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CATALYSIS AND SURFACE SCIENCE

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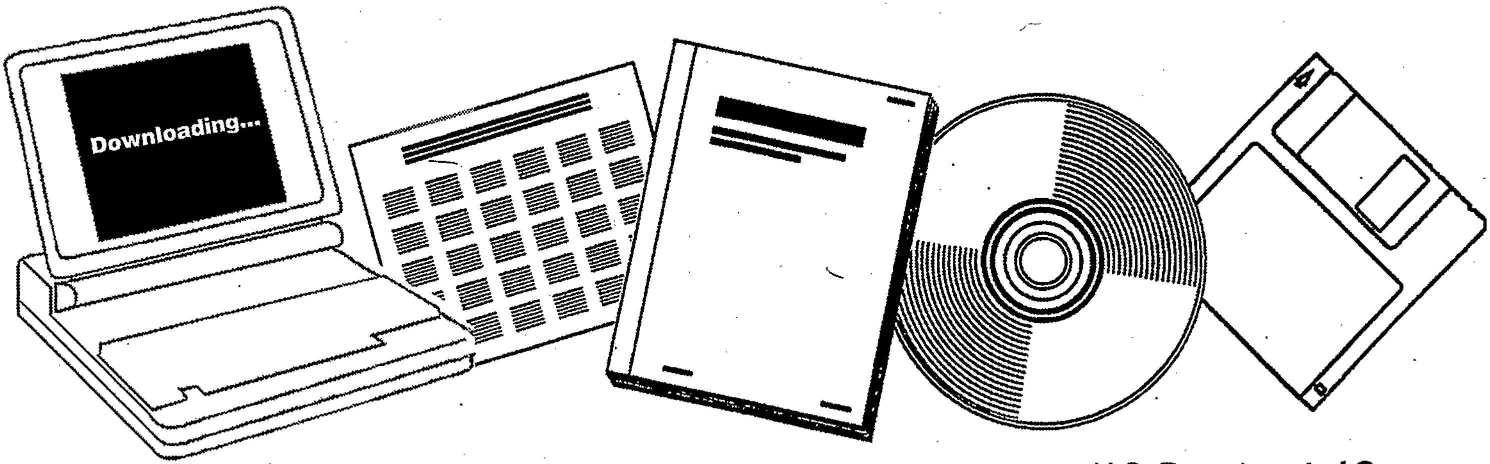

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CATALYSIS AND SURFACE SCIENCE

G.A. Somorjai

Department of Chemistry, University of California

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

Abstract

Catalysis science investigates the dynamics of the elementary surface reaction steps on the atomic scale and the relationship of the atomic surface structure and surface composition to the catalytic process. A large number of surface science techniques are employed for this purpose and special instrumentation has been developed to couple the low pressure environment necessary for the application of many of these techniques and the high pressure conditions utilized in catalysis. The small area (~ 1 cm^2) of the single crystal surfaces has yielded reaction rates identical to those on dispersed high area catalysts for several structure insensitive reactions. The model studies using well characterized surfaces reveal the special importance of (a) surface irregularities and (b) surface additives in controlling the rate and the product distribution in the surface reactions. Several examples will be shown to demonstrate this for hydrocarbon conversion and the carbon monoxide hydrogenation reactions. Present research approaches include (1) the atomic scale investigation of proven catalytic systems, (2) studies of catalyst deactivation and poisoning, and (3) attempts to build new catalysts. These along with likely directions of future research will be discussed.

Introduction

Modern catalysis science investigates the kinetics and mechanism of elementary surface reactions on the atomic scale and the relationship of the atomic surface structure and surface composition to the catalytic process. Thus, it is concerned with both static and dynamic measurements on well characterized surfaces in the case of heterogeneous catalysis. Perhaps the first high technology catalysts, catalysts that were prepared and improved using these principles were the zeolites.[1] These high surface area alumina silicates were synthesized with a variety of compositions (varied alumina-to-silica ratio) and pore sizes. The pore structure and size was controlled by organic molecules that were incorporated into these oxides during preparation and their skeletal structure left cavities and channels of well defined shape after they were decomposed by heating. These catalysts used in very large quantities for hydrocracking that may occur in a shape selective manner since the pore structure determines the size and shape of the organic molecules that may pass through the catalyst.

Surface science techniques were not necessary for the development of these alumina silica systems as their structure is readily accessible for studies by x-ray diffraction, electron spin resonance and other appropriate physical chemical techniques. The many modern techniques of surface science, however, are beginning to play important roles in the characterization of many other useful heterogeneous catalyst systems and in the development of new catalysts as they are overcoming the major problem that impeded their application before. That major difficulty in their applications involved the bridging of the pressure gap; the development of instruments that are capable of operating under both ultra high vacuum and high pressure conditions as these conditions are needed in surface analysis and for catalysis respectively. Figure 1 demonstrates one of these instruments that was developed in my laboratory.[2] The small area catalyst sample is enclosed in a cup situated in the middle of an ultra high vacuum chamber. 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. 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 rate and product distribution of high pressure catalyzed reactions that are obtainedusing well characterized surfaces can be correlated with the kinetics of catalyzed reactions carried out on large surface area dispersed systems on one hand, and with the kinetics of surface reactions studied at low pressure on the other. The importance of using high pressure in carrying out surface reactions is particularly well documented in the case of association reactions that are accompanied by a decrease in the number of moles in the reaction mixture as the product molecules are formed.[3] According to the LeChatelier principle, high pressure favors the formation of higher molecular weight products. Figure 2 shows that pressures in excess of 20 atm are desirable to produce high molecular weight benzene, for example, from carbon monoxide and hydrogen. Thus, catalysts that are utilized for carrying out association reactions must be studied at high pressures to be able to show what they can do without the thermodynamic limitations imposed on them.

At present, there are two major directions of atomic scale investigations of catalysts. One involves the study of the practical catalyst system that usually consists of small particles, 15-100Å diameter dispersed on high surface area supports. It has been very difficult to characterize these types of system on the atomic scale. Recently, however, extended x-ray absorption fine structure (EXAFS) studies using high intensity synchrotron radiation have resulted in major advances in the determination of the structure and composition of the catalyst particles deposited inside the pores of the support.[4]

The other major direction of atomic scale investigations is the study of model systems. In this research a small surface area ($\sim 1\ cm^2$) single crystal, thin film or polycrystalline foil is used for catalytic studies. Samples of this geometry can readily be characterized on the atomic scale by all the various techniques of surface science.[5]

This latter approach is being pursued in my laboratory. Single crystals are cut to expose different crystal faces and their catalytic activities explored and correlated with their surface structure and surface composition. Three different crystal faces of platinum that exhibit distinctly different catalytic activity are shown in Figure 3. Crystals can be cut to expose a surface in which one type of surface site predominates. The atomic surface 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 Figure 3a. 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 six-fold equilibrium positions. By cutting crystals along planes of lower atomic density (high Miller index), crystal faces that exhibit ordered steps and kinked structures, as shown in Figures 3b and 3c, can be prepared. 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 diffraction pattern from high Miller index surfaces exhibits diffraction beam doublets that appear at well defined electron beam energies. These are also shown in Figures 3b and 3c. The terrace widths are calculated from the doublet separation. The step height is obtained from the variation of the intensity maximum of the doublet diffraction beam features with electron beam energy. The detailed analysis of the surface structure based on the diffraction pattern is described elsewhere.[6] The terrace width does not have to be uniform to obtain satisfactory diffraction patterns. There may be a great deal of variation in the step width, about an average value, yet one still obtains a diffraction pattern of satisfactory quality. However, if the diffraction patter indicates that the terrace width is 6 atoms, that does not rule out the presence of a large number of terraces of 5 or 7 atoms.

It appears that the clean stepped or kinked surfaces of face centered cubic metals always have 1 atom height steps.[7] As we shall see later, this may be rearrangeed markedly when adsorbates, carbon or oxygen, are present on the surface.

When using model systems for catalytic studies, it is of utmost importance to establish the identity or the correlation between the rates and product distribution obtained over the model and real catalyst systems respectively. Table I compares the rates and activation energies for cyclopropane ring opening over platinum crystal surfaces with those obtained over dispersed high surface area supported catalysts.[8] The agreement is very good indeed. Table II shows excellent agreement for the carbon monoxide hydrogenation reaction over polycrystalline rhodium foils of small surface area and over silica supported high surface area rhodium particles.[9] The product distributions, activation energies for methane formation and rates are identical within the accuracy of the experiments. These correlations between the catalytic activity of the model systems and dispersed catalysts provide the necessary credibility so important to utilize the chemical information obtained from model studies to obtain an understanding of the complex supported catalyst systems.

Let us review what we have learned from modern studies of model systems about chemisorption and heterogeneous catalysis on the atomic scale over the past 10 to 15 years. The heats of adsorption of carbon monoxide and hydrogen and several other small molecules that were obtained by using polycrystalline and single crystal surfaces[10] have been compiled recently and some of the results are shown in Figures 4 and 5. Unlike the smooth curve obtained from 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. There are several bonding sites that may include a molecule bound on top of a surface atom, at a bridge or a three-fold site, all having different binding energies. The heats of adsorption for a given molecule may vary more than 20-30 kcal for a given transition metal fairly commonly. 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. This atomic scale phenomenon, indicating marked heterogenity of binding, is completely masked in studies of polycrystalline surfaces or of small particles that have many surface sites exposed simultaneously. In these cases the data obtained is averages over all these sites and mask the molecular scale reality.

Similar large differences in reactivity correlations are observed when comparing data obtained from polycrystalline transition metal catalysts and from single crystals.[11] The specific rates for hydrogenolysis of ethane to methane are plotted for different transition metal powders in Figure 6. There are eight orders of magnitude variations of catalytic activity and valuable studies of this type identify the most active catalyst systems. However, when these studies are carried out using single crystal surfaces of appropriate surface structure and

and with small amounts of additives that promote increased reaction rates, one to two orders of magnitude variation of reactivity can be obtained for a given transition metal catalyst. Several examples of these variations of rates with surface structure and surface composition will be shown later. Thus, there is no such thing as a unique rate for a given reaction--catalyst system, but the rate and selectivity are variable over a wide range by the control of the atomic surface structure and surface composition.

Studies of heterogeneous catalysis using model systems have revealed two main features of active surfaces that control catalytic behavior. These are (a) irregularities, and (b) additives. The irregularities that are catalytically most influential at the transition metal surfaces are steps and kinks. These are sites of low coordination as compared to atoms in the terrace. These sites are identified in Figure 7. Stable point defects may also play important catalytic roles at oxide surfaces as it was recently demonstrated.[12] However, their concentrations are likely to be too low at metal surfaces to be chemically significant in most cases. The additives that influence catalytic behavior are either deposited by the reaction mixture during the reaction (carbonaceous or oxide deposits, for example) or purposely added to the surface during catalyst preparation (promoters). These additives are generally electron acceptors (oxygen, chlorine, etc.) or electron donors (alkali metals). Alternatively, another metal may be used to block certain surface sites (gold on platinum or iridium surfaces, for example) or to stabilize an appropriate oxidation state or surface structure which would otherwise be unstable in the reaction mixture. The oxide support may also be employed for this latter purpose.

Below we shall give examples of the influence of irregularities and additives in controlling the catalytic activity of platinum for hydrocarbon conversion reactions and that of iron during the hydrogenation of carbon monoxide.

1. The Effect of Steps in Breaking H-H Bonds During H_2D_2 Exchange on Platinum Surfaces.

One method that was developed for studies of the dynamics of gas-surface interactions and the kinetics of elementary surface reactions is the molecular beam surface scattering technique.[13] This is schematically depicted in Figure 8. A well collimated beam of molecules of known velocity impinges 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 ultra high 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 disbribution 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. Using this technique the exchange reaction $H_2+D_2=2HD$ was studied as a function of the angle of incidence of the beam of reactants on various stepped platinum surfaces.[14] The reaction probability was found to depend markedly on the direction of approach of the reactants to the stepped structure. This is demonstrated in Figure 9. . The production of HD is highest when the reactants strike the open side of the stepped structure, decreasing by approximately a factor of 2 when the inner corner of the step is shadowed. The observed dependence can be accounted for in a simple model assigning different activity for H-H bond breaking to the step and terrace sites. For the best fit was the experimental data, it was found that the activity of a step site is 7 times that of a terrace site for breaking the H-H bond. The reasons for this large difference have been verified by recent studies as well.[15] The adsorption of hydrogen appears to be an activated process on the Pt(111) surface with a barrier height of 0.5 to 1.5 kcal/mole. On the step surface, however, the adsorption of hydrogen requires no activation energy. This small activation energy barrier on the (111) surface gives rise to the large difference in reaction probability that is associated with the dissociative adsorption of hydrogen. After this adsorption step, subsequent elementary surface reaction steps involving the diffusion and recombination of hydrogen atoms are all identical on the stepped and the (111) crystal faces of platinum.[15] The reaction mechanism is quite complicated, including parallel and branched reaction paths in the temperature range of 25-800°C.

2. The Effect of Steps and Kinks in Breaking C-H and C-C Bonds at Platinum Surfaces.

The dehydrogenation and hydrogenolysis of cyclohexane and cyclohexene have been studied on a series of stepped and kinked surfaces of platinum.[16] We shall present the results of reaction studies for dehydrogenation and hydrogenolysis of cyclohexane. By comparing the amount of benzene and n-hexane formed, the relative activities of these surfaces for C-C and C-H bond breaking can be determined. In Figure 10 the turnover numbers for dehydrogenation to benzene and hydrogenolysis to n-hexane are shown as a function of step density at 125°C. The dehydrogenation rate is independent of step density, while the hydrogenolysis rate increases with increased step density. The turnover numbers of dehydrogenation and hydrogenolysis on kinked surfaces are shown in Figure 10b. The kink density is defined as the number of kink sites per cm^2 (the total number of atoms on the surface is $\sim 1.5 \times 10^{15}/cm^2$). By comparing the turnover numbers with those obtained from stepped surfaces that are shown in Figure 10a, it appears that the rate of hydrogenolysis is markedly higher in the presence of kinks. The dehydrogenation rate is approximately constant and remains unaffected by variation of kink density, while the hydrogenolysis rate increases by an order of magnitude in the presence of kinks as compared to a surface that is almost free of steps (Pt(111)). The kinks in the stepped surface appear to be very effective in breaking C-C bonds leading to much enhanced hydrogenolysis rates, in addition to breaking H-H and C-H bonds. The steps, on the other hand, are active in breaking H-H and C-H bonds and are not so active in breaking the C-C bond. The selectivity of these bond breaking processes at different atomic surface sites on platinum is certainly significant in that the atomic surface structure of platinum may be properly tailored to provide selectivity in chemical reactions where C-H and C-C bond breaking processes are to be separated.

The uniquely strong bond breaking ability of kink sites is also demonstrated by photoelectron spectroscopy studies of carbon monoxide chemisorption on these surfaces as carried out by Professor Mason and his coworkers.[17] The photoelectron spectra was obtained upon exposing the kinked platinum surface to various exposures of carbon monoxide. At low coverages the adsorption is clearly dissociative as evidenced by the appearance of a carbide peak with a C_{1s} binding energy of 283.8 eV. Only after all of the kink sites are covered by carbon is the appearance of molecular CO is indicated from the photoelectron spectrum at higher coverages. Thus, while platinum is not known for being able to dissociatively adsorb carbon monoxide, the kink sites appear to be quite active in breaking the very strong CO bonds.

Marked effects of bond breaking behavior due to steps are also shown over nickel surfaces from high resolution electron energy loss spectroscopy studies from Professor Ibach's laboratory. In fact, it appears that for breaking C-H and C-C bonds steps at nickel surfaces are appreciably more active than steps at platinum surfaces when compared to the terrace sites of these two metals respectively.

3. Surface Restructuring During Catalytic Reactions.

The atomic surface structure of a freshly prepared catalyst is rapidly changed under the reaction conditions and may be changed again in the presence of hydrocarbons or upon cleaning the surface in oxygen, or heating it in hydrogen. This is revealed during studies of 22 single crystal surfaces of platinum that were studied in ultra high vacuum when clean in the presence of a monolayer of chemisorbed oxygen or carbon by low energy electron diffraction.[7] Most crystal surfaces restructure as the surface composition is changed. Some of the surface structures that are stable in ultra high vacuum and in the presence of oxygen reconstruct in the presence of carbon, while others are stable when clean and when carbon covered restructure when covered with oxygen. The type of changes of surface structure that occur most commonly are depicted schematically in Figure 11. A surface that exhibits a 1 atom heightstep-terrace configuration reconstructs into 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 can be reversible. Once the adsorbate, oxygen or carbon, is removed the surface returns to its original clean surface structure. There are few stable surfaces that do not restructure at all under conditions of experiments, Besides the low Miller Index surfaces, (111), (001) and (011), these are the (112), (133), (122) and (012) orientation crystal faces of platinum.

These crystal planes are characterized by a very high density of periodic steps, 1 atom in height or a complete lack of steps. Because of their structural stability it is expected that they may play important roles in the catalytic chemistry of platinum.

Restructuring in the presence of adsorbates serves as a mechanism for redispersion.[7] 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 reconstruction of the active catalyst structure upon adsorption of impurities. Sulfur is known to cause restructuring of metal surfaces.[18] Certainly studies of the correlation between restructuring and poisoning of catalytic activity is a major, important direction of modern surface science research into heterogeneous catalysis

4. The Carbonaceous Deposit

The platinum and other transition metal surfaces are covered with a near monolayer of carbonaceous deposit during the catalytic reaction.[19] The catalyst remains active in the presence of this deposit until it is heated to high temperatures, above 400°C, when the deposit becomes graphitized and catalytic activity ceases. We may ask whether the hydrocarbon surface reaction takes place on top of this carbonaceous overlayer or in exchange with it. Although there is not enough detailed experimental information, it appears that there are many reactions that may take place on top of this layer. These are also likely to be structure insensitive or less structure sensitive as the carbon containing deposit covers up many of the surface irregularities. Thus, research into the role of this deposit may reveal why certain catalytic reactions are not influenced by changes of catalyst particle size and structure while others are.

Recent low energy electron diffraction and high resolution electron energy loss spectroscopy studies of small hydrocarbon molecules also reveal the nature of the surface chemical bond between the metal and this carbonaceous monolayer.[20] When acetylene, C_2H_2, adsorbs on the Pt(111) surface,it forms an ordered (2x2) surface structure at 25°C. The molecule is bound to one platinum atom almost at an "on top" site at Pt-C distance of 2.5Å with its internuclear axis parallel to the metal surface. On heating to 75°C the diffraction beam intensity due to the C_2H_2 surface structure changed drastically, indicating that major restructuring of the surface layer has occurred, while the unit cell of the surface structure remains the same. The structure of this molecule which is more stable than the previous configuration that is produced at room temperature is revealed by a combin-- of LEED and HREELS studies and this is shown in Figure 12. Acetylene forms an ethylidine molecule with a 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. The short metal-carbon bond is characteristic of

carbene-like molecules that exhibit unique chemical activity in many displacement reactions. The C-C bond 1.5Å is a single bond in character and is perpendicular to the surface plane. There may be two or three hydrogen atoms depending on the hydrogen partial pressure on the surface. It appears that little activation energy is required to form either CCH_2 or CCH_3 species. This ethylidine platinum surface structure resembles the structure of several trinuclear metal acetylene complexes.[20]

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 Figure 12, a very strong metal-carbon bond is needed. The carbene-like Pt-C bond can be estimated to be stronger that 68 kcal/mole from thermodynamic arguments. However, on platinum the Pt-C bond is not strong enough to cause breaking of the C-C bond under our experimental circumstances. However, on nickel surfaces at similar temperatures the C-C bond breaking certainly occurs. The changes of bonding of acetylene to Pt with small variations of temperature and the sequential bond breaking of adsorbed molecules with increasing temperature demonstrate one of the most important properties of the surface chemical bond--its temperature-dependent character. At low temperatures the molecule may remain intact on an active metal surface. As the temperature is increased it dissociates by sequential breaking of C-H and C-C bonds, and an active carbon layer may form from the dissociated hydrocarbon molecules. On increasing the temperature further, the active carbon graphitizes and the graphitic overlayer exhibits little or no chemical activity.

Thermal desorption studies indicate that the bonding of molecules that are co-adsorbed in the presence of the active carbonaceous deposit is often different from that on the clean metal surface. Carbon monoxide exhibits a high temperature desorption peak on the partly carbon-covered rhodium surface indicating dissociative adsorption while only molecular species are present on the clean rhodium surface under the same experimental conditions.[9] This is shown in Figure 13. Benzene and other organic molecules also exhibit different bonding behavior on partially carbon-covered platinum crystal faces.

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.

5. The Effect of Oxygen on Hydrocarbon Catalysis by Platinum

It was found that small amounts of chemisorbed oxygen present on platinum surfaces in concentrations of 10-40% of a monolayer can markedly change the rate and product distribution in hydrocarbon reations.[21] In Figure 14 the turnover number for the dehydrogenation of cyclohexene is plotted as a function of the surface oxygen-platinum ratio. The value of 0.6 in the (O_{515}/Pt_{237}) Auger peak ratio (O_{515}/Pt_{237}) corresponds to a monolayer of oxygen. 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 45% of a monolayer on the kinked platinum surface that was studied. Similar effects were not observed on the (111) and stepped surfaces of platinum. Thus it appears that a combination of a kink site and oxygen are necessary to obtain this large increase in chemical activity. The oxygen may be introduced by heating the platinum in oxygen before the reaction, or by adding small amount of oxygen to the reaction mixture. As soon as the platinum is completely oxidiz catalytic activity is poisoned, as seen in Figure 14. Our studies therefore indicate that the oxygen species are not those of the oxide, but must be strongly bound chemisorbed oxygen.

In the presence of oxygen, the kinked platinum surface exhibits hydrogenation activity as well. This reaction had a very low rate in the absence of oxygen. This is also shown in Figure 14. Interestingly the optimum activity fo hydrogenation of cyclohexene to cyclohexane occurs at a lower oxygen surface concentration than the optimum activity for dehydrogenation of cyclohexene to benzen Thus, important selectivity can be obtained by small changes in the oxygen surfa concentration. At certain oxygen surface concentrations may be equal amounts benzene and cyclohexane could be formed from cyclohexene. At higher oxygen surf concentrations the hydrogenation activity is impeded while dehydrogenation appea to dominate. Since kinks play a significant role in the presence of oxygen in hydrogenation and dehydrogenation activity, it would be essential to study surfac with varied kinked concentrations, keeping the terrace width the same. This was carried out using a series of kinked platinum surfaces[22] that are shown in Figure 15. Surfaces that were studied had two, three and four atoms between the kinks respectively. Figure 16 shows the dehydrogenation rates as a function of oxygen surface concentration for these three kinked surfaces. It appears that the kinked surface with three atoms between kinks is the most active for dehydrogenation. Recent studies by Heine, et al,[23] of oxygen adsorbed on nickel surfaces indicate that the oxygen metal molecular orbitals overlapped the next nearest neighbor metal atoms. As a result it is not surprising that more than two atoms between kinks is needed to obtain the active sites at optimum concentrations to carry out the dehydrogenation reaction. It is also tempting to associate the distance between kink sites with the size of the molecule that is to be reacted. Models to explain the chemical effects of oxygen have been discussed by McCabe & Schmidt with respect to the enhanced bonding of H_2 and CO that they observed on oxidized platinum surfaces. One model postulates that the formation of the surface layer of oxide will result in a change in the electronic structure of the surface platinum atoms. In the oxide the adsorbed oxygen atoms would tend to remove platinum valence electrons and the surface platinum atoms would become more positively charged. This change in electronic structure could affect the binding of hydrogen and hydrocarbon reactants, intermediates and products to the catalyst surface which in turn could change the rates and selectivity of the observed reactions. Since the presence of high concentrations of step and kink defect sites has a large effect already on the electronic structure of the clean platinum surfaces, the formation of a surface oxide might change the electronic structure of each surface site differently giving rise to the observed structure sensitivity of hydrocarbon reactions upon preoxidation. McCabe & Schmidt have determined tha oxide covered platinum surfaces have new binding sites for both hydrogen and carbon monoxide with significantly higher binding energies than on the clean surfaces. In addition they observed that the initial sticking coefficient for hydrogen is higher by almost a factor of 2 on the oxidized surface, falling to a low value as soon as the higher binding energy state was populated. This enhanced bonding of hydrogen could explain the large increase in hydrogenation activity of cyclohexene to cyclohexane observed. Upon low temperature adsorption of oxygen on platinum, the work function increases by about 1 eV. With igh temperature oxidation, on the other hand, the work function has been shown to decrease by about 1 eV. This decrease would seem to indicate that oxidation leads to adsorbed oxygen atoms beneath the surface platinum atoms. The positively charged surface metal atoms would thus be readily available for bonding with hydrogen and hydrocarbons.

The second model proposes that strongly adsorbed oxygen atoms are active in compound formation with other adsorbates such as hydrogen and hydrocarbons; such oxygen containing compounds could provide alternate pathways for dehydrogenation or hydrogenation, thus changing the observed reaction rates and selectivity. For example, the formation of hydroxyl groups on the surface might enhance dehydrogenation activity of cyclohexene to cyclohexane. An oxygen atom strongly adsorbed at a step or kink platinum site might show different activity for compound formation than an oxygen atom at a (111) terrace site; this could provide an explanation for the observed structure sensitivity of the reactivity and selectivity on oxidized platinum catalysts.

The third model is that the oxidation of the platinum surface results in a reconstruction or rearrangement of the surface atoms. The enhancement of dehydrogenation activity and the change in selectivity could then be postulated to arise from the creation of new active sites during this rearrangement. The structure sensitivity could arise from a variation in the ease of reconstruction from surface to surface. Platinum dispersed as small particles on oxide supports has been observed to exhibit increased mobility under oxidizing atmospheres. LEED observations indicate that the Pt(110) surface reconstructs after extensive heating in oxygen. A similar surface rearrangement has been observed by Amariglio and coworkers[25] to occur on platinum and nickel during the synthesis of water from oxygen and hydrogen and they postulate that sites formed by this reaction are active for ethylene hydrogenation. The mechanism they propose cannot be used to explain our results, however, due to lack of reactivity of the strongly bound oxygen with hydrogen under our experimental conditions.

The enhancement of reactivity in all these hydrocarbon reactions by low oxygen coverages seems too large, on the kinked surface, to be explained by surface reconstruction with the creation of new active sites, especially in view of the observation that the LEED pattern from the platinum substrate did not change significantly with oxygen coverage for any of the surfaces studied. It seems that change in the electronic structure of the platinum surface atoms, due to the preoxidation and/or the formation of the surface compounds involving oxygen must be largely responsible for the observed enhancement and change in selectivity. Apparently the presence of platinum kink sites promotes particularly favorable surface electronic changes and enhances compound formation. Although the formation of hydroxyl groups might be important in the observed hydrogenation activity, the decrease in the work function observed with the strongly bound oxygen leads to an interpretation that a significant proportion of the adsorbed oxygen is below the platinum surface atoms and prompts us to believe that compound formation is not the primary mechanism for enhancement of dehydrogenation activity.

6. The Effect of Potassium During 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. The main product of the reaction is methane at 6 atm using a hydrogen-to-carbon-monoxide ratio of 3 to 1 at 300 C. A buildup of a carbon multilayer is the cause of the drastic reduction of the reaction rate. Similar poisoning occurs when the reaction is carried out on an iron surface that was 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.

The resistance to poisoning and the catalytic activity can be altered, however, by the addition of $\sim$0.5 to 1 monolayer of potassium.[5] 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 Figure 17. The clean iron is completely poisoned by the presence of potassium. 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 treated with potassium at a temperature of about 200 C however, the catalytic activity and resistance to poisoning is markedly improved. The initial high rates of hydrogenation of carbon monoxide may be maintained for days without any apparent deterioration. The reason for the maintenance of continued catalytic activity is clearly apparent from the Auger spectra of the potassium-treated iron oxide surface after the chemical reaction. All peaks, potassium, oxygen and iron, are clearly displayed indicating that potassium stabilizes the iron oxide that otherwise would be unstable in the CO/H_2 reaction mixture. It appears that by a catalytic side reaction potassium prevents the buildup of carbon on the transition metal surface.

7. The Effect of Small Amounts of Olefin Addition to CO/H_2 Mixture During Carbon Monoxide Hydrogenation over Iron Surfaces

During the H_2/CO reaction has been investigated over Fe(111) single crystal surfaces. Under the reaction conditions (6 atm, 3:1 H_2/CO, 300 C) the dominant product was methane (85 mole %) with small amounts of ethylene and propylene, (11 mole % and 3 mole % respectively). Due to the low surface area of our catalyst (approximately 1 cm^2) the total conversion was less than 1%. The addition of ethylene or propylene in small concentrations, 0.04 to 2.7 mole % to the reactant stream resulted in a product distribution with large concentrations of high molecular weight hydrocarbons.[26] Figure 18 shows how the product distribution changes as a function of partial pressure of ethylene. Clearly the addition of ethylene gives rise to the formation of higher molecular weight hydrocarbons that are the results of a polymerization reaction. It appears that ethylene and propylene act as chain initiator and propagators to form a variety of high molecular weight hydrocarbons. These results suggest that readsorption and secondary reaction of the initially produced olefins is an important pathway leading to the formation of large molecular weight hydrocarbons during Fisher-Tropsch synthesis. In the first step, CO and H_2 produces methane and small amount of olefins. The olefins, primarily ethylene and propylene, readsorb on the surface and form free radicals which help the polymerization of CO and H_2 to form high molecular weight, long chain hydrocarbons.

8. The Building of Platinum and Other Transition Metal Catalysis

The atomic scale investigation of the reactivities of well characterized platinum crystal surfaces revealed the importance of irregularities (steps and kinks) and additives (carbonaceous deposits, oxygen, etc.) to tailor the activity and selectivity of the catalyst. It appears that the catalyzed hydrocarbon conversion does not occur on platinum alone, but takes place on a complex platinum-additive system where both the surface structure and composition are finely adjusted to optimize activity and selectivity. In dispersed catalyst systems the support can also play a significant role in adjusting the catalytic behavior by aiding or eliminating side reactions or by stabilizing the structure and/or the oxidation state of the catalyst surface atoms by the metal support interaction.

Once these ingredients of hydrocarbon catalysis by platinum are uncovered, the question arises how we can put this information to the best use. It would be desirable to deposit platinum particles with controlled surface structure and additive composition. One may be able to minimize the amount of catalyst needed by depositing particles with surface structures of optimum activity, thereby saving much of this precious metal for other applications. Alternately, it might be possible to explore ways to substitute for platinum by systematically probing the effects of other metals and other additives on the platinum catalytic activity. Studies to build platinum and other catalysts to perform desired selective chemistry or to find substitutes for platinum or other precious catalysts (rhodium, palladium and iridium, for example) are in their infancy. Nevertheless, several approaches are being attempted and some of these will be described below.

Ultimately, one would like to maintain control over both the atomic surface structure and surface composition of the synthetic catalyst system. One way to achieve this is by epitaxial deposition of the metal, layer by layer, on ordered substrates (supports). Under proper circumstances the atomic surface structures of the substrate would control the surface structure of the deposited catalyst monolayer and multilayers. The catalytic activity of the condensed metal film can then be tested by varying its concentration from 10% of a monolayer to several layers and by variation of its surface structure using different atomic surface structure substrates.

Studies of this type have been carried out using gold, copper and tantalum single crystal surfaces as substrates for the deposition of single crystalline platinum film. It appears that platinum in monolayer amounts exhibits very different catalytic chemistry as compared to three or more layers of platinum as a result of strong interaction with the metal substrates. The catalytic activity of platinum monolayer on gold is markedly lower than three or more layers of platinum. As the thickness is increased, the activity of that of the dispersed platinum catalyst is approached.

Deposition of platinum thin films on oxide surfaces have also been carried out. Because of the differences in surface free energies of the oxide and the condensing metal, layer-by-layer growth does not readily occur. Nevertheless, changes in chemical behavior have been identified when the grain sizes of the platinum particles in the evaporated films have been altered.

The effects of adding a second metal to the active transition metal catalyst have been investigated in several laboratories. The two metals may be co-deposited from the vapor phase or from solution, or deposited separately one after the other. Perhaps the most successful approach in this direction of research on new catalyst systems was invented by Sinfelt who discovered vastly different chemical properties of small alloy particles as compared to the behavior of the macroscopic alloy system composed of the same metals. Gold-iridium, for example, when deposited as small particles exhibit complete miscibility as proven by chemisorption studies, while they are almost immiscible according to their bulk phase diagram. Although the structure of these bimetallic clusters, as they have become known, cannot readily be controlled, interesting systematic changes in their catalytic chemistry have been detected as the composition and their conditions of preparation are varied.

Another interesting approach to the synthesis of new catalysts were pursued by Boudart. By noting the similarity between the electronic structure and chemical activities of platinum and tungsten carbide, the chemistry of carbides is being explored in atomic detail in a systematic manner.

As more information becomes available on the role of surface structure, composition and oxidation state and additives in catalyst systems, new avenues to synthesized catalysts with desired selectivity and activity will be explored. There are many exciting discoveries in store for those pursuing these paths of catalytic investigations.

Conclusions

Additives, in addition to irregularities, clearly play significant roles in controlling the chemistry of catalytic reactions. There is an intimate interplay between bonding of 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 a stable reaction byproduct that would otherwise rapidly poison the catalytic reaction. These are some of the important properties of additives that are either deposited during the reaction or added purposely before the reaction commences. 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. ¶It appears that the working heterogeneous catalyst is a finely tuned, buffered system. The relative concentrations of various surface sites -- steps, terrace atoms and kinks--and appropriately placed additives determine the activity and selectivity of the catalyst. At present, most of the surface science research in heterogeneous catalysis is concerned with finding out how good catalysts work. Once an understanding of the working catalyst on the atomic scale is reached, improvement of catalytic activity is almost automatic. Research into ethylene oxidation by silver, hydrocarbon conversion by platinum and nickel, ammonia oxidation, hydrogenation of carbon monoxide by a variety of transition metals and studies of the amonia synthesis by iron and ruthenium are all in progress. Studies of catalyst deactivation and poisoning by sulfur and nitrogen are also major topics of modern surface science research. The next stage of development is to build new catalysts. This will be achieved by close control of the structure and, separately, the composition of the catalyst surface. Solid state chemistry and surface science will play significant roles in this endeavor. Epitaxial deposition of metals on other metal and on oxide substrates of well defined structure and composition is one of the approaches toward this goal. Studies of metal-organic clusters in solution and on a variety of surfaces is another approach to building new catalysts. Studies of alloy monolayers can also lead to great advances in discovering new catalytic behavior. These different research directions will likely also verify the correlations that exist between heterogeneous catalysis and catalytic reactions that take place at the solid-liquid interface. Correlations between heterogeneous and homogeneous catalysts are also likely to be uncovered in the near future. Relationships between heterogeneous and enzyme catalysis is another important area ripe for surface science studies. In all cases of basic studies of heterogeneous catalysis, one uses a combination of dynamic studies with static surface analysis. This combination is the key to the understanding of selective chemistry of a variety of catalytic systems.

The future of surface science, as applied to catalysis, is very bright indeed. Other fields, in addition to catalysis like corrosion, electrochemistry, adhesion, friction, studies of mechanical properties of interfaces as related to their chemical properties, will all benefit from a surface science approach. It has been recognized that many surface science based technologies are in the center of energy technologies as well.

In an atmosphere of great need for surface science knowledge in a variety of technologies, I would like to warn against the initiation of overly conservative research programs. It is important, especially for young scientists, to enter new fields of surface science and surface science related technologies. Young scientists could establish their own fields by studying a particular surface phenomena (antiferromagnetism at surfaces, the kinetics of melting or other orderdisorder phenomena, etc.) new materials (surfaces of organic solids, oxides, alloys, etc.) that have not been explored in detail before and new interfaces (solid-liquid, solid-solid). Only in this way will the promise of surface science to provide answers, on the atomic scale, to important questions of science and technology become a reality.

Acknowledgement

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Figure Captions

Figure 1. Apparatus for carrying out reactions at high and low pressures (10^{-8} and 10^5 torr) using small area (∿ 1 cm^2) samples that are characterizes with various disgnostic techniques.

Figure 2. Pressure dependence of the percent conversion of CO and H_2 to benzene.

Figure 3. LEED patterns and schematic representations of three types of fcc crystal surfaces: (a) $\bar{1}11$ orientation containing less than 10^{12} defects per cm^2; (b) $\bar{5}57$ with 2.5×10^{14} step atoms per cm^2 and 6 atom-wide terraces between steps; and (c) $\bar{6}79$ surface with 2.3×10^{14} step atoms per cm^2 and 7×10^{13} kink atoms per cm^2. The average spacing is 7 atoms between steps, and 3 atoms between kinks.

Figure 4a. Heats of chemisorption of carbon monoxide for polycrystalline surfaces of elements in the periodic table.

Figure 4b. Heats of chemisorption of carbon monoxide for various crystal faces of elements in the periodic table.

Figure 5a. Heats of chemisorption of hydrogen for polycrystalline surfaces of elements in the periodic table.

Figure 5b. Heats of chemisorption of hydrogen for various crystal faces of elements in the periodic table.

Figure 6. Catalytic activities of metals for ethane hydrogenolysis.

Figure 7. Schematic representation of the heterogeneous surface on the atomic scale. Terrace, step and kink atoms as well as point defects have been identified by experiments.

Figure 8. Scheme of the molecular beam-surface scattering experiment.

Figure 9. The reaction probability to produce H-D upon single scattering of a mixed H_2-D_2 molecular beam on a stepped platinum surface as a function of the angle of incidence.

Figure 10a. Cyclohexane dehydrogenation to benzene and hydrogenolysis to n-hexane as a function of step density.

Figure 10b. Cyclohexane dehydrogenation to benzene and hydrogenolysis to n-hexane as a function of kink density at constant step density of $2.0\times10^{14}/cm^2$.

Figure 11. Schematic representation of surfaces exhibiting 1 atom height step configuration, multiple height step structure and hill-and-valley configuration consisting of large facet planes. Reconstruction from one type to another type occurs on adsorption..

Figure 12. Ethylidine molecule that forms upon the adsorption of ethylene or acetylene on the Pt(111) crystal face.

Figure 13. Thermal desorption of CO from rhodium after various treatments (a) clean surface, (b) ion bombarded surfaces, (c) heated in $CO-H_2$ at 10^6 torr, 300C for 10 minutes, (d) as in (c) but pure CO, and (e) as in (c) but pure CO_2.

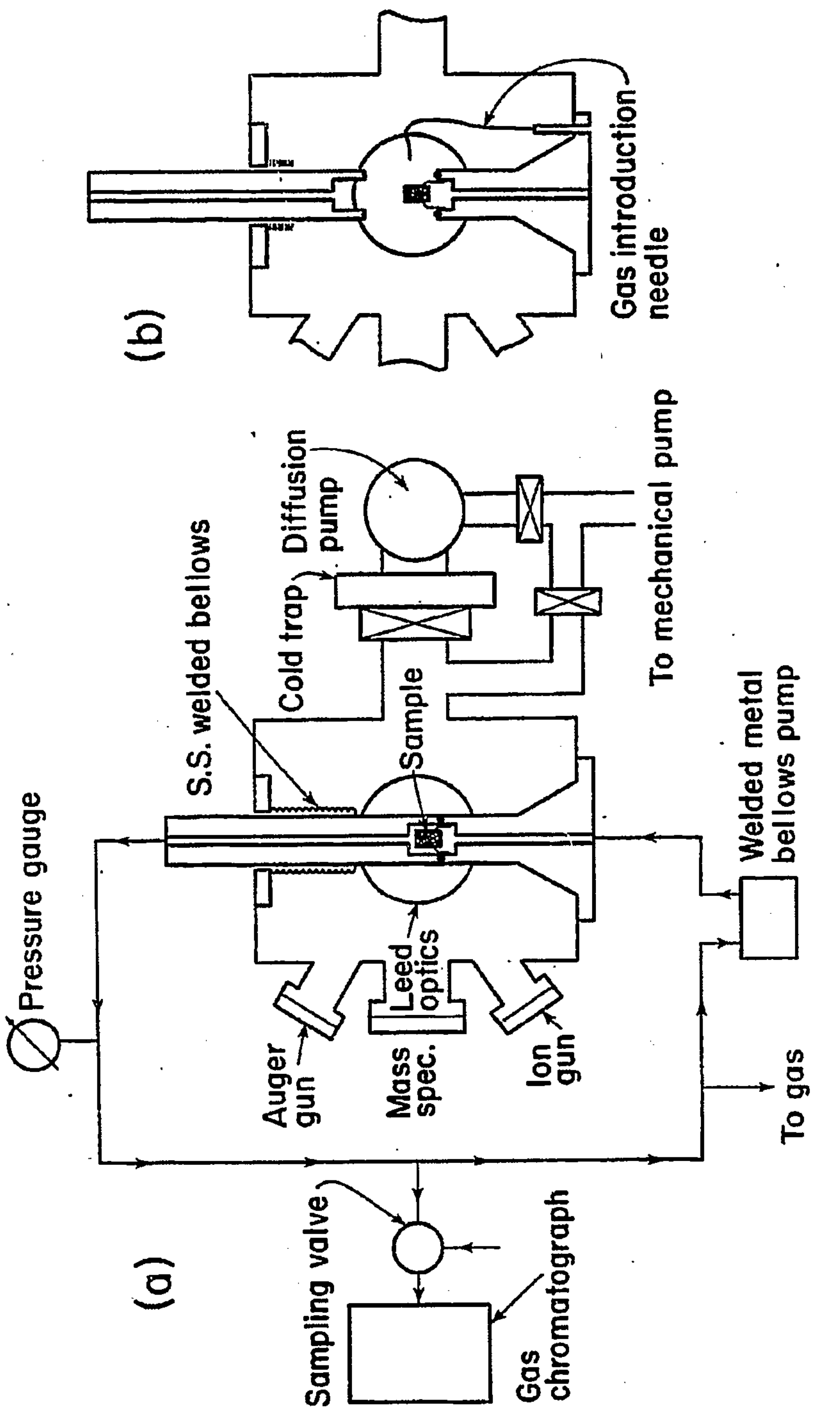
Figure 14. Maximum turnover numbers for benzene production from cyclohexene and for cyclohexane production from cyclohexene as a function of oxygen coverage on the Pt(S)-[7(111)x(310)] kinked surface showing the change in selectivity of dehydrogenation over hydrogenation. Reaction conditions: catalyst temperature 150°C, cyclohexene pressure $6x10^{-8}$ torr, hydrogen pressure $1x10^{-6}$ torr.

Figure 15 Schematic diagrams of atomic surface structures from kinked platinum surfaces and LEED patterns from the same surfaces.

Figure 16. The effect of oxygen on the dehydrogenation of cyclohexene at 150°C on the four different kinked platinum surfaces.

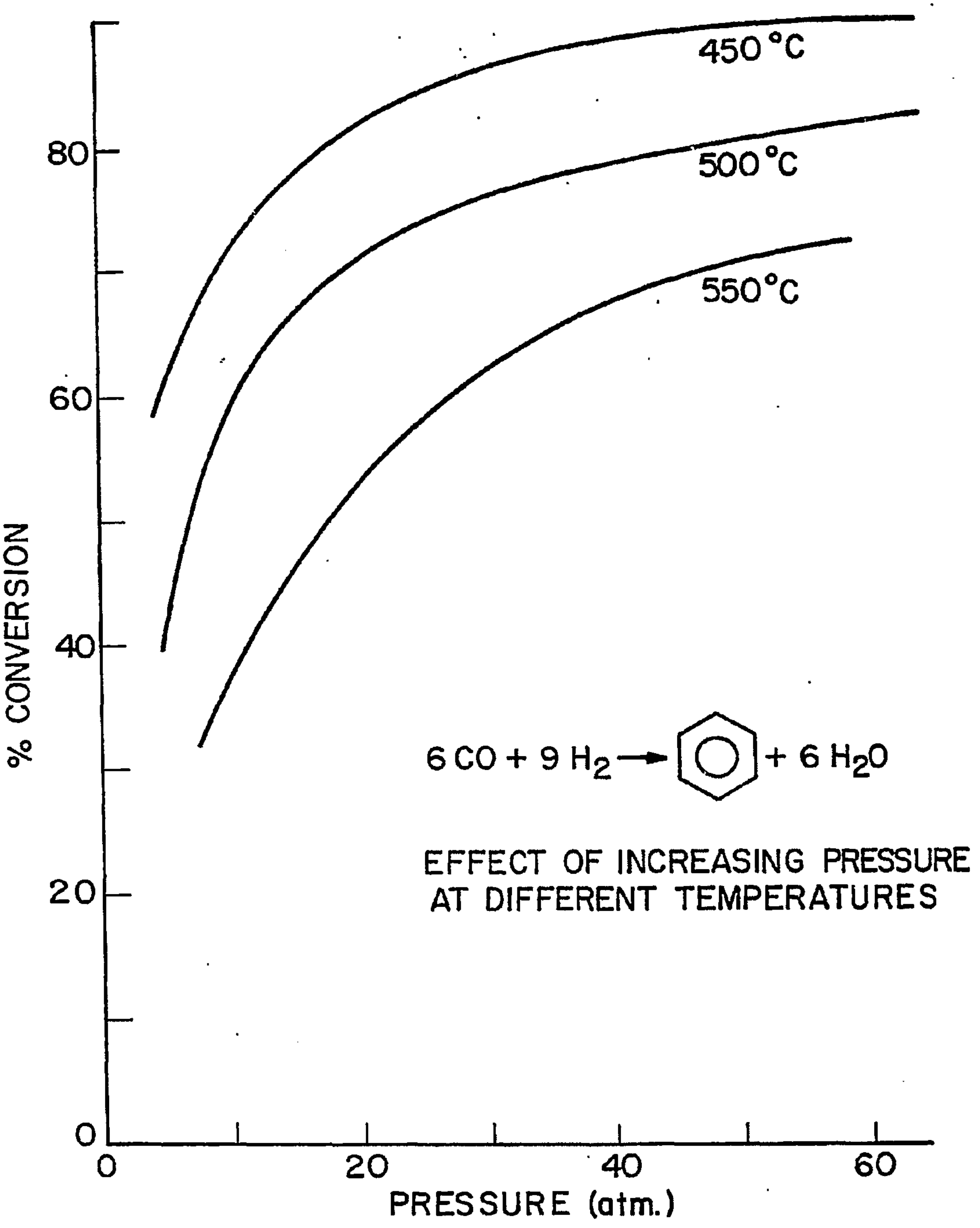
Figure 17. Methane production from $CO-H_2$ mixtures using potassium covered iron and oxidized iron surfaces.

Figure 18. Product distribution for fixed reaction conditions (6 atm. 3:1 H_2/CO) 300°C) as a function of added ethylene over iron surfaces.



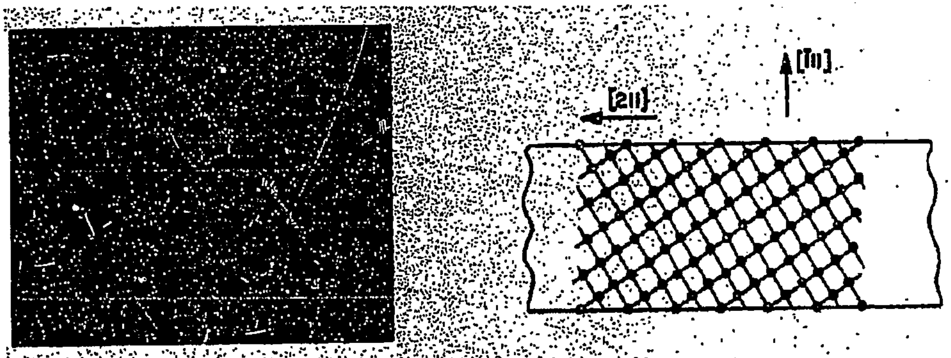
XBL 756-3160

Fig.1

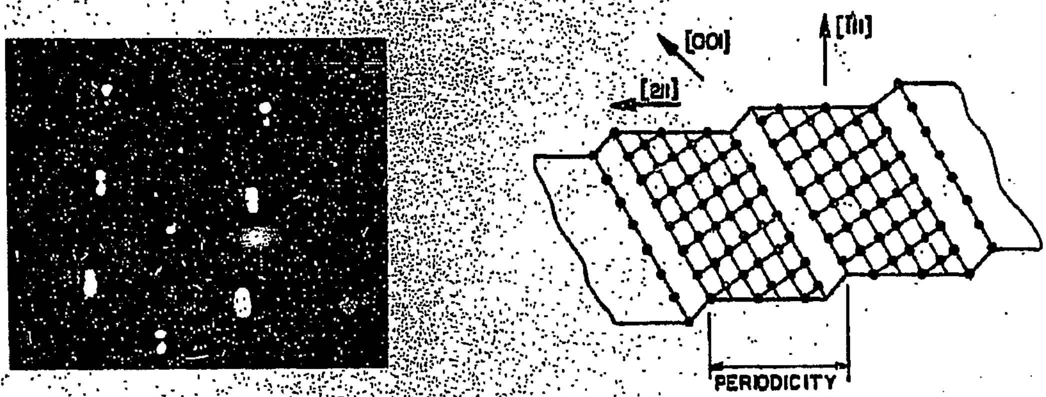


XBL 762-590

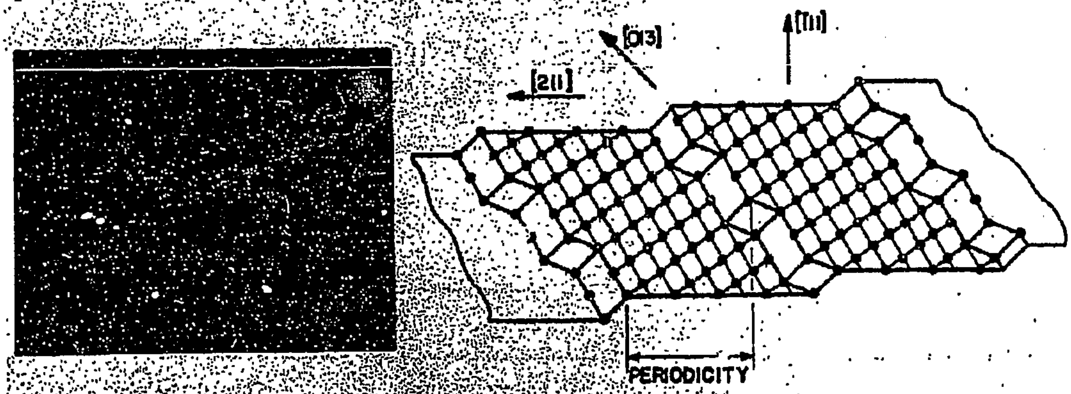
Fig.2



a) Pt-($\bar{1}$11)



b) Pt-($\bar{5}$57)



c) Pt-($\bar{6}$79)

XBB 758-5903

Fig.3

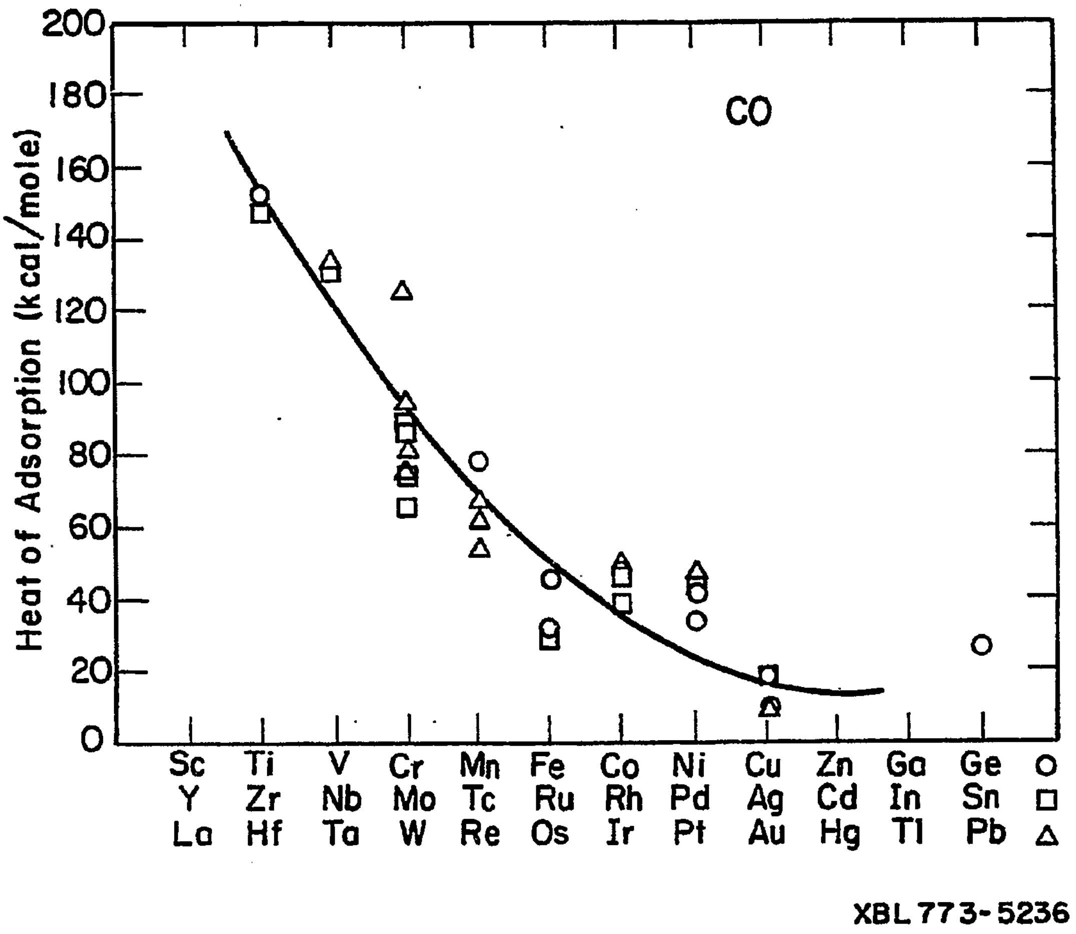
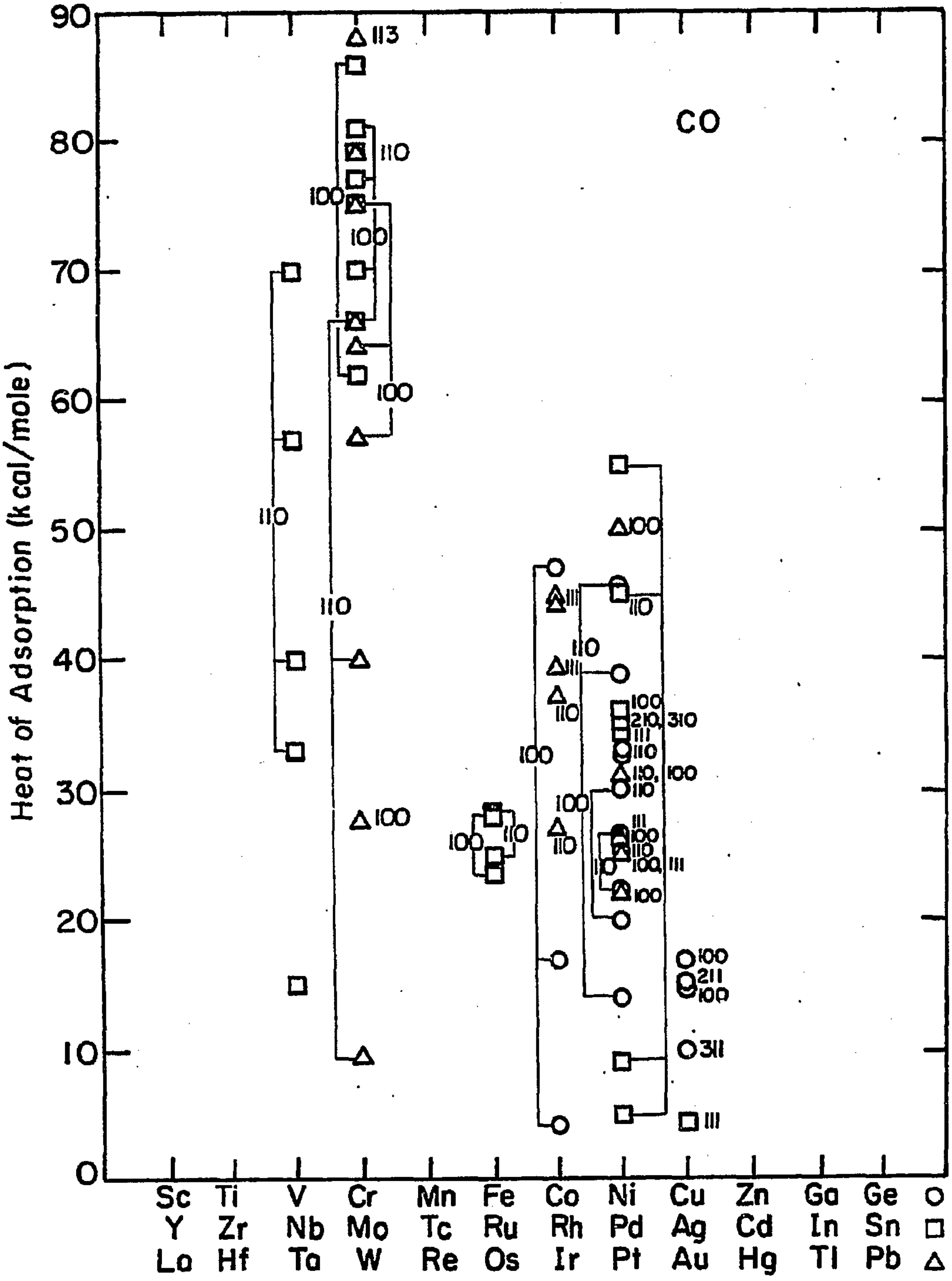
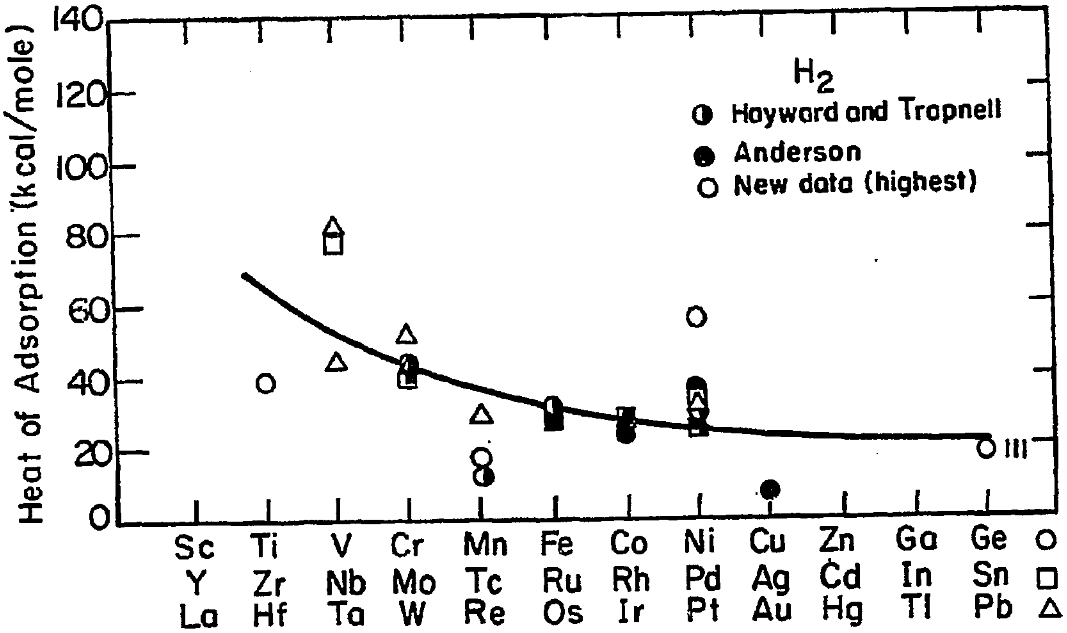

CO
Heat of Adsorption (kcal/mole)
200
180
160
140
120
100
80
60
40
20
0
Sc Y La
Ti Zr Hf
V Nb Ta
Cr Mo W
Mn Tc Re
Fe Ru Os
Co Rh Ir
Ni Pd Pt
Cu Ag Au
Zn Cd Hg
Ga In Tl
Ge Sn Pb
○ □ △
XBL 773-5236

Fig.4a



XBL777-5699

Fig.4b



XBL 777-5700

Fig.5a

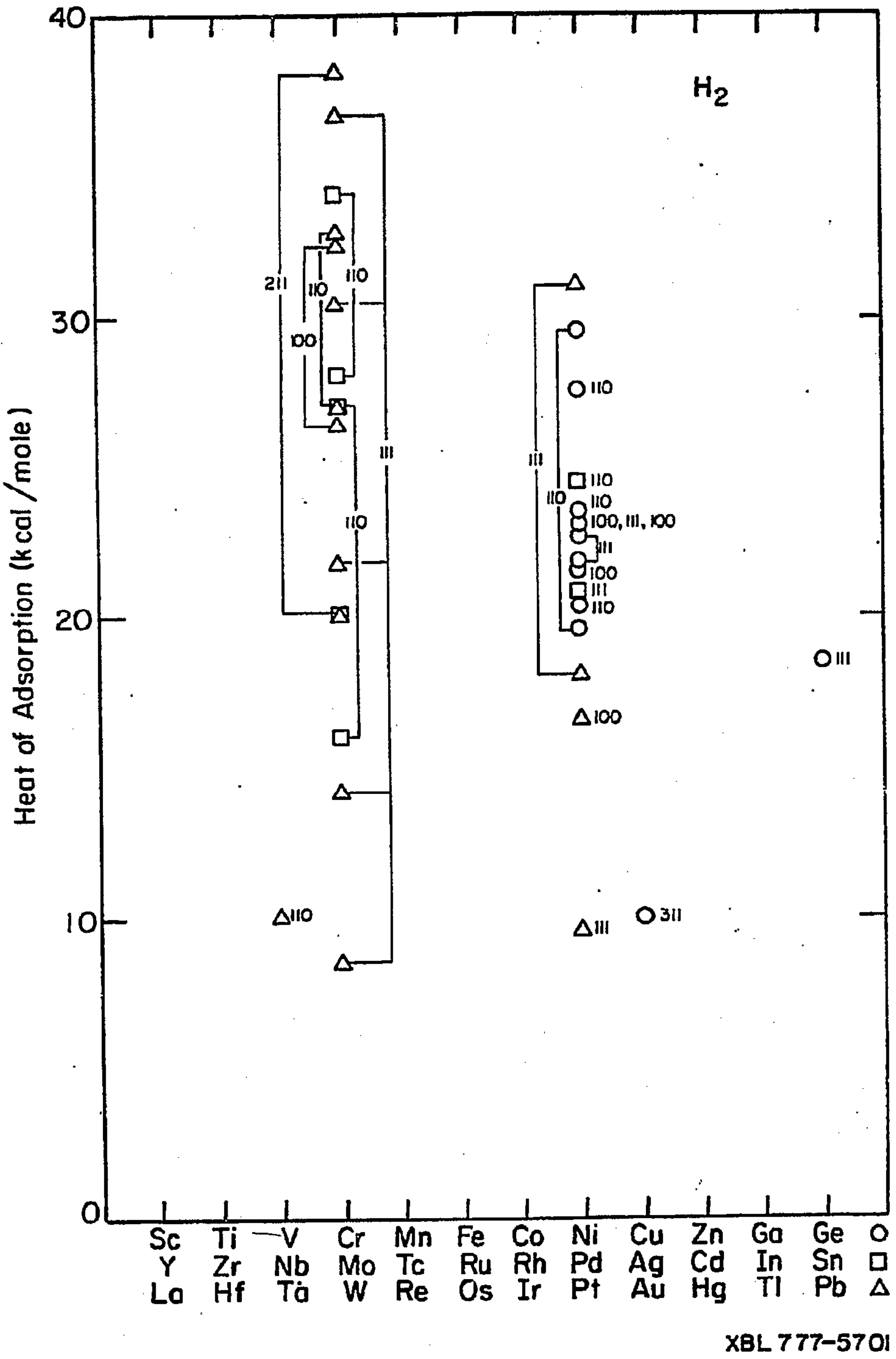

H2
Heat of Adsorption (kcal/mole)
0
10
20
30
40
211
110
100
110
111
110
111
110
110
110
100, 111, 100
111
100
111
110
100
111
111
311
110
Sc Y La
Ti Zr Hf
V Nb Ta
Cr Mo W
Mn Tc Re
Fe Ru Os
Co Rh Ir
Ni Pd Pt
Cu Ag Au
Zn Cd Hg
Ga In Tl
Ge Sn Pb
○ □ △
XBL 777-5701

Fig.5b

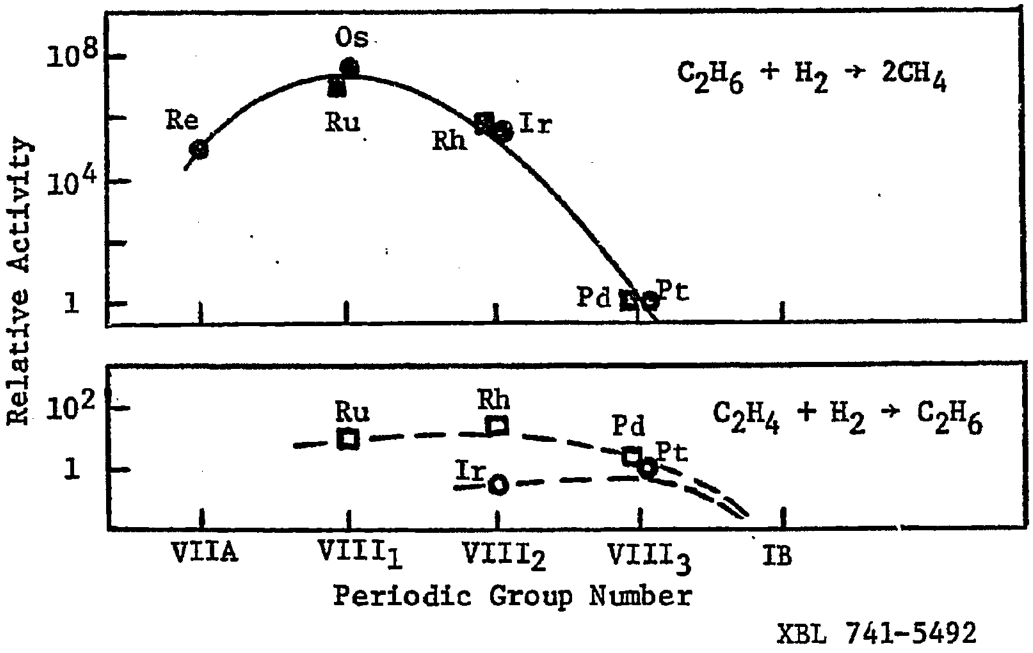
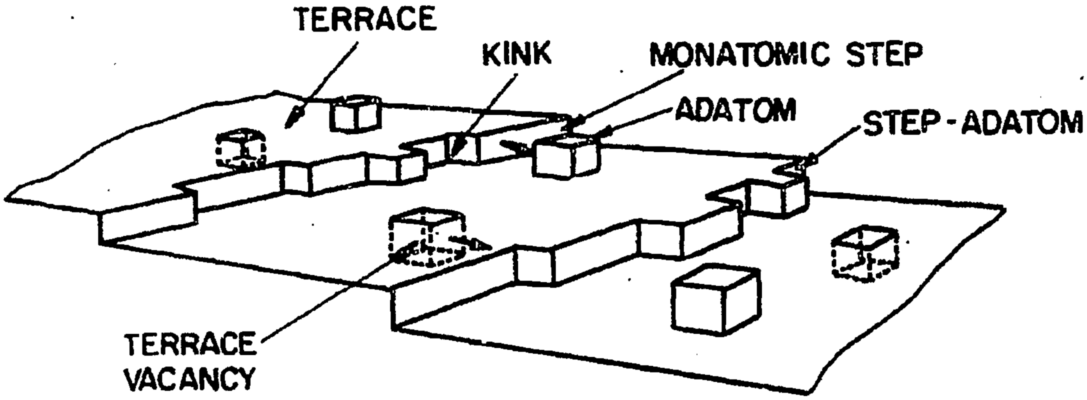

Relative Activity
10^8
10^4
1
10^2
1
Os
Re
Ru
Rh
Ir
Pd
Pt
$C_2H_6 + H_2 \rightarrow 2CH_4$
Ru
Rh
Pd
Pt
Ir
$C_2H_4 + H_2 \rightarrow C_2H_6$
VIIA
$VIII_1$
$VIII_2$
$VIII_3$
IB
Periodic Group Number
XBL 741-5492

Fig.6



XBL 708-1717A

Fig.7

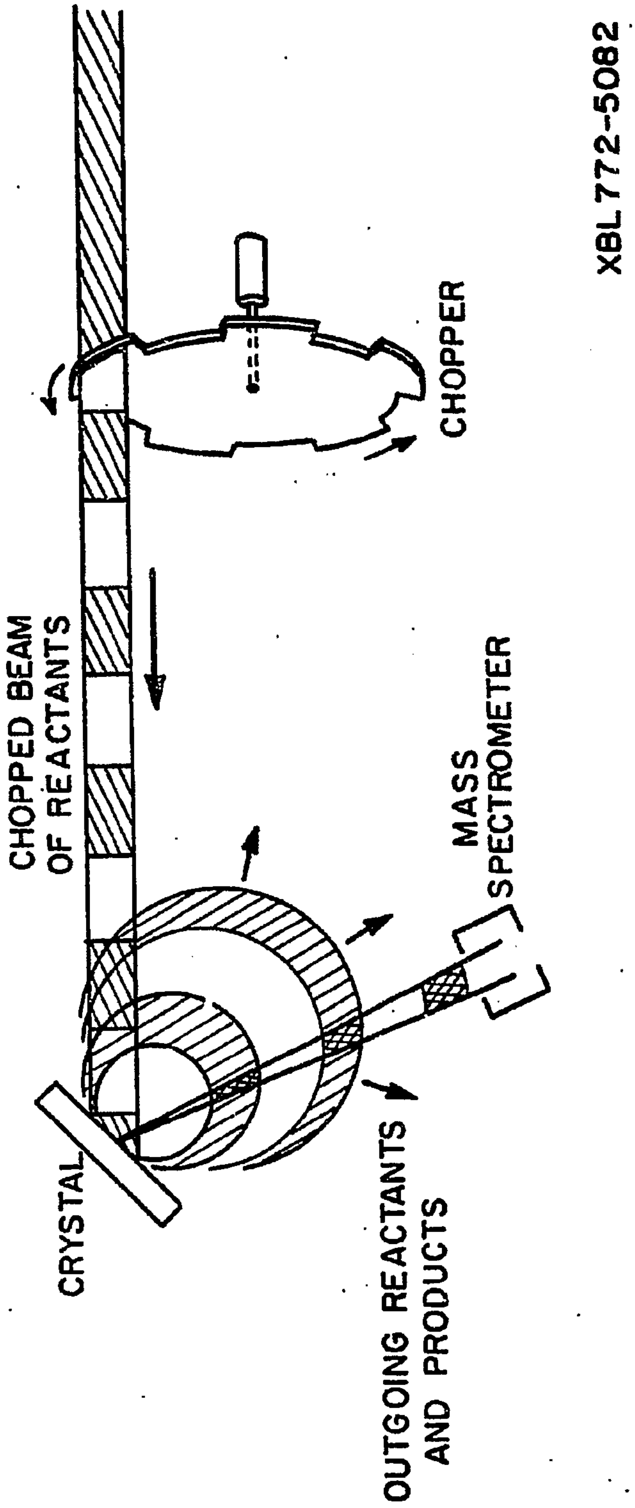

CHOPPER
CHOPPED BEAM OF REACTANTS
MASS SPECTROMETER
CRYSTAL
OUTGOING REACTANTS AND PRODUCTS
XBL 772-5082

Fig.8

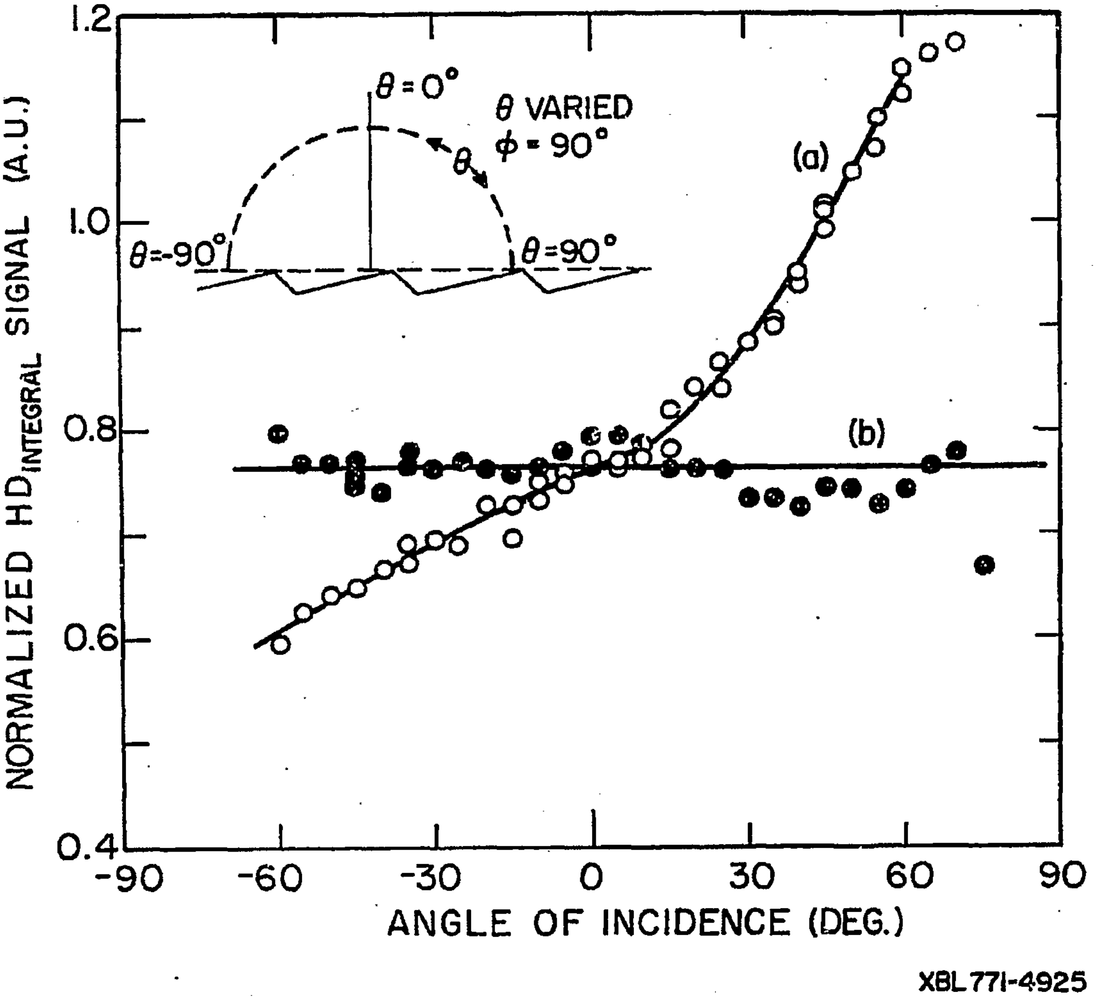

θ = 0°
θ VARIED
φ = 90°
θ
θ=-90°
θ=90°
(a)
(b)
1.2
1.0
0.8
0.6
0.4
-90
-60
-30
0
30
60
90
NORMALIZED HD$_{INTEGRAL}$ SIGNAL (A.U.)
ANGLE OF INCIDENCE (DEG.)
XBL 771-4925

Fig.9

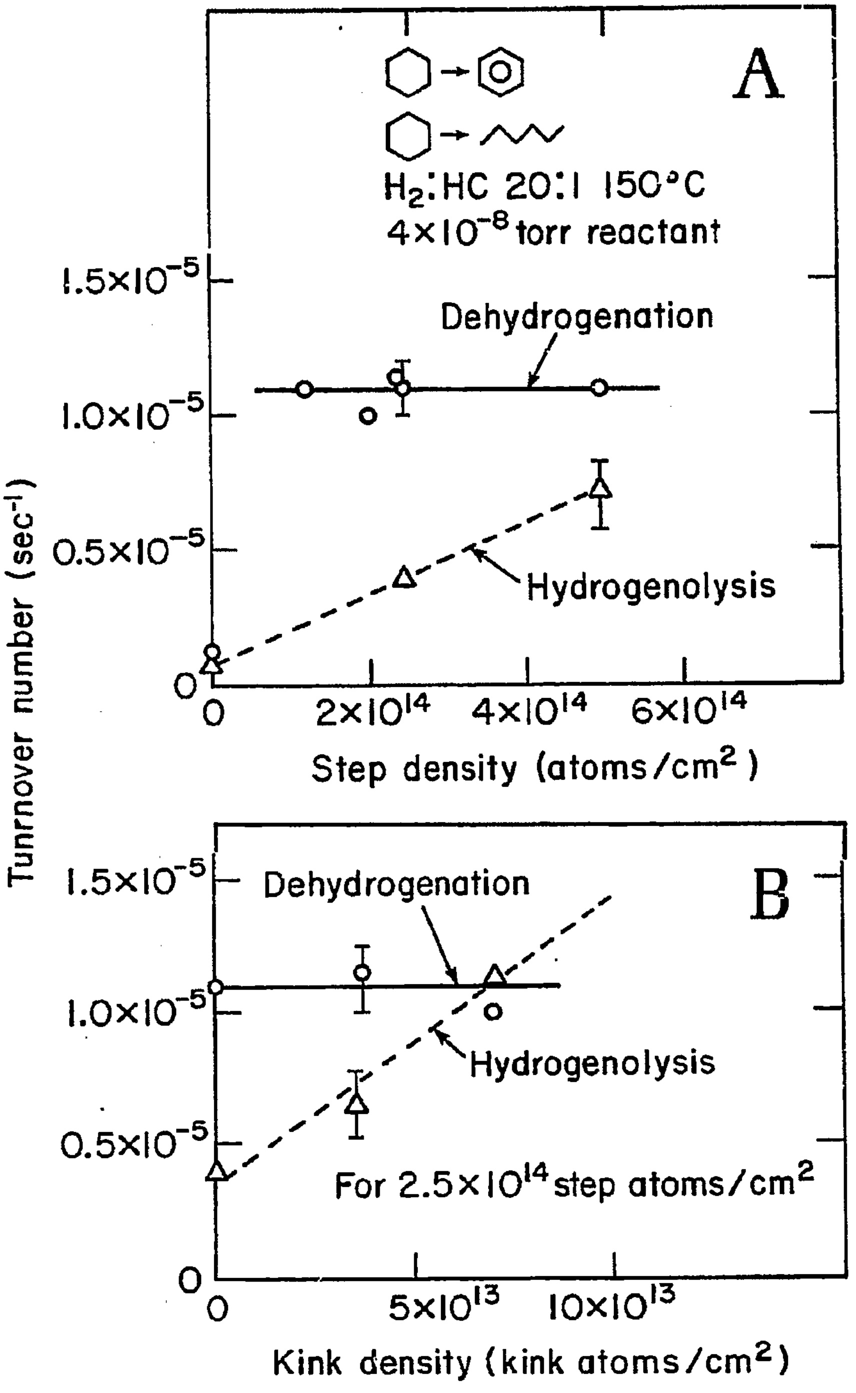
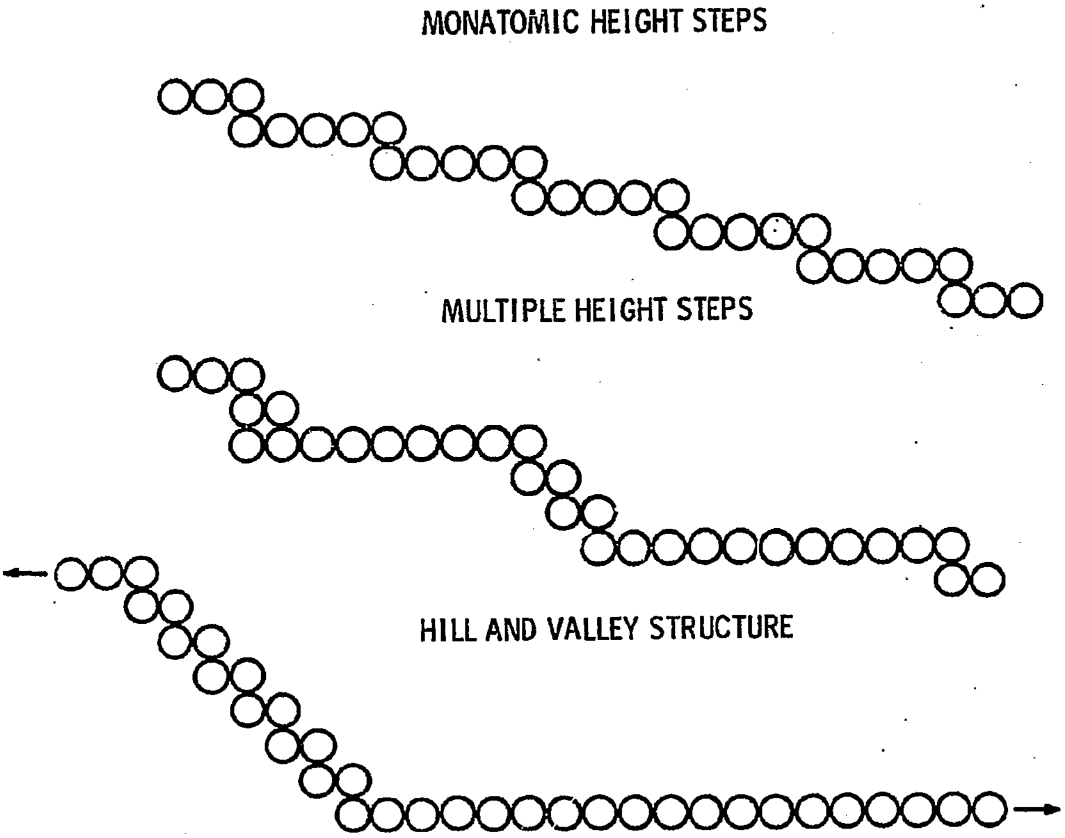


Fig.10a

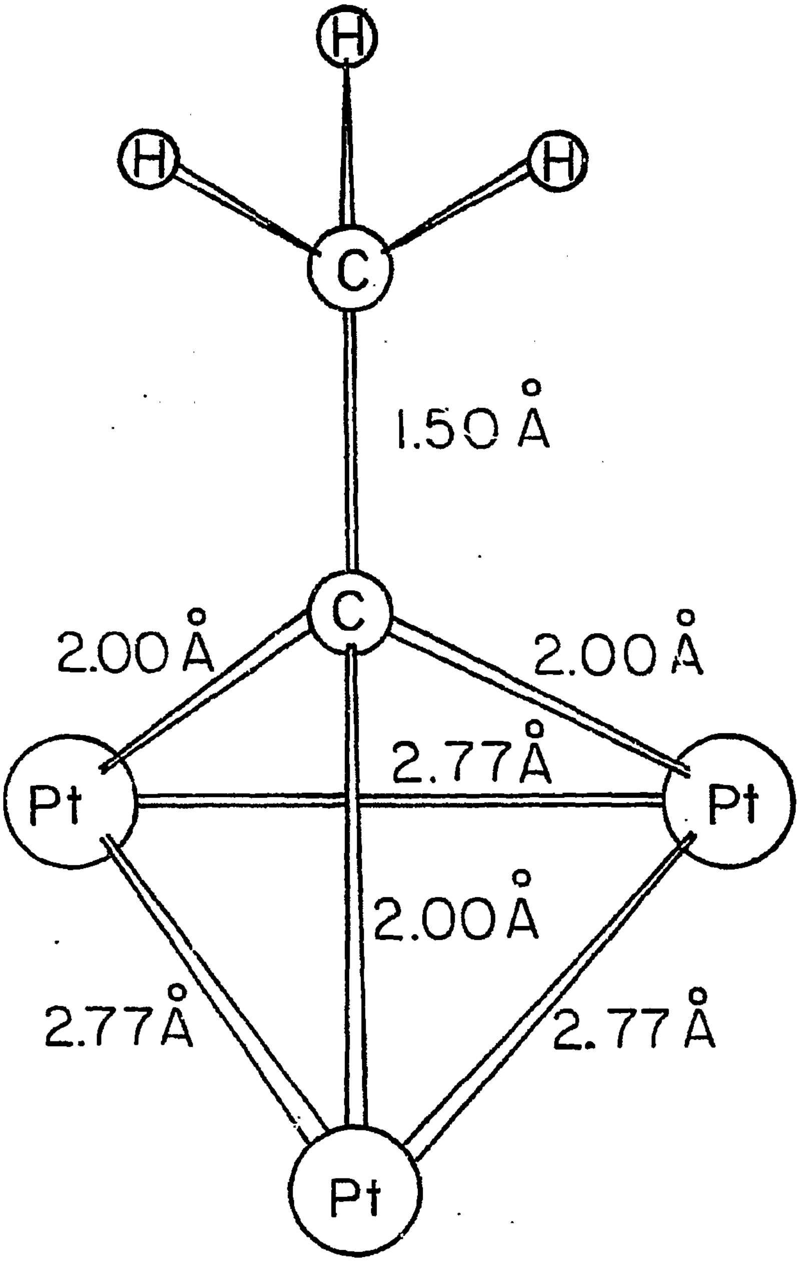
Fig.10b

XBL 756-3163



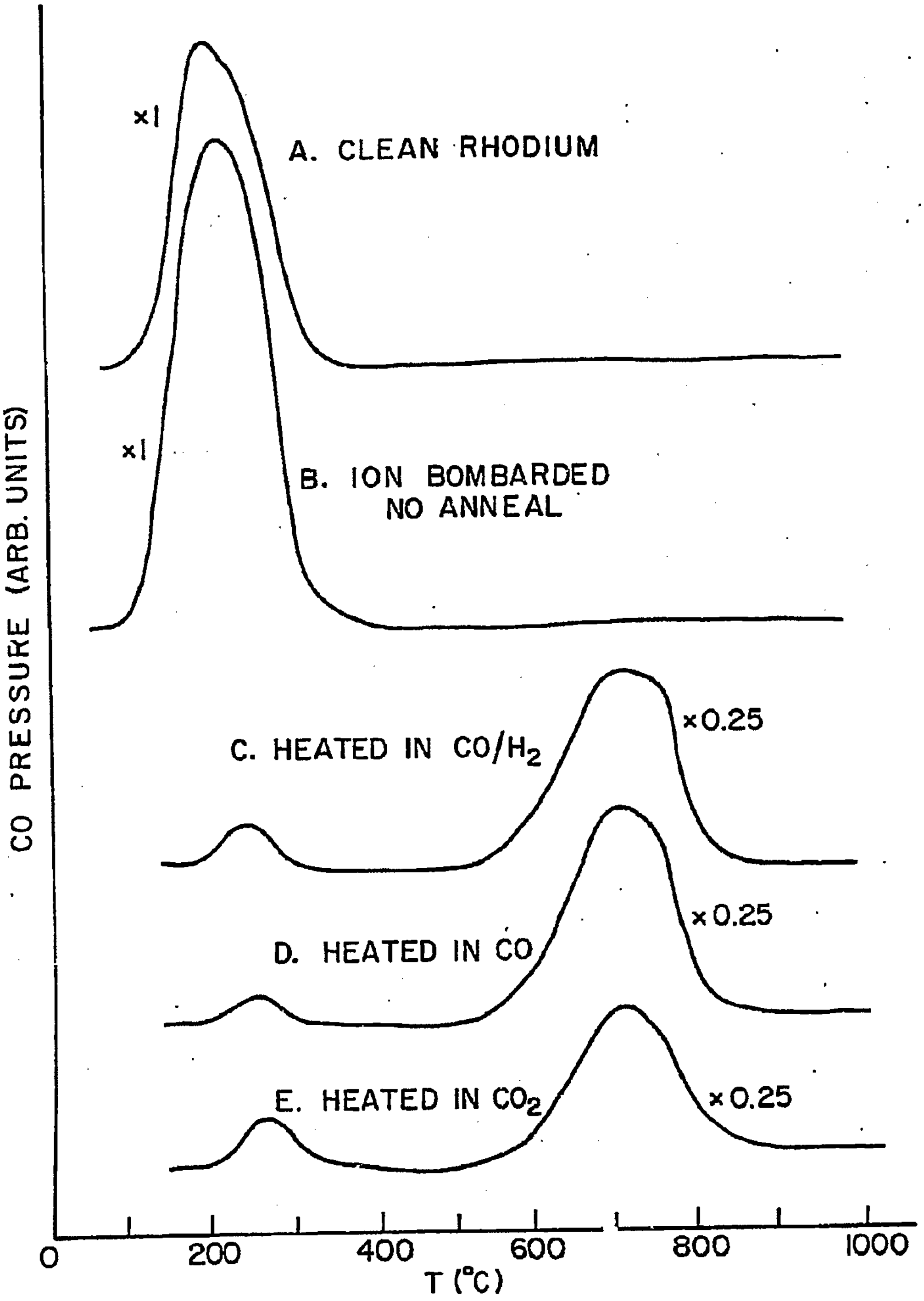
XBL 7612-10984

Fig.11



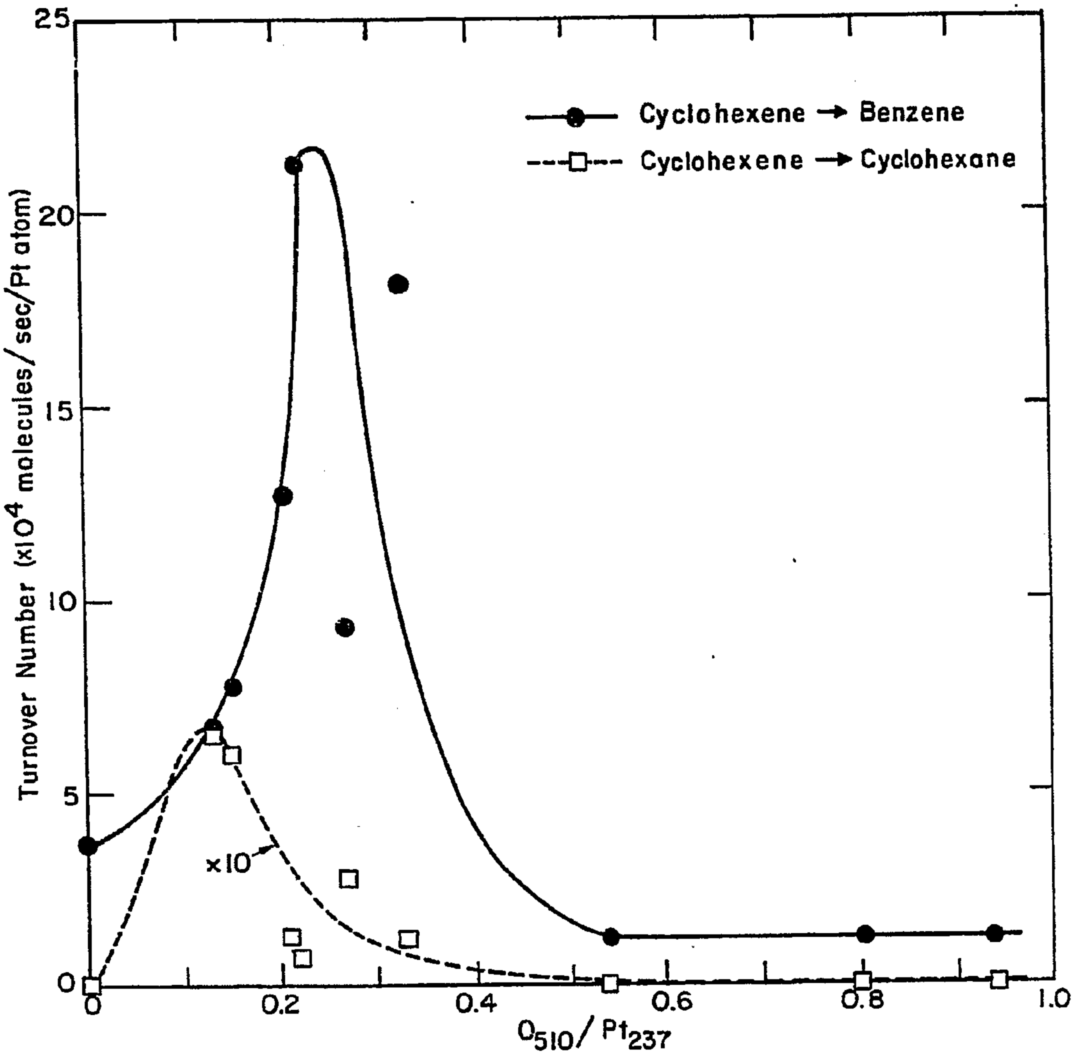
XBL 7712-6591

Fig. 12



XBL 765-6863

Fig. 13



XBL 785-4958

Fig.14

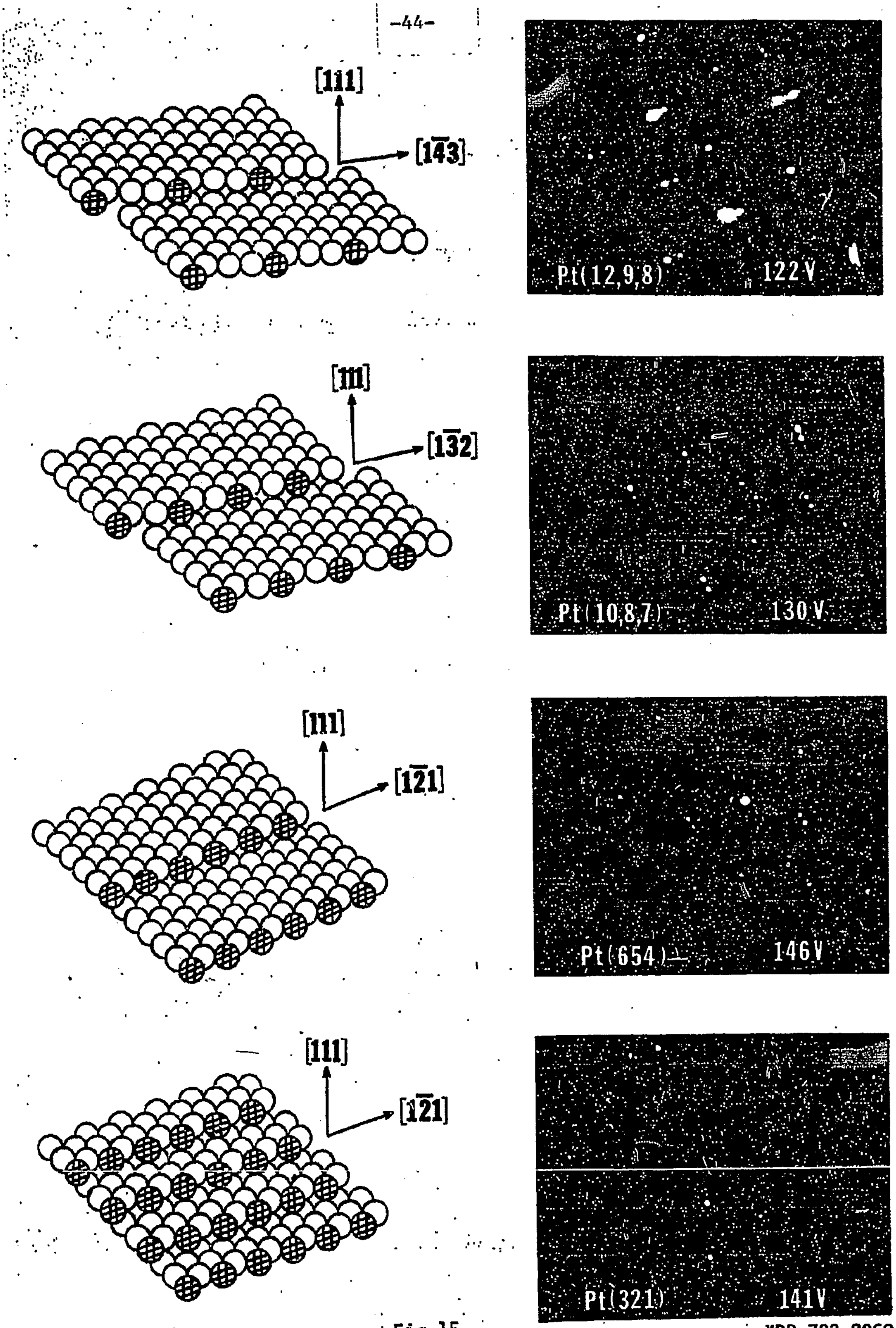
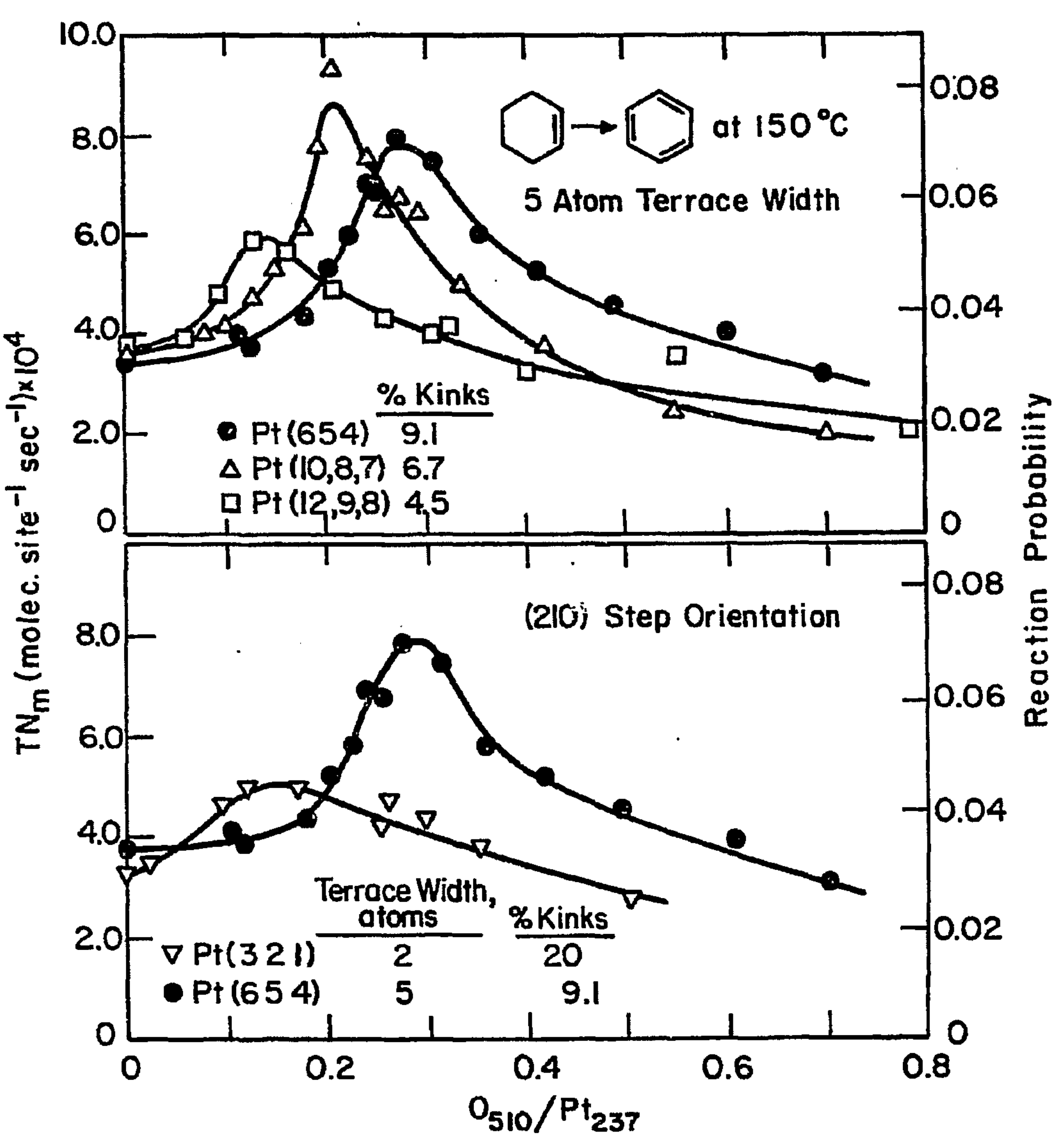


Fig.15

XBB 793-2960



XBL792-5824

Fig.16

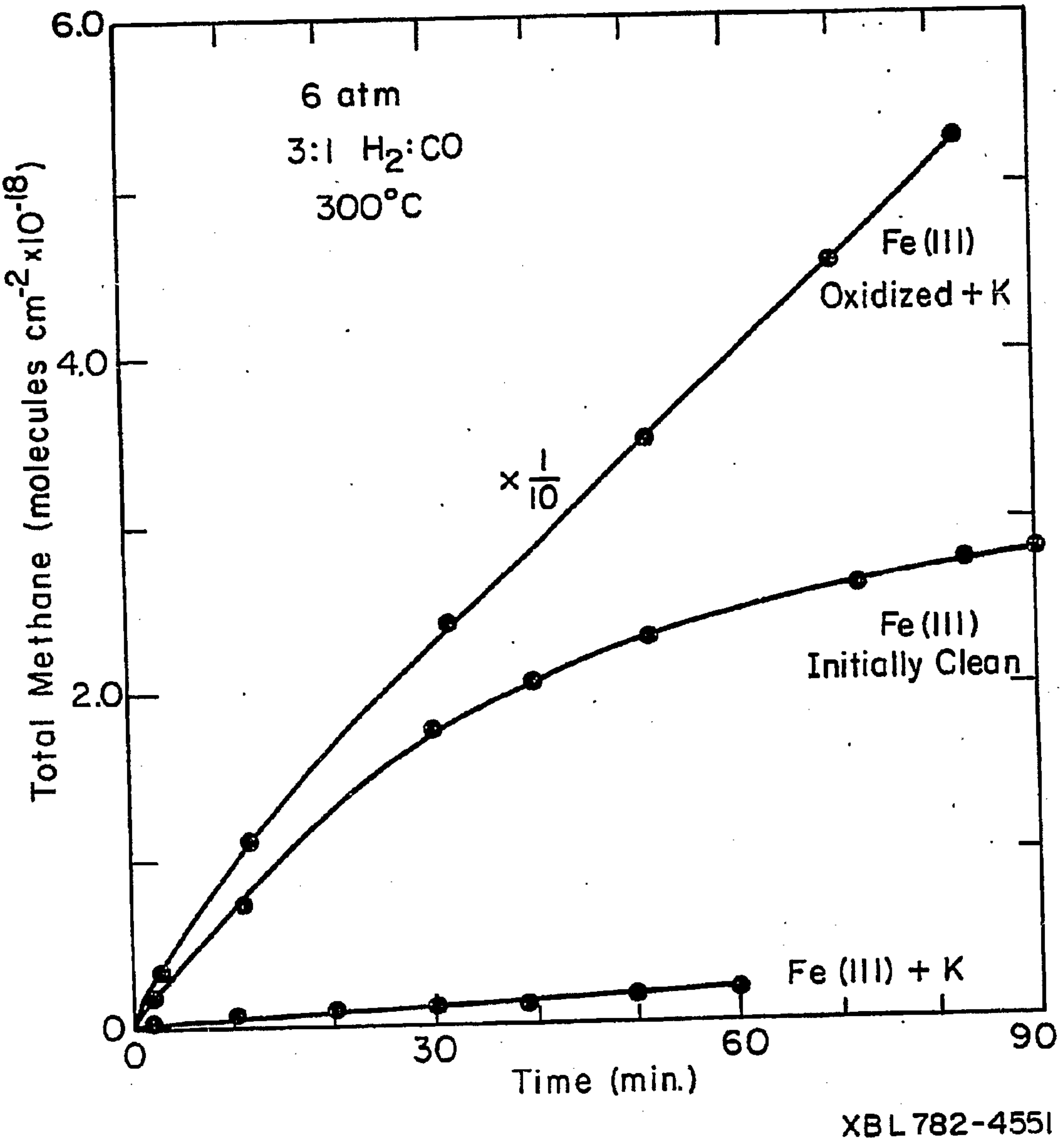

6 atm
3:1 H_2:CO
300°C
Total Methane (molecules $cm^{-2} \times 10^{-18}$)
6.0
4.0
2.0
0
Time (min.)
0
30
60
90
$\times \frac{1}{10}$
Fe (III) Oxidized + K
Fe (III) Initially Clean
Fe (III) + K
XBL 782-4551

Fig. 17

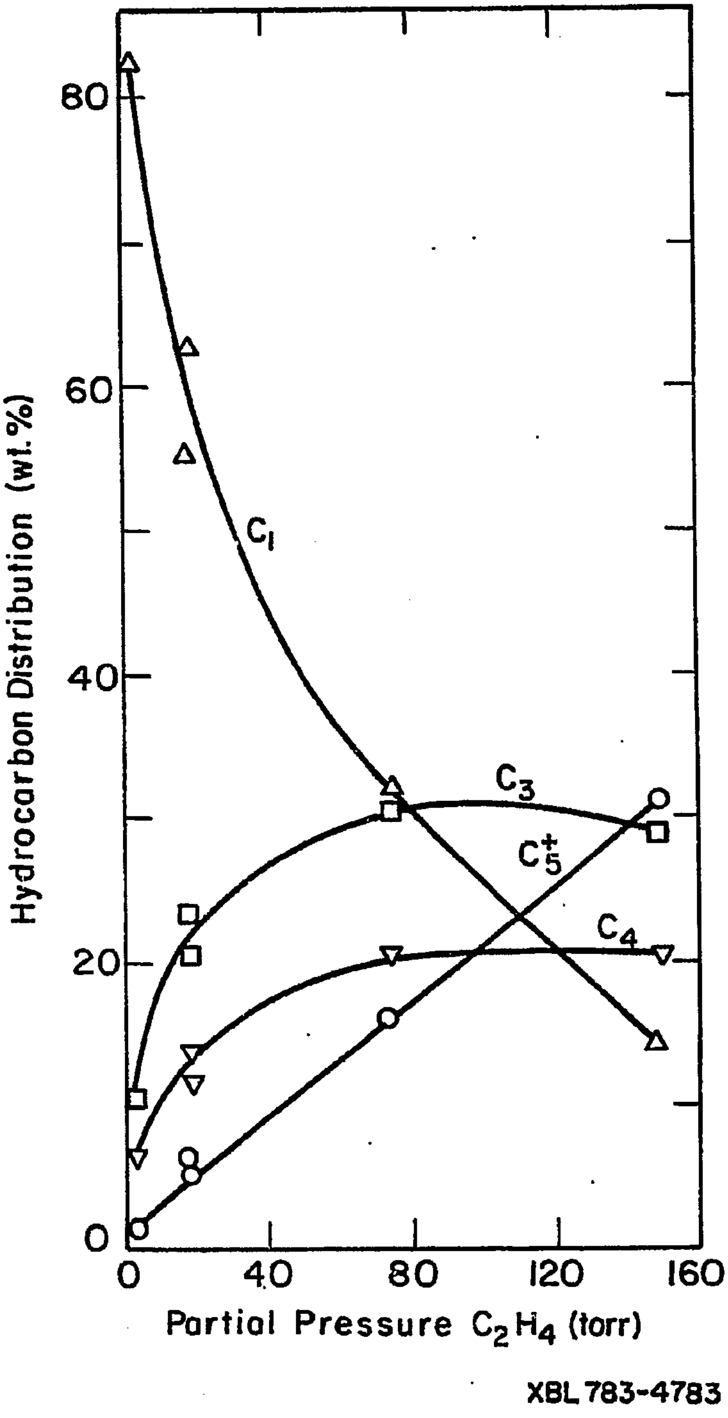

Hydrocarbon Distribution (wt.%)
80
60
40
20
0
0
40
80
120
160
Partial Pressure C_2H_4 (torr)
C_1
C_3
C_5^+
C_4
XBL 783-4783

Fig.18

Table Captions

Table I	Comparison of initial specific rate data for the cyclopropane hydrogenolysis on platinum catalysts.
Table II	Comparison of polycrystalline rhodium foil with 1% rhodium-Al_2O_3 catalyst in the Co-H_2 reaction at atmospheric pressure.

TABLE I

COMPARISON OF INITIAL SPECIFIC RATE DATA FOR THE CYCLOPROPANE HYDROGENOLYSIS ON PLATINUM CATALYSTS

		Calc'd spec reaction rate @ $P_{cp}^0 = 135$ Torr and $T = 75°C$		
Data source	Type of catalyst	(moles C_3H_8/min-cm² Pt)	(molecules C_3H_8/min-Pt site)	Comments
Present study	Run 10A	2.1×10^{-4}		Rate on Pt(s)-[6(111) × (100)] single crystal based on $E^* = 12.2$ kcal/mole.
	Run 12A	1.8×10^{-4}		
	Run 15	1.8×10^{-4}		
	Run 16	2.1×10^{-4}		
	Av	1.95×10^{-4}	812[a]	
Hegedus (*30, 49*) (see Table III-5)	0.04 Wt% Pt on η-Al_2O_3	7.7×10^{-7} based on 100% Pt dispersion	410[b]	
Boudart *et al.* (*17*) and Dougharty (*28*)	0.3% and 2.0% Pt on η-Al_2O_3;	8.9×10^{-7}	480	$\eta_{cp} = 0.2$, $E^* = 8.5$ kcal/mole.
	0.3% and 0.6% Pt on γ-Al_2O_3	2.5×10^{-6}	1340	$\eta_{cp} = 0.6$, $E^* = 8.5$ kcal/mole. (Dougharty reports $E^* = 8$-9 kcal/mole and $n = 0.2$-0.6)

[a] Value based upon 87% (111) orientation and 13% polycrystalline orientation.

[b] Based upon av Pt site density of 1.12×10^{15} atoms/cm². This value would be nearly equal to average of above values if dispersion was approximately 50%.

Table II

Comparison of polycrystalline Rh foil with a 1% Rh/Al_2O_3 catalyst in the $CO\text{-}H_2$ reaction at atmospheric pressure.

	polycrystalline Rh foil (this work)	supported 1% Rh/Al_2O_3 (Vannice)$^{(10)}$
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% $CH_4 \pm 3$ 5% $C_2H_4 \pm 1$ 2% $C_2H_6 \pm 1$ 3% $C_3H_8 \pm 1$ $<1\%$ 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^{-1} sec^{-1}	.034 molecules site^{-1} sec^{-1}
Activation Energy (kcal)	24.0±2	24.0

*data adjusted from 275°C

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