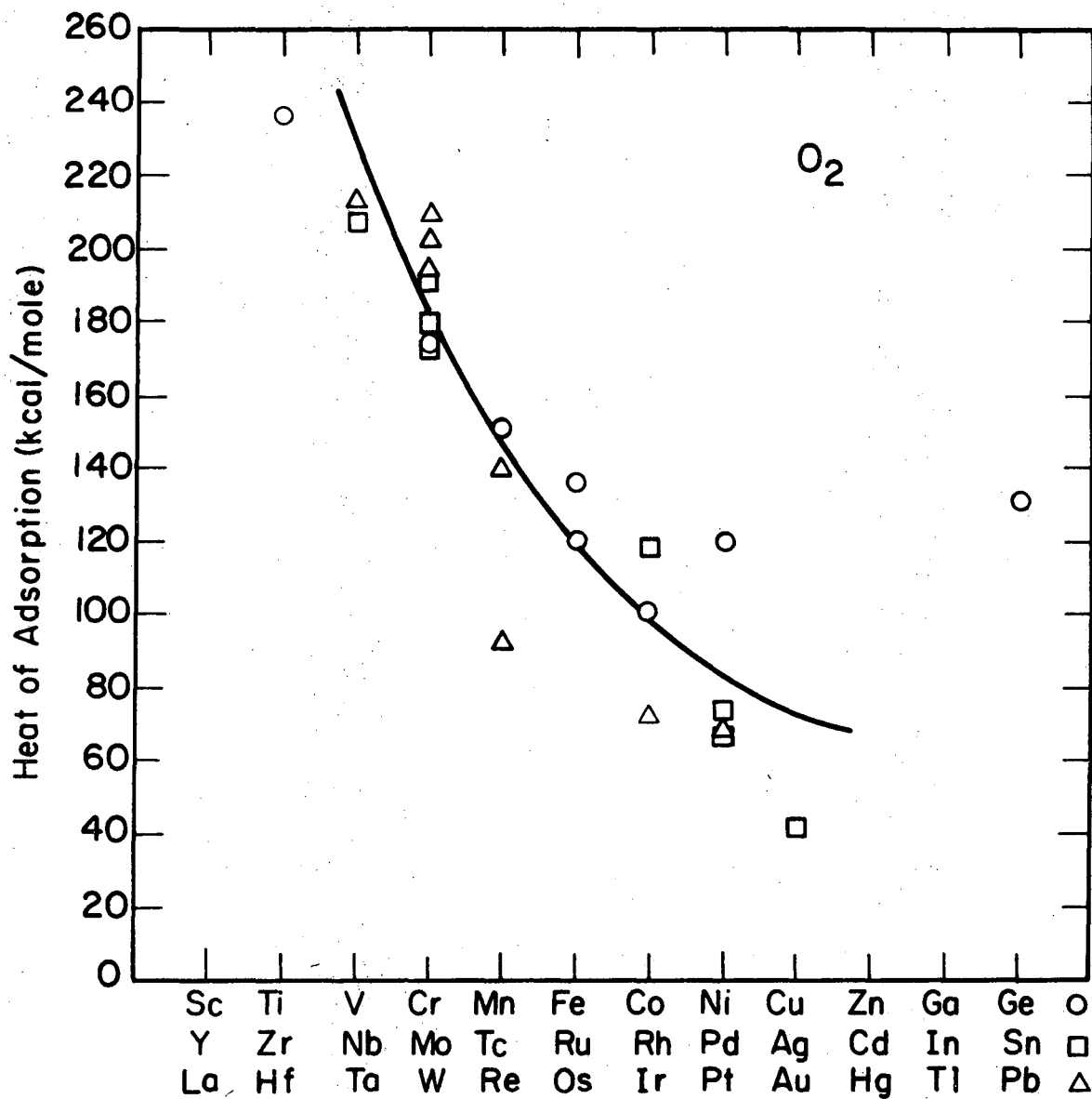
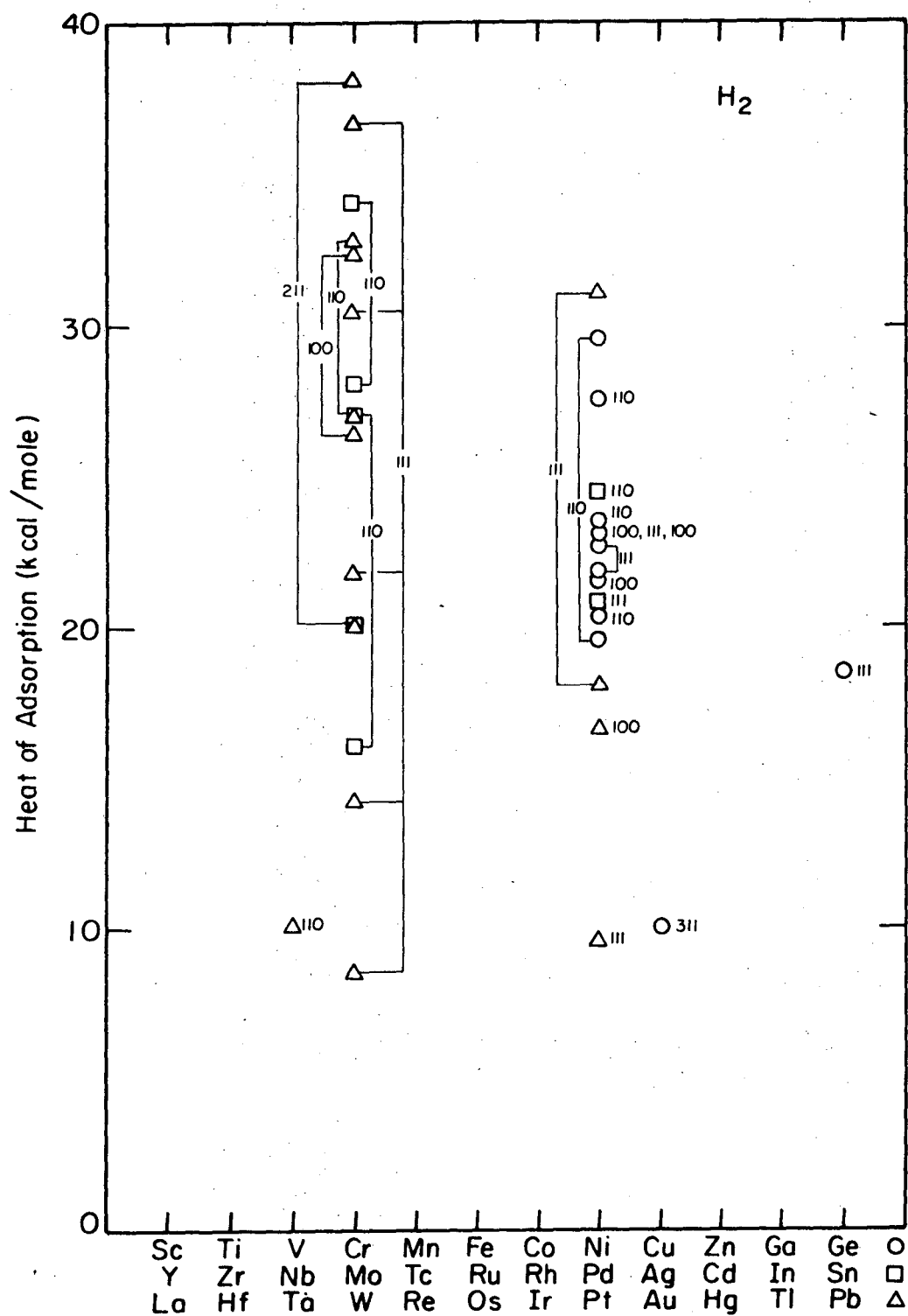


Fig. 6a



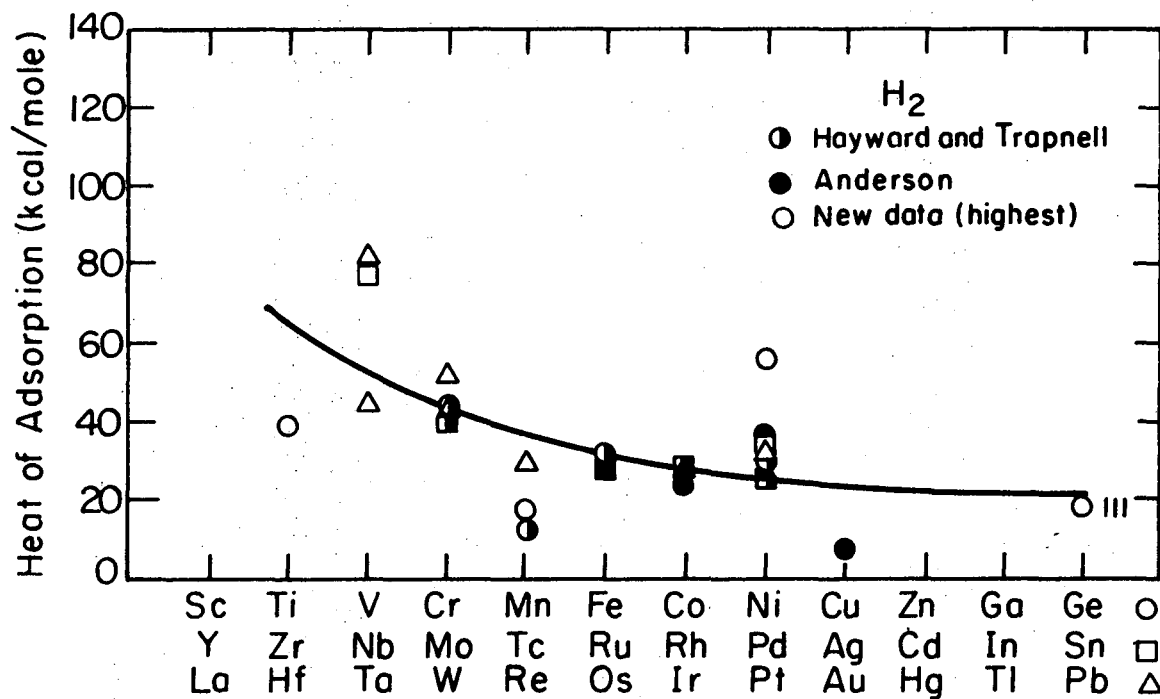
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Fig. 6b



XBL 777-5701

Fig. 7a



XBL 777-5700

Fig. 7b

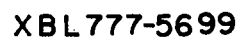
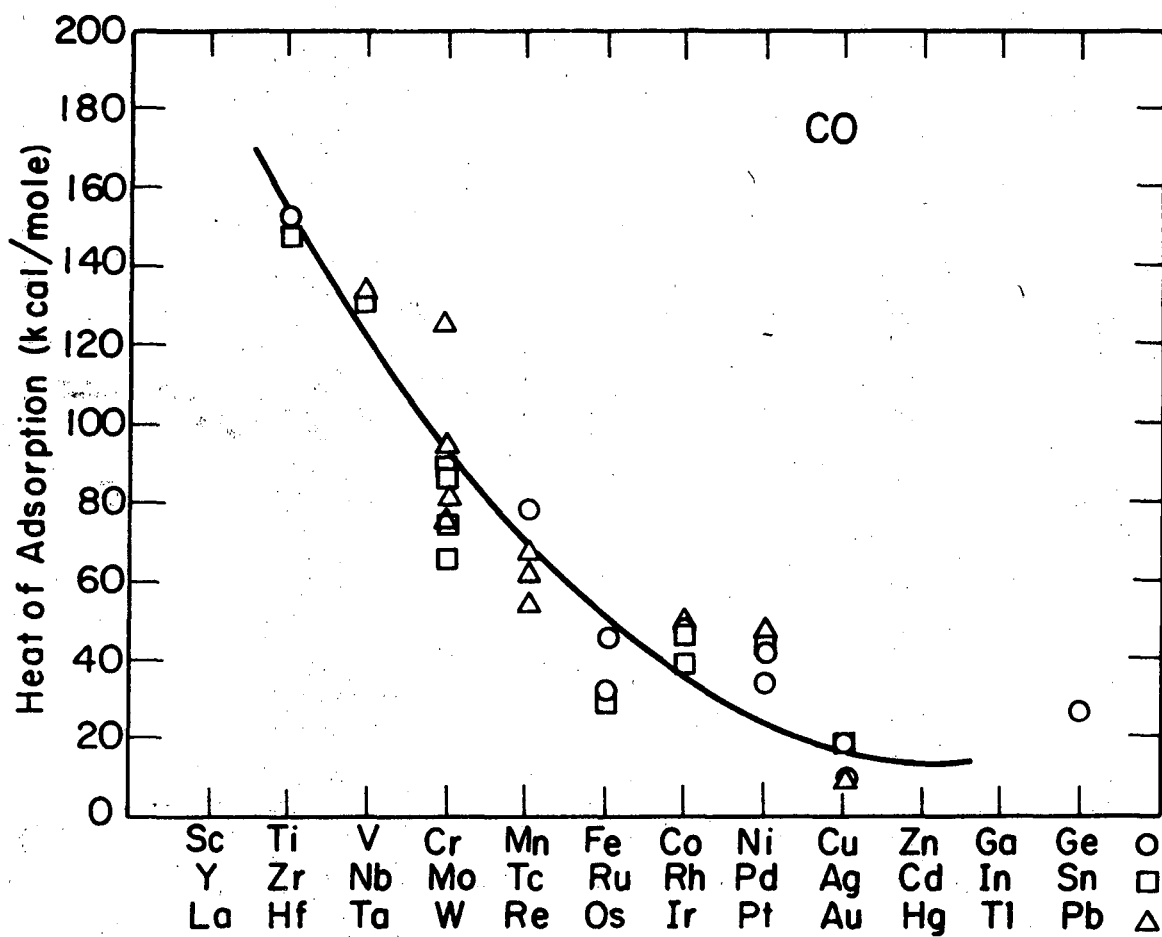
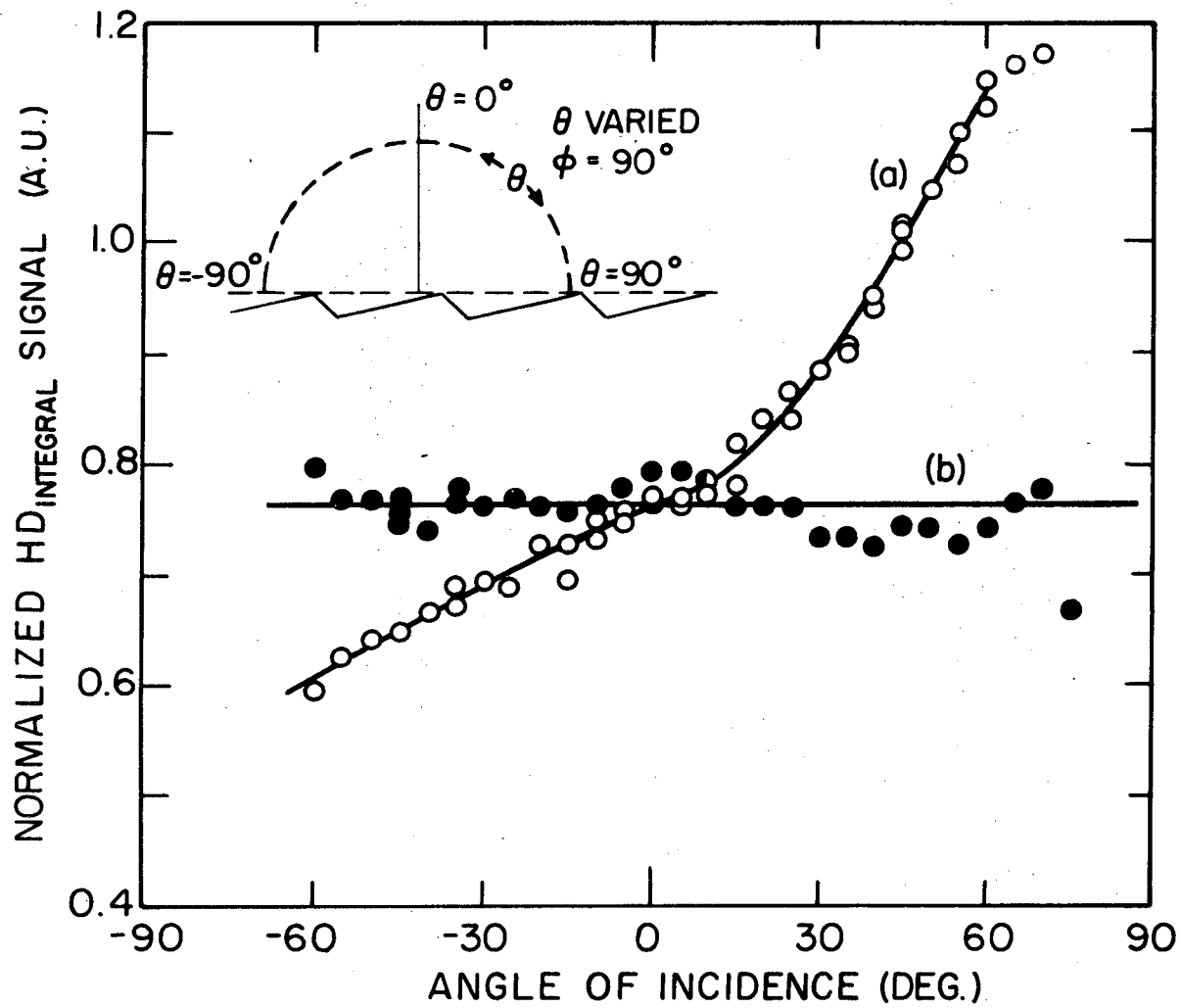


Fig. 8a



XBL 773-5236

Fig. 8b



XBL 771-4925

Fig. 9

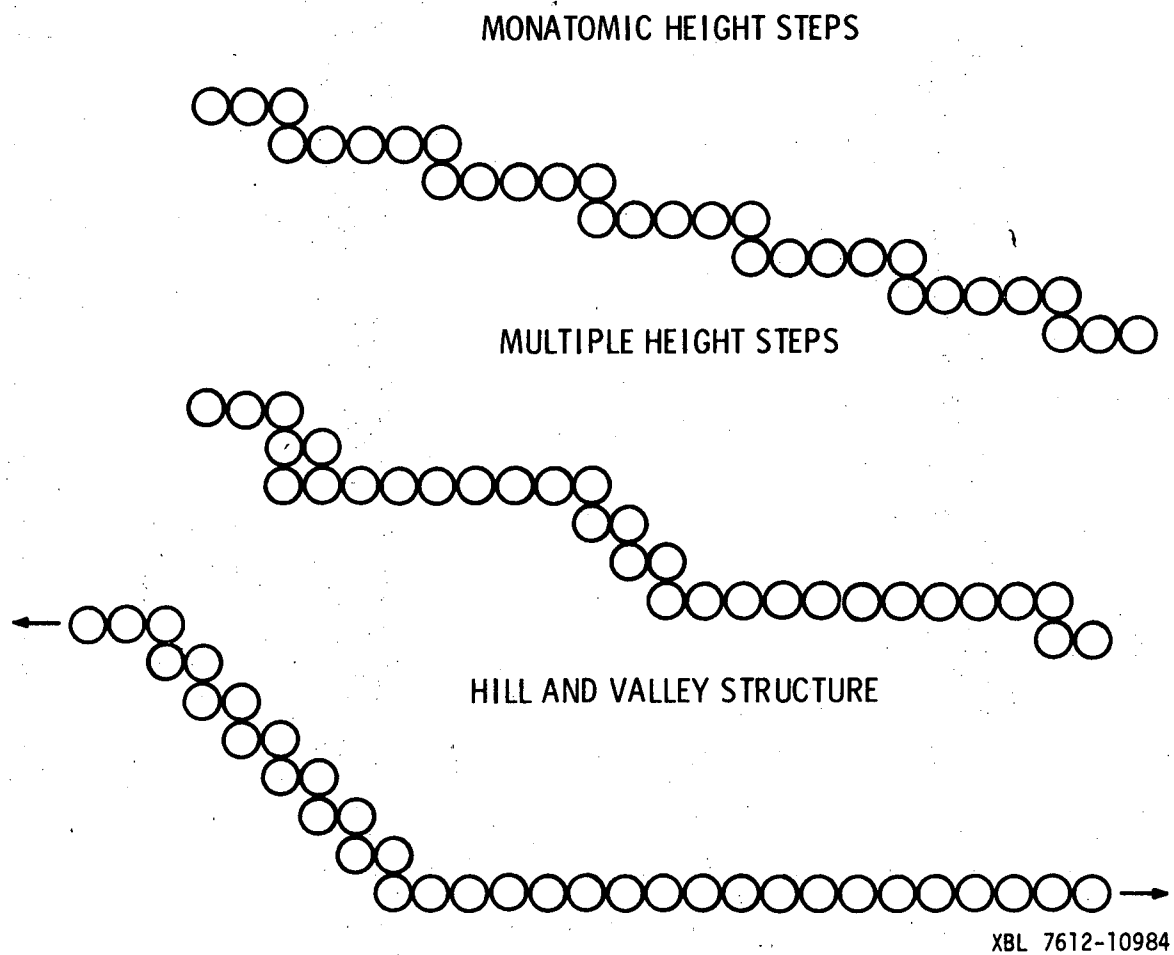
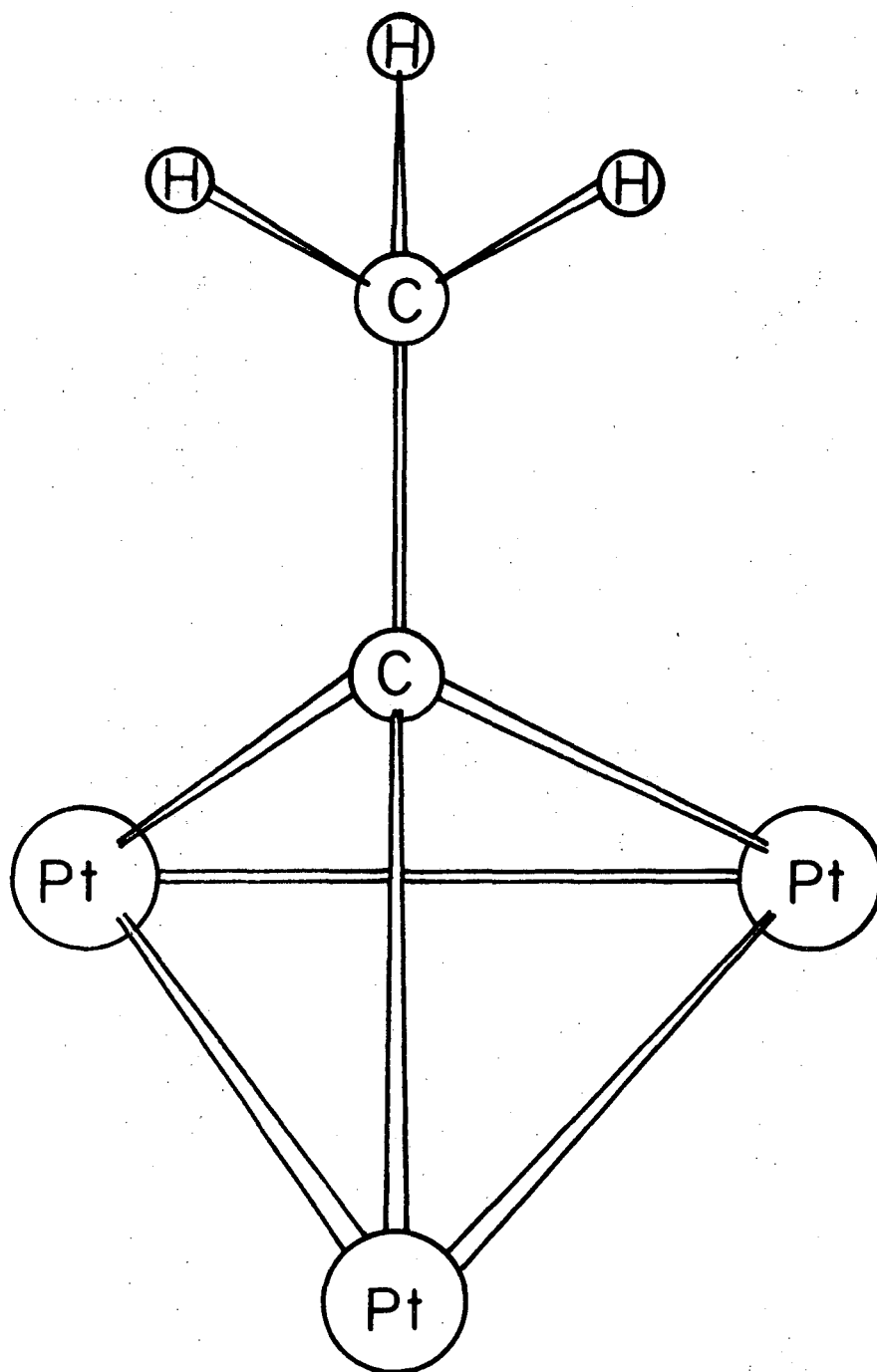


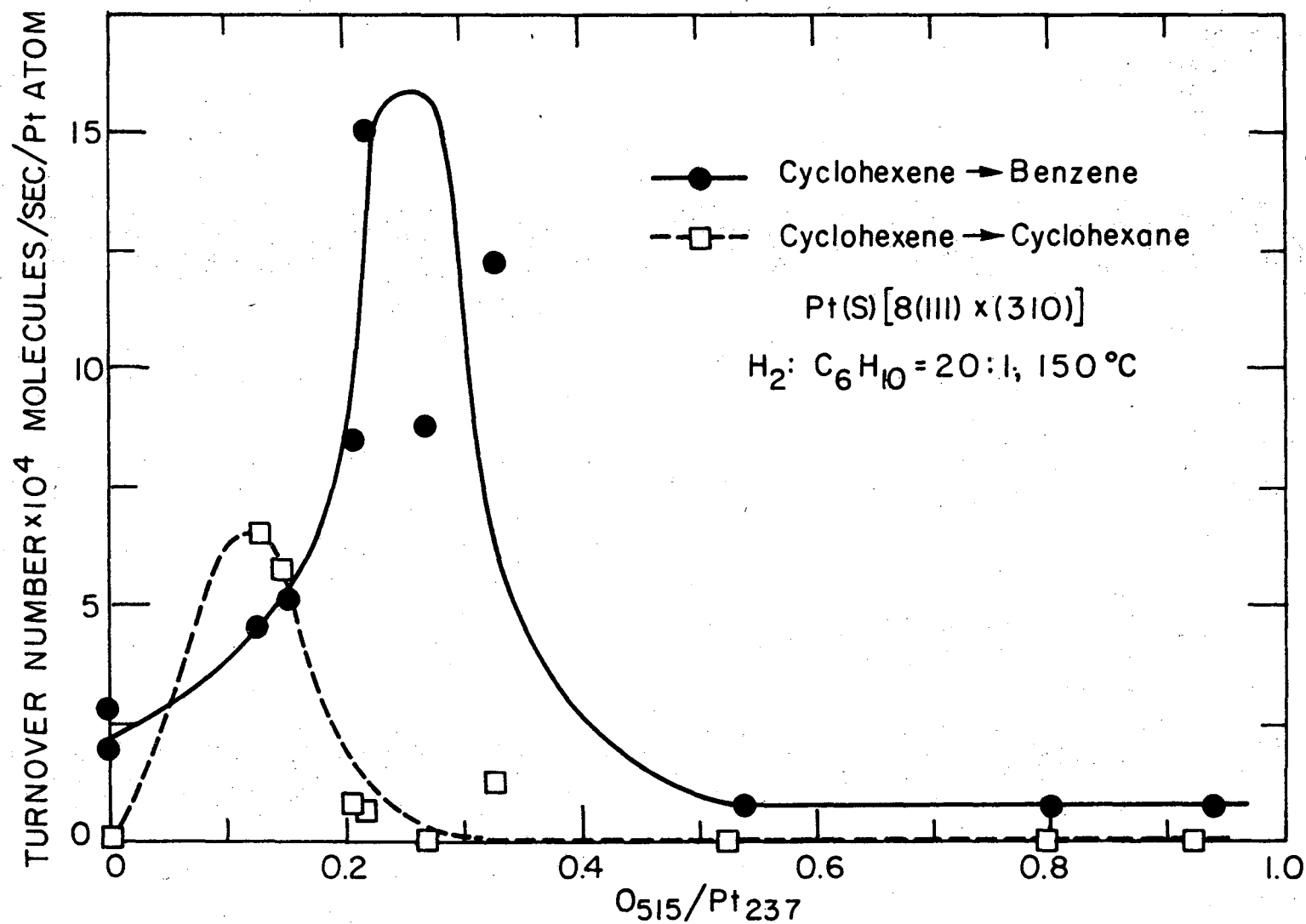
Fig. 10



XBL 7712-6591

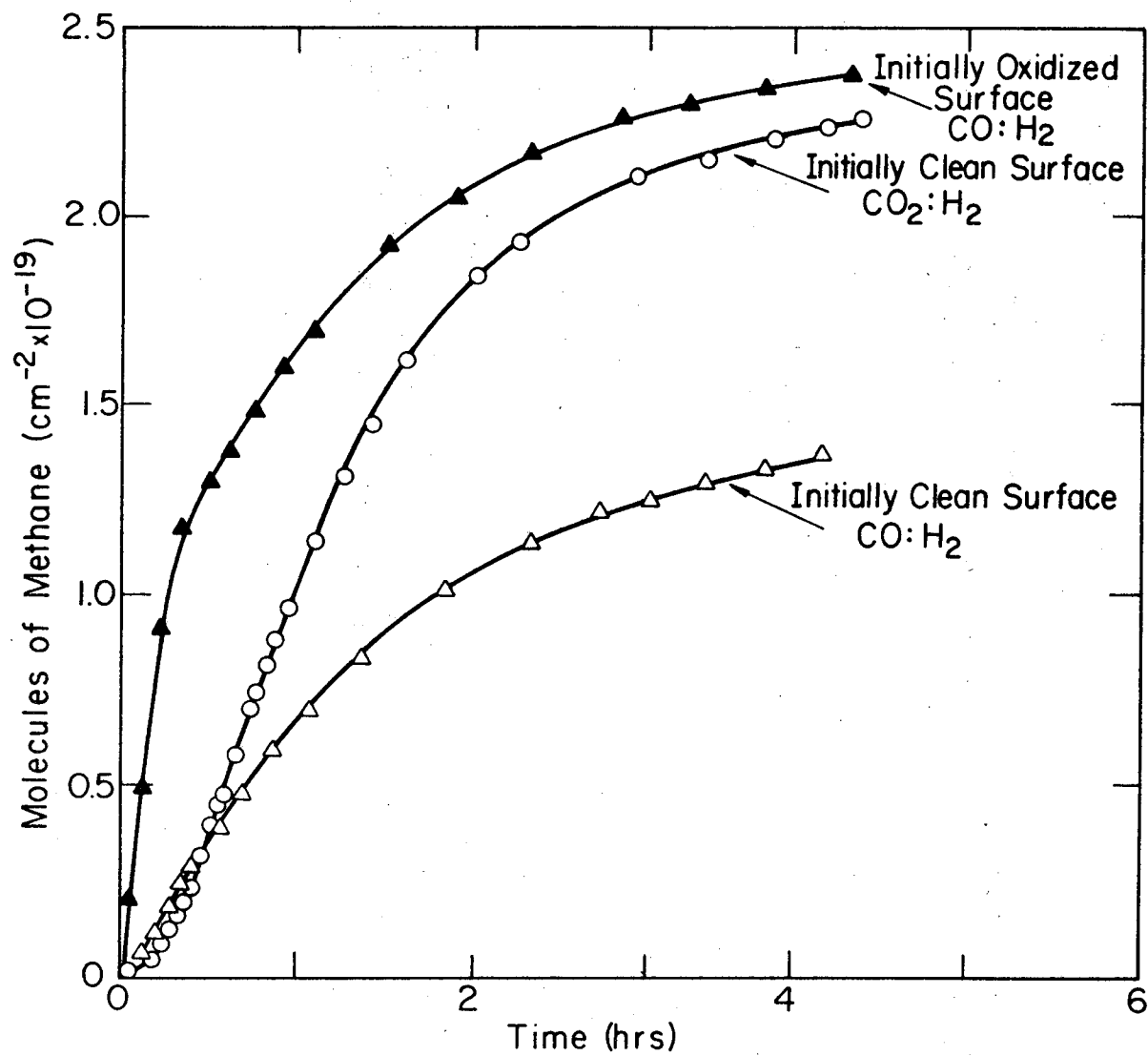
Fig. 11

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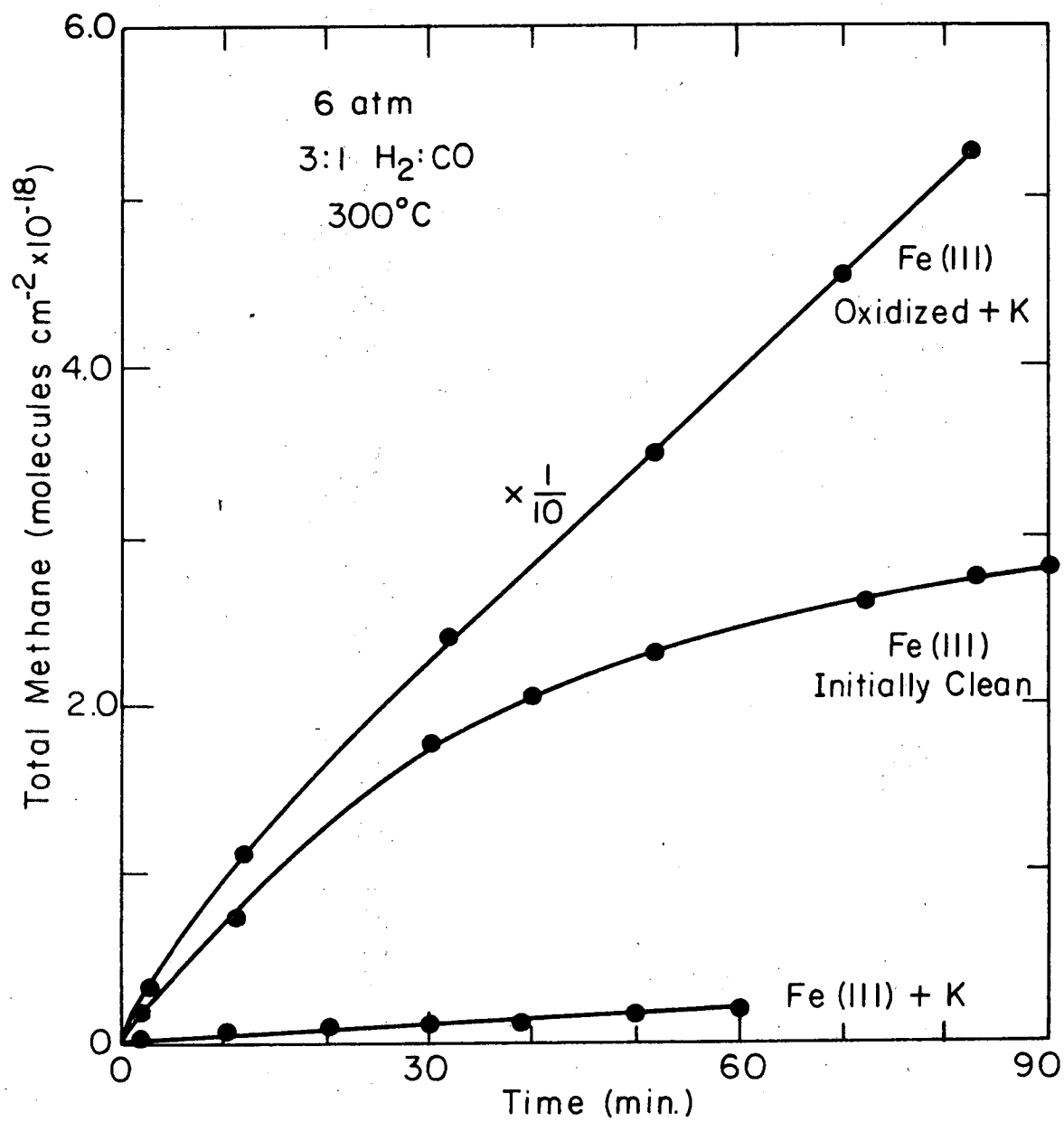
XBL 782-4547

Fig. 12



XBL 779-6024

Fig. 13



XBL 782-4551

Fig. 14

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