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Gabor A. Somorjai

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Gabor A. Somorjai
 Department of Chemistry, University of California, and
 Lawrence Berkeley Laboratory, University of California,
 Berkeley, CA 94720

1. PREAMBLE

The purpose of this paper is to present a review and status report to my colleagues in theoretical chemistry of the rapidly developing surface science of heterogeneous catalysis. The art of catalysis is developing into science. This profound change provides us with opportunities not only to understand the molecular ingredients of important catalytic systems but also to develop new and improved catalyst. The participation of theorists to find answers to important questions is sorely needed for the sound development of the field. It is my hope that some of the attendees of this conference may be persuaded to tackle some of the outstanding problems of heterogeneous catalysis that I attempt to identify in this paper.

For this purpose the paper is divided into several sections. The brief Introduction to the methodology and recent results of the surface science of heterogeneous catalysis is followed by a review of the concepts of heterogeneous catalysis. Then, we describe the experimental results that identified the three molecular ingredients of catalysis. The a) structure, b) carbonaceous deposit and c) the oxidation state of surface atoms. Each section is closed with a summary and a list of problems that, in my view, require theoretical and experimental scrutiny. Finally we describe attempts to build new catalyst systems and the theoretical and experimental problems that appeared in the course of this research.

2. INTRODUCTION

Modern surface science during the past 15 years developed a large number of techniques that can be utilized to uncover the molecular ingredients of heterogeneous catalysis. The atomic surface structure, the chemical bonding of adsorbates, the composition and oxidation states of surface atoms can all be determined within the sensitivity of less than 1% of a monolayer (about 10^{13} atoms per cm^2) (1). A partial list-

ing of the most frequently employed techniques for surface analysis is displayed in Table 1.

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

The small area single crystals are model catalysts. Models are used frequently in physical sciences to uncover the workings of a complex system. Of course, it must be ascertained that the model system behaves similarly to that of the more complex chemical system that is to be ultimately utilized. The model small area catalysts were compared with dispersed high surface area catalysts in the same reaction under identical experimental conditions. The same turnover rates, product distributions and activation energies were obtained for the ring opening of cyclopropane (3), and the hydrogenation of benzene over platinum (4), and for carbon monoxide hydrogenation over rhodium (5). It appears that for catalyzed reactions that do not exhibit much structure sensitivity, small area crystal and large area dispersed particles of the same metal yield identical catalytic reaction parameters.

We have concentrated our studies of molecular scale catalysis on transition metals which catalyze hydrocarbon conversion reactions and on the hydrogenation of carbon monoxide. Platinum, an excellent catalyst for dehydrocyclization reactions that produce aromatic molecules from alkanes, or for isomerization, was one of the metals we studied intensively. The other was rhodium, which was found to produce oxygenated organic molecules from carbon monoxide and hydrogen, selectively.

Iron that catalyzes ammonia synthesis from nitrogen and hydrogen as well as the CO/H_2 reaction and was also a focus of our investigations. We investigated in detail the photodissociation of water over oxide surfaces and the hydrogenation of graphite to methane; both reactions are catalyzed by alkali metal ions. Out of these studies came the identification of three necessary ingredients of selective molecular scale catalysis.

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

We shall review each of these reaction parameters in order to understand how the catalytic reactions occur after describing some of the important concepts of heterogeneous catalysis.

3. CONCEPTS OF HETEROGENEOUS CATALYSIS

The word "catalyst" was introduced by Berzelius (1836) to describe the property of certain substances which facilitate chemical change without being consumed during the reaction. The original definition has stood the test of time; catalysts aid the attainment of chemical equilibrium by reducing the potential energy barriers in the reaction path. For example, hydrogen and oxygen will remain as an unreacted mixture indefinitely, although in the presence of a platinum or nickel gauze, they react instantaneously to produce water (1).

Catalysis is a kinetic phenomenon. The speed of a catalysed reaction is often described in terms of a "turnover rate", which reveals how many product molecules form per second at a given temperature and pressure.

Since the catalytic action occurs at specific sites on solid surfaces, often called "active sites", the rate can be increased phenomenally by using very high surface area catalysts. Catalysts with surface areas of $1-10^2 \text{ m}^2/\text{gm}$ are quite common. These are usually prepared by finely dispersing the active metal or compound catalyst on high surface area "supports", which usually consist of refractory oxides or oxyhydroxides (alumina, zirconia, silica, etc.) The catalyst dispersion, defined as the number of surface atoms per total number of atoms, may range from unity (all of the atoms are on the surface) to ~ 0.01 and the catalyst particles may range in size between $10-200\text{\AA}$. This dispersed system must maintain structural and chemical stability for thousands of hours under the conditions of high temperature ($400-900\text{K}$) and high pressure ($1-10^2$ atmospheres) frequently encountered in the chemical technology. The design of new, more stable, catalysts which resist chemical attrition and sintering of the small particles is a constant concern of the catalytic scientist.

The specific rate, the number of product molecules per catalyst unit area per second, (or the number of product molecules per surface atom per second) at a given temperature and pressure provides a figure

of merit to compare the "activity" of different catalysts for the same reaction under similar experimental circumstances. Although only a fraction of the catalyst surface is active during the reaction this fraction is usually unknown; thus the specific rate provides a lower limit of the catalyst's activity.

Specific rates must be in the range of 10^{-4} - 10 to be part of a viable process in chemical technology. As a consequence, most catalytic reactions that involve the breaking or rearrangements of C-H, C-C, H-H, C=O and N=N bonds are carried out in the temperature range of 400-900K since activation energies range from a low of 10-15 kcal/mole (for hydrogenation of unsaturated hydrocarbons) to a high of 40-50 kcal/mole (for dehydrocyclisation or hydrogenolysis of hydrocarbons). There are, of course, several exceptions; the catalytic isotope exchange of hydrogen ($H_2 + D_2 \longrightarrow 2HD$) occurs at temperatures as low as 77K on most transition metal surfaces and the hydrogenation of ethylene to ethane is readily performed at 300K. The oxidation of ammonia to nitric oxide, a highly exothermic reaction, is usually carried out in the range 1100-1200K.

By multiplying the specific rate by the reaction time used in a given study, the turnover number, T.N. (number of product molecules per catalyst surface site) can be obtained. The T.N. must be greater than unity to assure that the reaction is catalytic (i.e. that there is more than one "turnover".) If the T.N. is less than unity we may be dealing with a stoichiometric reaction and our solid surface may be acting as a reactant rather than a catalyst. Thus, to demonstrate its catalytic character, the reaction must be carried out for long enough to obtain a turnover number that is greater than unity.

Many chemical reactions of interest lead to the formation of several different, but all thermodynamically feasible, products. It is often of greater interest to produce one of the many different molecules selectively, rather than increasing the overall rate. A selective catalyst will facilitate the formation of one product molecule while inhibiting the production of other, different molecules, even though the formation of all of the species is thermodynamically feasible. Thus, the blocking of reaction pathways which lead to the formation of unwanted molecules is as important an attribute of a good catalyst as the lowering of the potential energy barrier along the reaction pathway to the desired product molecule.

The reaction probability, R.P., is defined as the number of product molecules formed per number of reactant molecules incident on the catalyst surface. It is readily obtained by dividing the specific rate of catalysis by the incident reactant flux. R.P. is generally very low, and varies in the range 10^{-12} - 10^{-6} for most catalytic reactions in the pressure and temperature ranges generally employed in the chemical industry. The reason for this is the long surface residence time for the adsorbed molecules and reaction intermediates, (usually in the range of 10^{-1} - 10^3 sec.) which leads to a surface which is covered and inacces-

sible to the impinging molecules. The desorption of the product molecules from the catalyst surface frees surface sites, onto which the reactant molecules may adsorb. The desorption is always an endothermic reaction and appears to be the slow step in the catalytic process for most reactions running at high pressures.

The long surface residence times of adsorbed intermediates have another interesting consequence. The molecules may diffuse over long distances (10^{-10} Å) within their surface lifetime, visiting many catalytic sites where they can undergo consecutive reactions and molecular rearrangements. Thus, a catalyst surface may possess many different active sites, all of which are likely to be accessible to the adsorbed reactants.

The coverage of adsorbed molecules, σ , [molecules/cm²] is usually determined by multiplying the incident flux, F , [molecules/cm² sec] by the surface residence time, τ , [sec].

$$\sigma = F \times \tau$$

The flux can be estimated from the reactant pressure, $F = P(2\pi MRT)^{-1/2}$, and the residence time $\tau = \tau_0 \exp[\Delta H_{ads}(0)/RT]$ depends on the heat of adsorption, ΔH_{ads} , the temperature, T , and the preexponential factor, τ_0 , (which varies in the range 10^{-17} - 10^{-15} (6) depending on the degree of mobility of the adsorbed molecules). The heat of adsorption is a measure of the strength of the chemical bond between the adsorbed molecule and the surface. It depends on both the coverage and the structure of the catalyst surface. As the coverage is increased the adsorbed molecules are packed closer together in the surface monolayer. If the interaction among the adsorbates is repulsive, the heat of adsorption per molecule decreases as the coverage in the monolayer is increased. This is the case for molecular CO adsorption on most metal surfaces (7). If the adsorbate-adsorbate interaction is attractive, the heat of adsorption per molecule may increase with coverage. This occurs, for example, during the growth of oxide monolayers on metal surfaces, (8).

The surface structure sensitivity of bonding of adsorbed molecules and as a result, the structure sensitivity of catalytic reactions is well documented, (9,10). The surface structure is heterogeneous on the atomic scale (Fig. 2) and there are many surface sites that are distinguishable by their number of nearest neighbours: there are surface atoms that can form terraces, steps and kinks, and these structures may, in turn, contain point defects, adatoms and vacancies. The binding of adsorbed atoms or molecules at each site may be different, giving rise to heats of adsorption that vary with the surface structure. This effect is particularly noticeable in adsorption and desorption studies carried out on single crystal surfaces. These surfaces can be prepared with different relative concentrations of terrace, step and kink sites. The structure sensitivity of bonding can lead to structure sensitivity in many catalytic reactions. These have been described in the literature (11).

It is often thought that the most active catalysts consist of surfaces which can form bonds of intermediate strength with adsorbates. If the surface chemical bonds are too strong, the reaction intermediates either have surface lifetimes which are much too long, or they may simply never come off the surface, forming stable surface compounds such as oxides, carbides or nitrides instead. On the other hand, if the surface bonds to adsorbates are too weak, the needed chemical bond-breaking or rearrangements might not occur before desorption. Chemical experience is in agreement with the contention that intermediate bond strength leads to superior catalyst activity. The structure of the catalyst surface, however, is one of the key factors which control chemical selectivity.

The catalytic process may be subdivided into several elementary reaction steps. These are a) adsorption, b) surface diffusion, c) molecular rearrangements at active surface sites and d) desorption. There are several techniques capable of studying the elementary reaction step. Predominant among them are (1) molecular beam surface scattering and (2) thermal desorption. The reader is referred to recent review papers describing these methods of investigation (12,13)

The catalyst, unfortunately, does not have an indefinite life, but becomes "poisoned" or deactivated after a certain period of time. It is thought to reflect good catalyst performance if seven pounds of products are produced per pound of catalyst before the catalyst must be regenerated. Catalyst deactivation and regeneration are important and major fields of catalysis science. There are many possible reasons for deactivation. For example, the catalyst may restructure as a consequence of selective adsorption of impurities from the reactant stream, such as sulphur or nitrogen. Alternatively, carbon may be deposited, blocking the active surface, due to side reactions leading to complete dehydrogenation and decomposition of organic molecules during hydrocarbon conversions. The use of additives, (introduced either during catalyst preparation or with the reactants) to prevent restructuring of the catalyst or the blocking of active sites is being explored intensively by many research laboratories.

3.1. Summary

Single crystal surfaces of small area ($\sim 1 \text{ cm}^2$) can be used as model catalysts in studies of the surface science of heterogeneous catalysis. The structure, composition and oxidation states of surface atoms can readily be determined by the various techniques of surface science that were developed in recent years. A new technology that permits in situ determination of catalytic reaction parameters (rates, activation energies, product distributions) at high pressures (atmospheres) and the surface properties at low pressures ($\sim 10^{-9}$ torr) has been employed. Molecular information about the elementary surface reaction's steps, adsorption, surface diffusion, chemical rearrangement and desorption becomes increasingly available. The reaction probabilities of most heterogeneous catalyzed reactions under industrial

conditions used at present are very low (10^{-12} - 10^{-6}) and the surface residence times of reacting molecules are long (seconds). The causes of the catalyst activity (specific rates), selectivity (desired product distribution) and resistance to poisoning (to assure long lifetimes) are the subjects of most research studies. The atomic structure, the carbonaceous deposit that forms during hydrocarbon reactions and the oxidation states of surface atoms are the molecular ingredients of heterogeneous catalysts that have been identified.

3.2. Questions that need theoretical and experimental scrutiny

- Are the desorbing molecules in energy equilibrium with the surface (translational and internal energy content)? What is the nature and efficiency of energy transfer among the reactants, the surface and the products?

- Improvements in the theories that underlie many surface science techniques are needed. Ion scattering from surfaces and high resolution electron energy loss spectroscopy are foremost among them!

- How does bonding to the solid surface change when adsorption occurs at the solid-liquid instead of the solid-gas interface?

4. STRUCTURE SENSITIVITY OF CATALYTIC REACTIONS

4.1. The structure sensitivity of ammonia synthesis over iron catalysts

Single crystal catalysts can be prepared with a variety of surface structures by cutting the solid along different crystallographic orientations. We have studied ammonia synthesis over the (111), (100) and (110) crystal faces of iron at operating pressures approaching those used industrially (20 atm) (9). The structure of these different crystal faces are shown in Figure 3. The Fe(111) face was found to be the most active. It catalyzes the synthesis of ammonia from hydrogen and nitrogen at a rate which is at least 420 times faster than that of the ordered (110) surface. The rate of ammonia synthesis is 32 times faster over the Fe(100) face than that over the ordered (110) surface. These results are consistent with the low pressure chemisorption studies of Ertl and his co-workers (14) who reported that the rate of dissociative chemisorption of nitrogen is greatest on the (111) face of iron and least on the (110) face and with previous suggestions that this step is rate determining in the ammonia synthesis reaction. The (111) plane of iron contains both 7-coordinated and 4-coordinated atoms, whereas the (100) and (110) planes contain only 6-coordinated and 4-coordinated atoms, respectively. The large variation in the rates of ammonia synthesis on the various iron crystal planes lend considerable support to the proposals by Boudart and others (15) regarding the importance of iron clusters and 7-coordinated iron atoms as components of the active site on the catalyst surface.

4.2. The structure sensitivity of hydrocarbon conversion reactions on platinum surfaces.

The surface structures of platinum crystals that display different catalytic behavior are shown in Figure 4. The two flat surfaces, the (111) and (100) crystal faces, have hexagonal and square atomic arrangements respectively. Each surface atom is surrounded by six or four nearest neighbors in the surface plane. There (lower two sketches in Figure 4) are also surfaces with periodic arrays of steps of one atom in height. The structure of the terraces and steps can have the same six-fold or four-fold symmetry as the flat surfaces. The widths of the terraces are variable depending on the angle of cuts of the single crystal surface which determines the crystallographic orientation of the surface. There may be kinks or ledges in the steps that can be present in large concentrations if the surface is suitably prepared (1). The step and ledge sites have fewer nearest neighbors (lower coordination number) and lower symmetry when compared to atoms in the flat surfaces.

The reactions of n-hexane or n-heptane over platinum surfaces are excellent probes of structure sensitivity (16). The various reactions of n-hexane are displayed in Figure 5. The reactions leading to branched isomers (isomerization) and cyclic molecules (dehydrocyclization) are especially desirable for producing high octane gasoline from petroleum naphtha. The third type, hydrogenolysis reactions that involves the scission of C-C bonds yields low molecular weight gaseous products that are undesirable when producing gasoline. The reactivity of the flat (111) and (100) surfaces for the dehydrocyclization of n-hexane and n-heptane are compared in Figure 6. The hexagonal (111) surface is 3 to 7 times more active than the platinum surface with the square unit cell (16). In Figure 7 the selectivity of stepped platinum surfaces are compared with the flat surfaces under identical conditions for the same reaction. Maximum aromatization activity is obtained on stepped surfaces with terraces about 5 atoms wide with hexagonal orientations as indicated by reaction rate studies over more than 15 different crystal surfaces with varied terrace orientations and step and kink orientations.

The reactivity patterns displayed for alkane isomerization reactions is completely different to that for aromatization (17). Our studies revealed that maximum rates and selectivity (rate of desired reactions/total rate) for butane isomerization reactions are obtained on flat crystal faces with square (100) unit cell. Isomerization rates for this surface are 4 to 7 times higher than those for hexagonal surfaces as shown in Figure 8.

For the undesirable hydrogenolysis reactions that require C-C bond scission we found that the two flat surfaces exhibit very similar reaction rates. However, the distribution of hydrogenolysis products varies sharply over these two surfaces. The hexagonal surface displays high selectivity for scission of the terminal C-C bond whereas the (100) square surface always prefers cleavage of C-C bonds located in the

center of the reactant molecule (18). The hydrogenolysis rates increase markedly (3-5 fold) when kinks are present in high concentrations on the platinum surfaces (Figure 8).

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

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

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

It should be noted that the metal surface structures that are stable in the presence of an adsorbed layer of hydrocarbons may be unstable in an oxidizing environment (19). In the presence of chemisorbed oxygen other crystal faces may be more stable. As a result, changing the reducing chemical environment into oxidizing or the other way around could cause a massive reorganization of the surface structure. One should not expect all the catalyst surfaces to remain stable under the varied conditions encountered during catalytic reaction studies. One of the reasons for the application of certain additives or the use of appropriate oxide supports is to stabilize the surface structure of the catalyst as more extreme conditions for the catalytic chemistry and for its regeneration are used.

4.3. Summary

The ammonia synthesis over iron, and most complex hydrocarbon reactions over transition metal catalysts are surface structure sensitive. The selectivity to obtain the desired products can be controlled

by tailoring of the catalyst structure. Surface irregularities, steps and kinks can be present in large surface concentrations and are especially active in breaking large binding energy chemical bonds (N=N, C=O, C-C, C-H) with near zero activation energy. Additives are often used to stabilize the desired surface structure of catalysts.

4.4. Questions that need theoretical and experimental scrutiny

- How does the chemical bonding of small molecules to the surface vary with the atomic structure of sites?
- What are the electronic ingredients (charge density and angular charge distribution) that make such a site active for bond breaking?
- How charge donor or acceptor species influence the catalytic activity at these sites? How selective adsorption of atoms (O, S, K, C) aid or poison bonding at the active surface sites?
- Are surface atom mobilities great enough under catalytic conditions to generate new active sites continuously?

5. CARBONACEOUS OVERLAYERS

Within milliseconds after the start of a hydrocarbon reaction at atmospheric pressures an equivalent of a carbonaceous layer is deposited on a catalyst surface and the reaction then occurs in the presence of this deposit (20). Indeed a clean platinum or other clean transition metal surface can not readily catalyze hydrocarbon conversion reactions. Most organic molecules adsorb irreversibly and form strong metal-carbon bonds. Upon heating, and in the absence of hydrogen, sequential dehydrogenation occurs until a graphitic overlayer remains (21). Figure 9 shows the sequential dehydrogenation of several alkenes that were adsorbed on platinum at low temperatures, and then heated.

Our studies using C-14 labeled organic molecules (16), thermal desorption and hydrogen-deuterium exchange (17) indicate a strong temperature dependence for the residence time and the composition of the organic deposit on platinum surfaces. Below about 120°C the layer can be rehydrogenated and removed from the metal surface as rapidly as the turnover time for organic reactants. Thus, at these low temperatures the metal surface remains clean during facile reactions, like the hydrogenation of ethylene that takes place with a low activation energy (less than 15 kcal/mole) at these low temperatures. The temperature programmed thermal desorption (22) of hydrogen and AES studies indicate that the stoichiometry of this mobile layer is C₂H₃. With increasing temperature above 120°C an increasingly larger fraction of the surface carbon becomes irreversibly adsorbed as it loses more hydrogen. This layer resides on the surface much longer than the turnover time of the organic reactants that may undergo isomerization, dehydrocyclization or hydrogenolysis. These reactions have high activation energy (20-45

kcal/mole) and are, therefore, carried out at higher temperatures, in the range of 150-400°C, to obtain reasonably high turnover numbers. Figure 10 shows the increase of the concentration of an irreversibly adsorbed carbonaceous layer and the simultaneous decline of the reversibly adsorbed mobile organic layer as a function of temperature (23). The stoichiometry of this tenacious layer on the catalytically active metal is C_2H . Our detailed investigations exploring the catalytic effect of preparing the carbon deposit from a variety of preadsorbed organic molecules show relatively minor alterations of the selectivity of hydrocarbon conversion reactions. The activity of the catalyzed reaction was inversely proportional to the concentration of the irreversibly adsorbed carbon layer.

The structure of the adsorbed hydrocarbon monolayers was submitted to detailed studies by LEED and HREELS (25). In the temperature range of 300-400 K the adsorbed alkenes form alkylidyne molecules that are shown in Figure 11. The C-C bond closest to the metal is perpendicular to the surface plane and its 1.5Å length corresponds to a single bond. The carbon atom that bonds the molecule to the metal is located in a three-fold site equidistant 2.0Å from the nearest metallic neighbors (24). This bond is appreciably shorter than the covalent metal-carbon bond (2.2Å) and is indicative of multiple metal-carbon bonds of the carbene or carbyne type. While this layer is ordered, on heating to about 100°C it disorders and hydrogen evolution is detectable by a mass spectrometer that is attached to the system. As the molecules dehydrogenate the disordered layer is composed of CH_2 , C_2H and CH type fragments that can be identified by HREELS (25). Only after heating to about 400°C do the fragments loose all their hydrogen and the graphite overlayer forms. These sequential bond breaking processes which occur as a function of temperature are perhaps the most important and unique characteristics of the surface chemical bond. While the surface remains active in the presence of organic fragments of C_2H stoichiometry it loses all activity when the graphitic monolayer forms.

Thus, we have two seemingly contradictory experimental observations. On the one hand many catalyzed reactions are strongly dependent on the structure of the surface. On the other hand, the surface that is catalytically active is covered with about a monolayer of carbonaceous deposit that seem to mask the structure of the solid catalyst. In order to maintain the observed structure sensitivity not all the metal surface sites are likely to be covered by the organic layer, but some of them must be available to perform the catalytic function. We have been able to titrate the remaining clean platinum surface sites by CO adsorption (20) which adsorbs readily on the uncovered metal at low pressures, about 10^{-6} torr and 25°C, but does not adsorb on the organic overlayer under these conditions. Figure 12 shows a fraction of the clean platinum surface as a function of the carbon surface concentration. (θ/θ_{clean}) is the fraction of bare platinum surface as compared to the site concentration on the initially clean metal surface. This fraction decreases rapidly with increasing temperature as seen in Figure 11. At about 400°C the carbonaceous overlayer that is irreversibly adsorbed

gradually loses its remaining hydrogen and becomes graphitized. The graphite layer is a catalyst poison and the catalytic activity is irretrievably lost when the surface is covered with graphite.

Hydrocarbon reactions are always carried out in the presence of excess hydrogen. Increased hydrogen concentration in the reactant feed helps to rehydrogenate a larger fraction of the irreversibly adsorbed carbonaceous layer and to slow the rate of graphitization. In the absence of excess hydrogen in the reactant mixture a complete monolayer graphitization is fast.

As a result of these studies a molecular model (20) of the working platinum catalyst can be proposed and is shown in Figure 13. Most catalyzed reactions could not occur on either the bare metal surface or on the surface that is completely covered by the irreversibly deposited organic layer. Hydrocarbon conversion must occur on the bare metal islands that are kept clean by the presence of hydrogen in the reactant mixture. However, the intermediates or the products that form may not readily desorb from the bare metal sites because they are too strongly bound. It is likely then that these species diffuse over onto the carbonaceous overlayer from which desorption commences perhaps with the additional transfer of hydrogen. By providing sites at which the reaction products are bound only weakly the carbonaceous overlayer facilitates the desorption of the organic molecules. It should be noted that the active carbonaceous deposit that contains CH and CH₂ fragments stores about ten times more hydrogen than the clean metal surface which could be made available to the desorbing organic molecules.

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

5.1. Summary

The metal surface is largely covered with a carbonaceous deposit during hydrocarbon reactions. The stoichiometry of this layer changes as a function of temperature ($C_2H_3 \longrightarrow C_2H \longrightarrow C$) as the layer dehydrogenates with increasing temperature. The residence times of the dehydrogenated species (C_2H , CH, C) are greater than the reaction turnover time. Hydrogen transfer and hydrogen storage appears to be the main functions of this deposit. Under catalytic reaction conditions only 5-10% of the metal surface is uncovered and responsible for much of the catalytic chemistry. The structure of adsorbed organic molecules change with increasing temperature. Each structural intermediate

is stable in a finite temperature range while the thermodynamically most stable configuration is attained at the highest temperatures. A molecular model of the working metal catalyst is proposed, consisting of bare metal islands in the carbonaceous deposit.

5.2. Questions that need theoretical and experimental scrutiny

- Why do adsorbed molecules undergo sequential bond breaking and structural rearrangements as the temperature is increased instead of forming their more stable configuration at lower temperatures? Why is there a small activation energy (on the order of RT) to form the more stable molecular structure or change location on the surface?
- Explain the bonding trends of molecules on transition metals across the periodic table and their relation to atomic and band structure properties of the metals.

6. THE OXIDATION STATE OF SURFACE ATOMS

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

6.1. Carbon monoxide hydrogenation over rhodium

Rhodium was reported to yield predominantly C₂ oxygenated products, acetaldehyde and acetic acid (26) when prepared under appropriate experimental conditions. Our studies using unsupported polycrystalline rhodium foils (27) have detected mostly methane along with small amounts of ethylene and propylene under very similar experimental conditions. This product distribution was identical to that obtained by Vannice (28) over supported rhodium catalyst as was the activation energy for methanation (about 24 kcal/mole). It appears that most of the organic molecules form following the dissociation of CO by the rehydrogenation of CH_x units in the manner similar to alkane and alkene production from CO/H₂ mixtures over other more active transition metal catalysts (iron, ruthenium and nickel).

However, when rhodium oxide, Rh₂O₃, was utilized as a catalyst, large concentrations of oxygenated C₂ or C₃ hydrocarbons were produced, including ethanol, acetaldehyde and propionaldehyde (29). Furthermore, the addition of C₂H₄ to the CO/H₂ mixture yielded propionaldehyde, indicating the carbonylation ability of Rh₂O₃. Under similar experimental conditions over rhodium metal C₂H₄ was quantitatively hydrogenated to ethane and carbonylation activity was totally absent. Clearly, higher oxidation state rhodium ions are necessary to produce the oxygenated organic molecules. Unfortunately, Rh₂O₃ reduced rapidly in the CO/H₂ mixture to the metallic state with drastic alteration of the pro-

duct distribution from oxygenated hydrocarbons to methane. In order to stabilize the rhodium ion, lanthanum rhodate, LaRhO_3 , was prepared by incorporating Rh_2O_3 into La_2O_3 at high temperatures (30). Over this stable catalyst the formation of oxygenated products from CO/H_2 predominated.

The reason for the change of selectivity in CO/H_2 reactions upon alteration of the oxidation state of the transition metal is due largely to the change of heats of absorption of CO and H_2 as the oxidation state of the transition metal ion is varied (30). This is demonstrated in Figure 14. The CO adsorption energy is decreased upon oxidation while the heat of adsorption of H_2 is increased, presumably due to the formation of hydroxyl groups. This, in turn, changes the relative surface concentrations of CO and H_2 . In addition, the metal is primarily active for hydrogenation and CO dissociation while the oxide can perform carbonylation and has reduced hydrogenation activity. As shown in Figure 11, the active LaRhO_3 catalyst seems to have both rhodium metal and rhodium ion sites, as indicated by the presence of the thermal desorption peaks of CO and H_2 , to provide both optimum carbonylation as well as hydrogenation activity so necessary to obtain C_2 or C_3 oxygenated hydrocarbon molecules.

We have also found that the product distribution that results from the CO/H_2 reaction at high pressures over LaRhO_3 is highly temperature dependent (30). At low enough temperatures, below 250°C , the formation of methanol predominates. This can occur by the direct hydrogenation of the undissociated carbon monoxide molecule. As the temperature is increased from 250 to 300°C , the formation of C_2 or C_3 oxygenated hydrocarbon molecules ethanol, propanol, acetaldehyde and propionaldehyde predominates. These molecules need the presence of both CH_x units that form as a result of the dissociation of carbon monoxide followed by the partial rehydrogenation of the surface carbon and the insertion of CO into these fragments to form the oxygenated product. In a finite temperature range between 250 and 350°C the CO dissociation and hydrogenation ability and the carbonylation ability of the catalyst are about identical. As the temperature is increased to above 350°C , the formation of methane predominates. The CO concentration is too low on the surface at these temperatures to produce CO insertion and the rehydrogenation characteristics of the material control the product distribution (29,30).

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

6.2. Photodissociation of water over reduced SrTiO₃ surfaces

When strontium titanate is illuminated with band gap radiation, about 3.1 electron volts, in the presence of water vapor or aqueous alkali hydroxide solutions hydrogen and oxygen are detected (31). The presence of Ti³⁺ ions at the surface plays a crucial role in dissociating water and is a necessary ingredient of the photocatalytic process (32). Figure 15 shows the catalytic cycle that explains most of the experimental results found so far (33). The reduced SrTiO₃ surface, which has a high concentration of oxygen vacancies and Ti³⁺ ions, readily adsorbs water and dissociates it in the dark. As a result the Ti³⁺ species are oxidized to Ti⁴⁺ and the oxygen vacancies are filled with the fragmented adsorbates. Upon illumination, the photoelectron generated reduces H⁺ to H and the electron vacancy traps the negative charge of the hydroxyl ion to convert it to OH radical which in turn produces oxygen through, presumably, a peroxide intermediate. As both hydrogen and oxygen desorb after atom recombinations the Ti³⁺ surface sites and the oxygen vacancy are regenerated. There is evidence for the rapid exchange of oxygen from the water molecules with the oxygen ions at the surface and for the reduction and oxidation of Ti³⁺ sites during the photochemical reaction (34). Thus the importance of the proper oxidation state of transition metal ions to carry out catalyzed reactions is again demonstrated.

6.3. Summary

The catalytic reaction path changes markedly with the oxidation state of the surface atoms. While many transition metals dissociate CO and readily hydrogenate organic molecules, higher oxidation state metal ions insert molecular CO into alkene double bonds or into organic fragments and show reduced hydrogenation ability. Redox catalytic reactions at surfaces often require changes of oxidation states of transition metal ions at the catalyst surface. Often surface atoms must be present in several different oxidation states (metal and metal ion) at the catalyst surface to be able to carry out complex catalytic reactions. A major challenge of catalyst preparation is to find ways to stabilize surface atoms in the desired oxidation states.

6.4. Questions that need theoretical and experimental scrutiny

- How do carbon monoxide and dinitrogen dissociate at the metal surface?
- How does chemical bonding change with the oxidation state of the metal ions? How do electron donors (alkali metals) and electron acceptors (halogens, oxygen, sulfur) adsorbed on the surface alter the oxidation states of surface atoms?

7. THE BUILDING OF NEW HIGH TECHNOLOGY HETEROGENEOUS CATALYSTS

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

There exists, already, a group of high technology catalysts that has been in use in the chemical industry over the past 12 years. These are the zeolites (35), one of which is shown in Figure 16. Zeolites are aluminum silicates that can be prepared with variable pore sizes which have molecular dimensions. This gives rise to size and shape selectivity in hydrocarbon conversion reactions since molecules that are small enough to enter the pores can undergo catalyzed reactions. In addition, by controlling the silicon to aluminum ratio of the zeolite crystal the catalytic behavior of these aluminum silicates can be drastically altered. Zeolites, at present, are the largest volume heterogeneous catalysts in use.

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

7.1. The catalytic activity of the gold-platinum system

Bimetallic alloy systems are noted for their higher activity and selectivity for many hydrocarbon reactions as compared to single metal component catalysts. In order to explore the reasons for this we studied the gold-platinum system (36,37). Gold was epitaxially deposited on the (100) and (111) crystal faces of platinum and the structure of the monolayer and the activity for various hydrocarbon reactions as a function of gold surface concentration was monitored. Then by heating the system gold was diffused into platinum and the catalytic activity of

the freshly formed alloy was again determined for the same chemical reaction as that used in the presence of the gold overlayer on platinum. Gold forms an ordered overlayer on the platinum surfaces (28). Figure 17 shows the activity for dehydrogenation, hydrogenolysis and isomerization of n-hexane as a function of gold coverage in the epitaxial case. It appears that the activity of platinum is linearly decreased by the presence of a gold overlayer at high reactant pressures. This result, of course, is not surprising as gold is inactive for all these catalytic reactions (37).

Very different results are obtained when gold was diffused into platinum at elevated temperatures. The gold-platinum alloy that forms showed a much higher activity for isomerization than clean platinum (29).

Simultaneously the activity for dehydrocyclization and hydrogenolysis decreased exponentially with gold coverage. As a result, the selectivity for isomerization became very large. Gold tends to break up the large coordination number sites by substitution more than the lower coordination number sites; thus reactions that require three-fold sites are more likely to be affected by the presence of gold in the crystal lattice than those reactions involving one or two neighboring platinum atoms. This simple argument can explain the observed selectivity (29). However, this cannot explain the observed increase in chemical activity; the gold alloy is a more active catalyst than clean platinum for isomerization. The presence of gold may decrease the concentration of the carbonaceous deposit and the residence times of the reaction intermediates. The presence of gold may inhibit the formation of carbonaceous polymers, which allows more facile rehydrogenation of the carbon. This can certainly account for the increased rates obtained on the gold alloy surface for isomerization. It is also known that bimetallic alloys poison more slowly than pure metallic catalysts in many hydrocarbon conversion reactions. Perhaps the presence of a second component metal also decreases the rate of conversion of the active carbonaceous fragments to the inactive graphitic phase.

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

7.2. The effect of alkali metals on the chemisorption of CO and on the reactivity of surface carbon

Alkali metals are frequently used as promoters in many catalyzed surface reactions. These include the ammonia synthesis on iron, the catalyzed hydrogenation of carbon monoxide on various transition metal surfaces and coal gasification in the presence of water. Alkali metals when present on transition metal surfaces affect the catalytic activity in several ways. One important effect is their influence on the heats of absorption of adsorbates such as carbon monoxide. HREELS and TDS

studies showed (38) that the coadsorption of potassium and carbon monoxide on platinum surfaces decreased the CO stretching frequency by about 400 wave numbers as compared to the stretching frequency on the clean platinum, in the absence of potassium. This effect is shown in Figure 18. A decreased CO stretching frequency indicates a weakening of the CO bond and simultaneously it implies an increased metal-carbon bond strength. Thus, potassium seems to increase the bonding energy of CO to the surface, thereby improving the dissociation probability significantly. During ammonia synthesis the presence of potassium on iron surfaces increases the binding energy of dinitrogen and reduces the activation energy for its dissociation to produce atomic nitrogen on the surface (7). Since the dissociation of dinitrogen is the rate limiting step the ammonia synthesis rate is accelerated.

Another effect is the alkali metal catalyzed interaction of water vapor with carbon at the surface. It was reported recently (39) that when alkali hydroxides or carbonates are adsorbed on the surface of graphite they catalyze its reaction with water vapor. At low temperature in the range 200-250°C methane and carbon dioxide are produced. This reaction is an alternate route for the gasification of carbon that is usually carried out without a catalyst around 1000°C with water vapor to produce carbon monoxide and hydrogen. It is clear that by the low temperature reaction alkali hydroxides (potassium, lithium, etc.) act as catalysts for both the reduction of carbon to CH_4 and for its oxidation to CO_2 or CO. This reaction involves ionic intermediates, H^+ and OH^- , which form from water as catalyzed by the alkali hydroxides. These then, by a series of complex reactions that follow, can hydrogenate and oxidize the surface carbon. This low temperature reaction has an activation energy of about 11 kcal/mole and can be responsible for the removal of the carbonaceous deposit from various transition metal surfaces when water vapor is present.

7.3. Strong metal-support interaction

Control of the oxidation state of surface transition metal ions has been reported by Tauster and coworkers (40). By using relatively basic oxides, titanium oxide, zirconium oxide, etc. they find very different chemisorption and reactivity properties of transition metal ions. The influence of these refractory oxide supports on the catalytic activity was called "strong metals support interaction" (SMSI). Thus, using the support, higher oxidation state transition metal ions can be stabilized in addition to the presence of the same transition metals in the zero valent state.

7.4. Summary

Binary alloys (Au, Cu and Pt) have very different catalytic selectivities, improved rates and resistance to chemical degradation when compared with the one-component metal catalysts (Pt). Alkali metal additives to transition metals change the bonding of many adsorbates by charge transfer. In addition, alkali metal catalyzed reactions of

water vapor with graphite to produce methane aids the cleaning of the metal catalyst surfaces during hydrocarbon reactions and the low temperature gasification of carbonaceous materials. Compound formation between the metal catalysts and the oxide support can be responsible for marked changes in the product distribution during catalytic reactions and maintaining the higher, desired oxidation state of the transition metal ions.

7.5. Questions that need theoretical and experimental scrutiny

- What are the structural and electronic changes that occur upon alloying at each metal surface site (terrace, step, ledge) that are responsible for the change of bonding and reactivity of adsorbates?

- What is the mechanism of the water-carbon reaction that produces gaseous hydrocarbons and is catalyzed by alkali metals?

- What is the nature and conditions of compound formation between the metal and oxide support. Is the alloy catalyst a two phase or multiphase system that is produced from a single intermediate phase under reaction conditions? If so, is the composition of the multimetallic catalysts predictable from their phase diagram?

- Is there charge transfer between the insulator catalyst support (oxide) and the metal catalyst? If so, how is this charge transfer modifying the bonding of adsorbates?

- Are the structures of organic molecules modified when inside a zeolite cage? What are the mechanisms of alkylation, hydrogen transfer and molecular rearrangements in zeolites?

8. ACKNOWLEDGMENTS

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TABLE 1

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

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

10. FIGURE CAPTIONS

- Fig. 1: Schematic diagram of the low pressure-high pressure apparatus for combined surface analysis and catalysis studies.
- Fig. 2: Model of a heterogeneous solid surface, depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.
- Fig. 3: Idealized atomic surface structure for the low-index planes of Iron Fe(100), Fe(111) and Fe(110).
- Fig. 4: Idealized atomic surface structures for the flat Pt(111) and Pt(100), the stepped Pt(755) and the kinked Pt(10,8,7) surfaces.
- Fig. 5: Skeletal rearrangement reactions of hydrocarbons are catalyzed by platinum with high activity and unique selectivity. Depicted here are the several reaction pathways which occur simultaneously during the catalyzed conversion of n-hexane, C_6H_{14} . The isomerization, cyclization and aromatization reactions that produced branched or cyclic products are important in the production of high octane gasoline from petroleum naphtha. The hydrogenolysis reaction that involves a C-C bond yields undesirable gaseous products.
- Fig. 6: Dehydrocyclization of alkanes to aromatic hydrocarbons is one of the most important petroleum reforming reactions. The bar graphs shown here compare reaction rates for n-hexane and n-heptane aromatization catalyzed at 573K and atmospheric pressure over the two flat platinum single crystal faces with different atomic structure. The platinum surface with the hexagonal atomic arrangement is several times more active than the surface with a square unit cell over a wide range of reaction conditions.
- Fig. 7: The selectivity of various platinum surfaces for the dehydrocyclization reaction. The stepped (557) surface with five atom wide terraces of (111) orientation appears to be the most active.
- Fig. 8: Reaction rates are shown as a function of surface structure for isobutane isomerization and hydrogenolysis catalyzed at 570K and atmospheric pressure over the four platinum surfaces. The rates for both reaction pathways are very sensitive to structural features of the model single crystal catalyst surfaces. Isomerization is favored on the platinum surfaces that have a square (100) atomic arrangement. Hydrogenolysis rates are maximized when kink sites are present in high concentrations as in the Pt(10,8,7) platinum crystal surface.

- Fig. 9: Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of ethylene, propylene, and cis-2-butene chemisorbed on Pt(111) at about 120 K ($\beta = 12$ K/sec).
- Fig. 10: Composition and reactivity of ^{14}C -ethylene chemisorbed on Pt(111) at temperatures between 20 and 370°C; the irreversibly adsorbed fraction determined by radiotracer analysis displays an excellent correlation with the average hydrogen content (H/C) of the strongly adsorbed species.
- Fig. 11: Atomic surface structure for alkylidyne species chemisorbed on Pt(111).
- Fig. 12: Fractional concentrations of uncovered platinum surface sites determined by CO adsorption-desorption as a function of surface carbon coverage on the (100), (111) and (13,1,1) platinum surfaces. A comparison is made between the CO uptake determined following n-hexane reaction studies and CO uptake determined when CO was coadsorbed with "graphite" surface carbon.
- Fig. 13: Model for the working surface composition of platinum reforming catalysts.
- Fig. 14: Heat of desorption (kcal/mole) of CO and D₂ from La₂O₃ fresh and used LaRhO₃, used rhodium oxide and rhodium metal. The spread of each value represents the variation with surface coverage rather than experimental uncertainty.
- Fig. 15: The suggested mechanism for the catalyzed photodissociation of water on Titanium oxide surfaces.
- Fig. 16: One of the important zeolites, mordenite. Na₈ Al₃ Si₄₀ O₉₆ · 24 H₂O, viewed along (001) axis.
- Fig. 17: Activity and selectivity changes for n-hexane conversion as a function of gold coverage in the gold-Pt(111) alloy system.
- Fig. 18: Vibrational spectra of the saturation CO coverage chemisorbed on Pt(111) at 300K as a function of preadsorbed potassium.

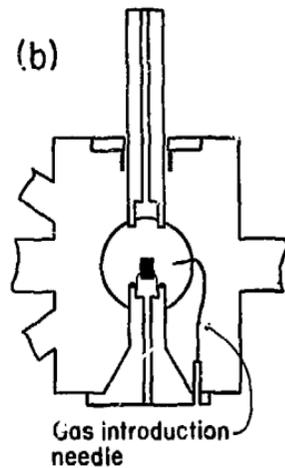
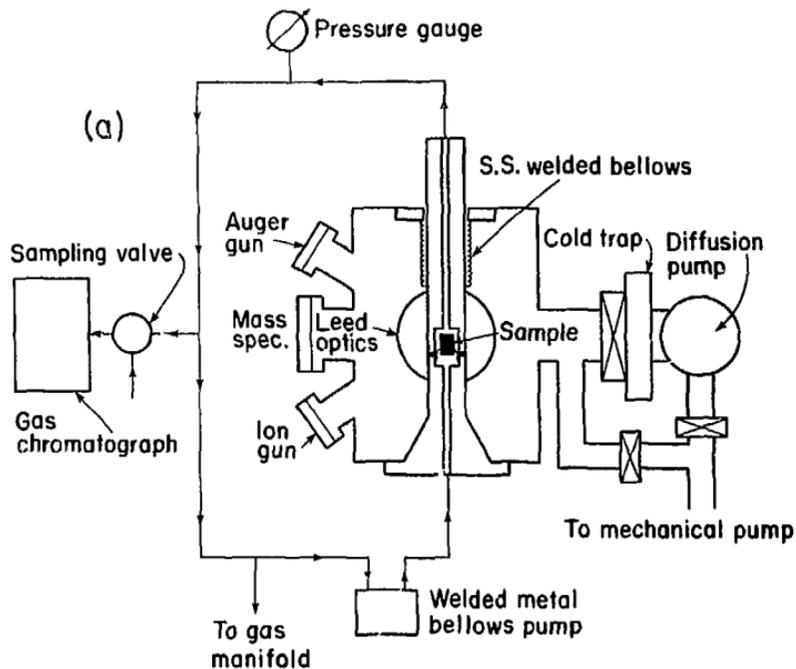


Fig. 1

XBL 756-3160

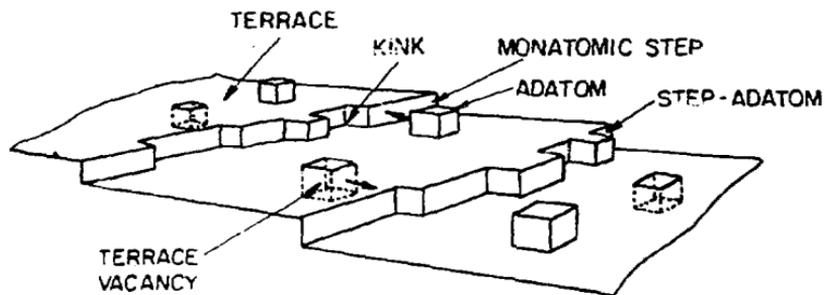


Fig. 2

XBL 708-1717 A

LOW-INDEX PLANES OF IRON

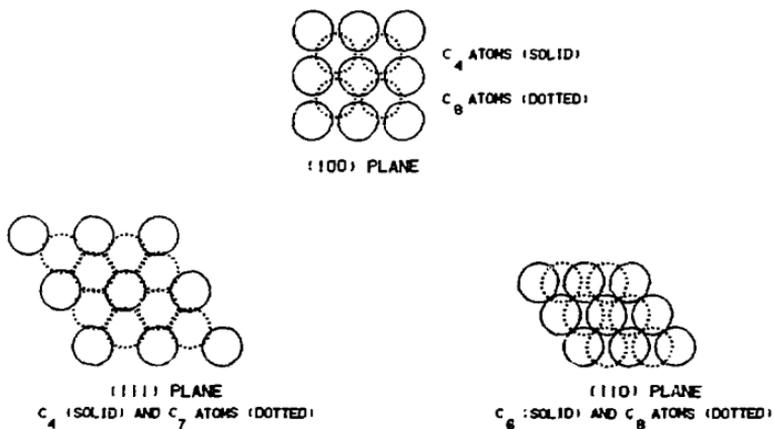
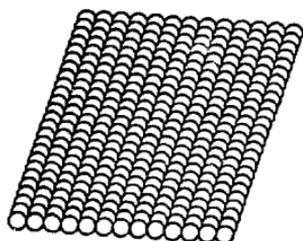
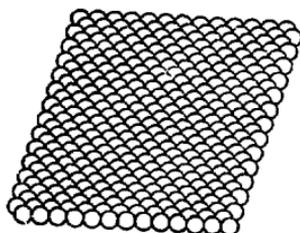


Fig. 3

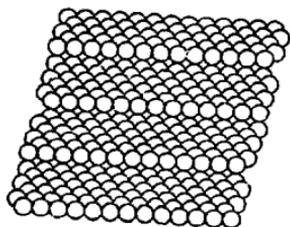
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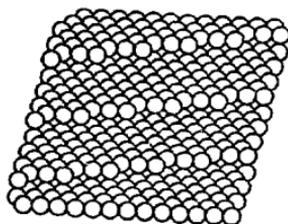
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fcc {111}



fcc {110}



fcc {110,0,7}

Fig. 4

XBL 8112-13009

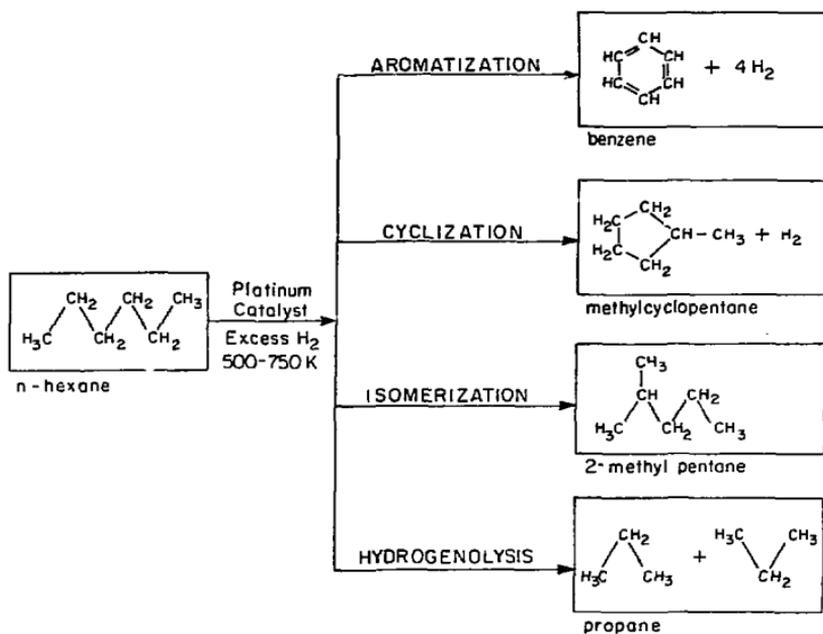


Fig. 5

XBL 822-5139

STRUCTURE SENSITIVITY OF ALKANE AROMATIZATION

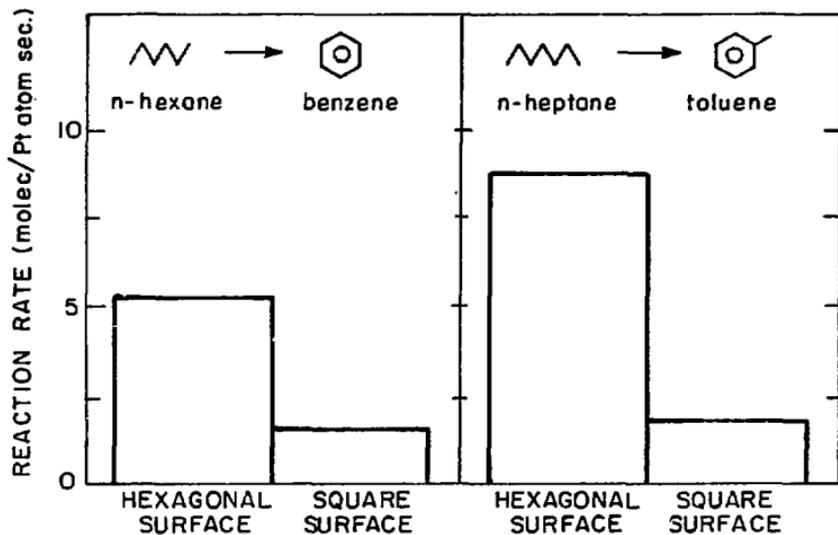


Fig. 6

XBL 82 2-5137

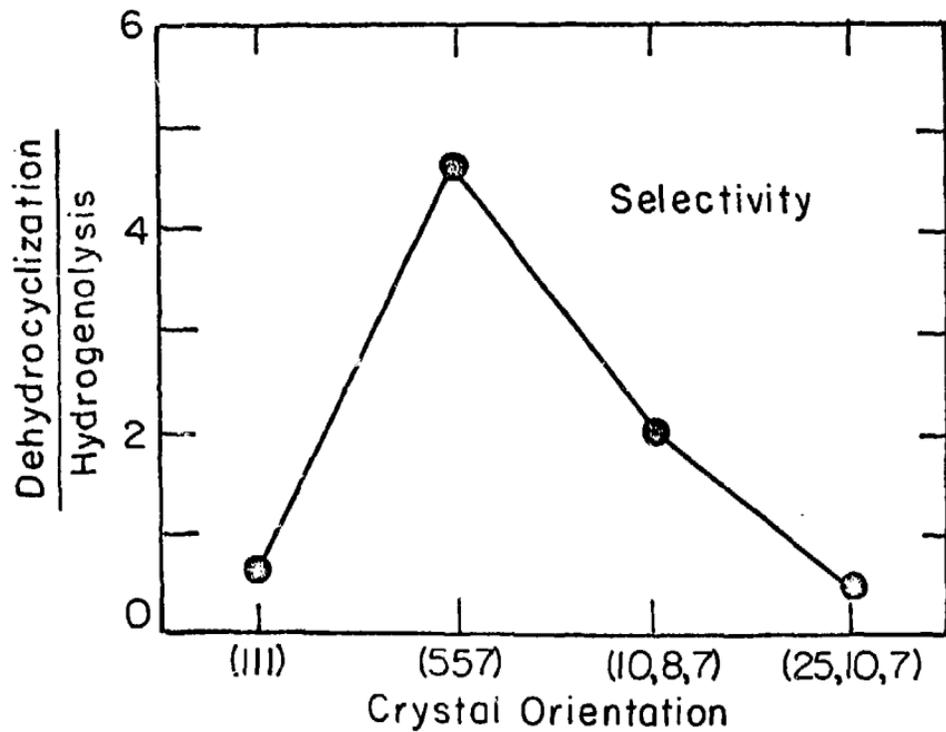


Fig. 7

X BL 807 5520A

STRUCTURE SENSITIVITY OF LIGHT ALKANE SKELETAL REARRANGEMENT

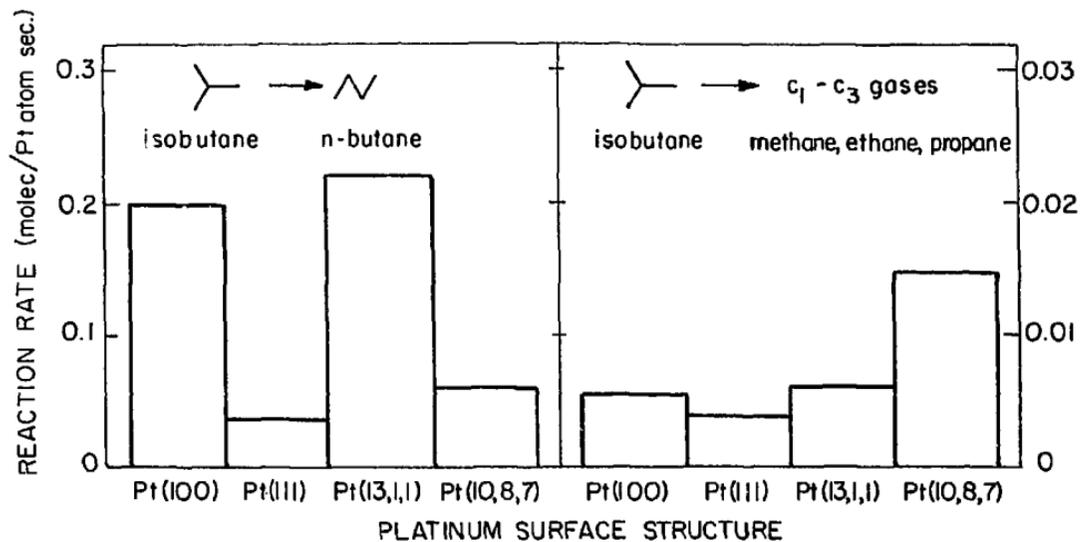


Fig. 8

XBL 8 22 - 5 13 6

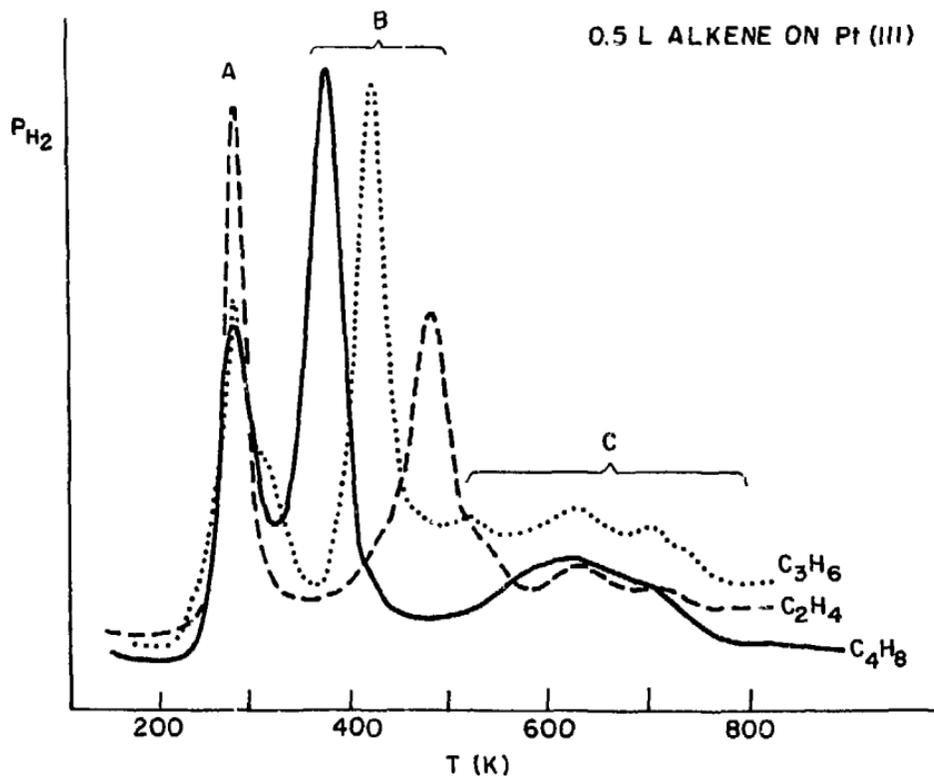


Fig. 9

XBL 814-5475

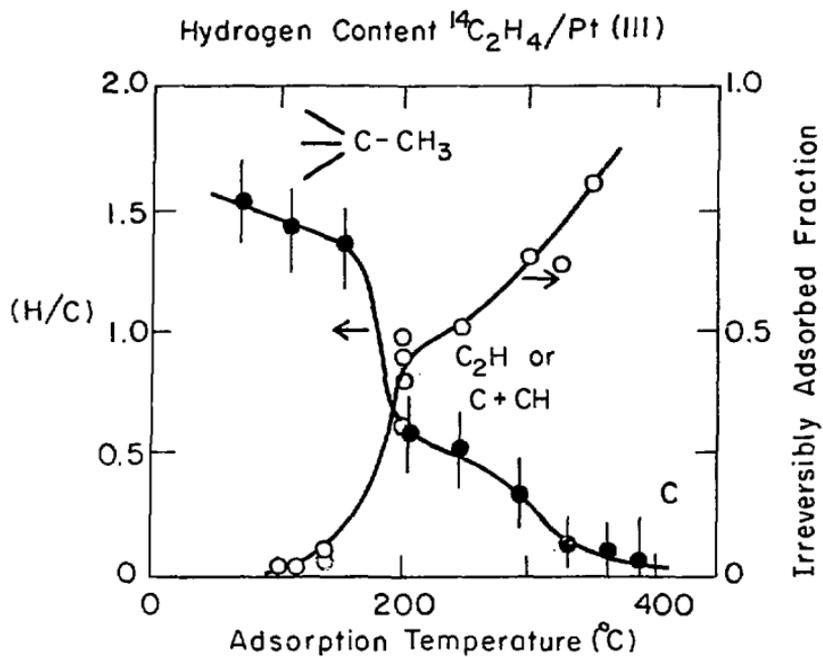
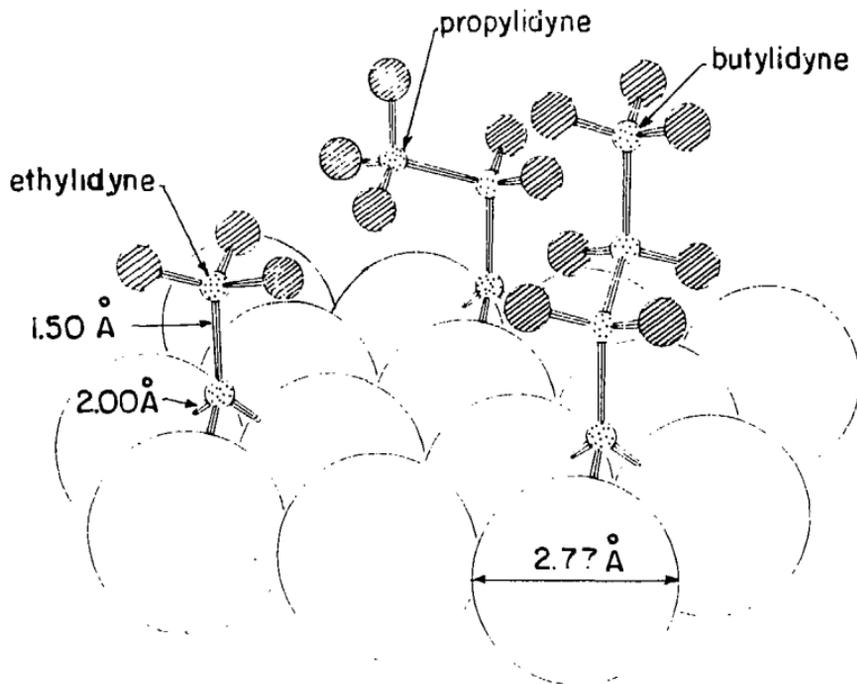


Fig. 10

XBL 812-5151



Pt(III) + ethylidyne, propylidyne and butylidyne

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

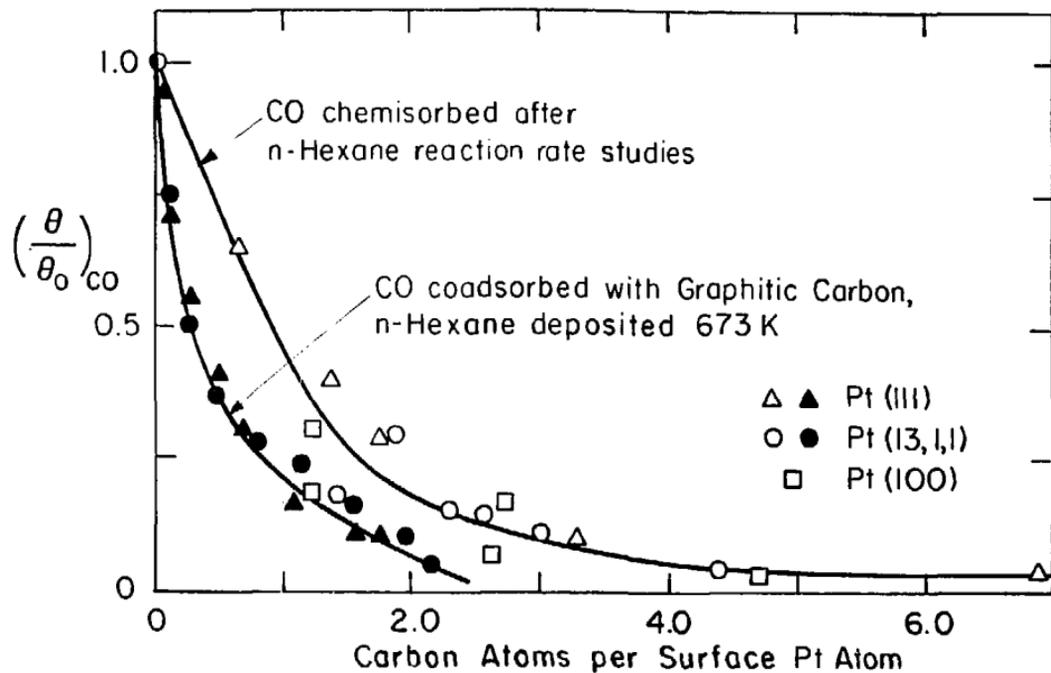


Fig. 12

XBL 816-5851

MODEL FOR THE WORKING PLATINUM CATALYST

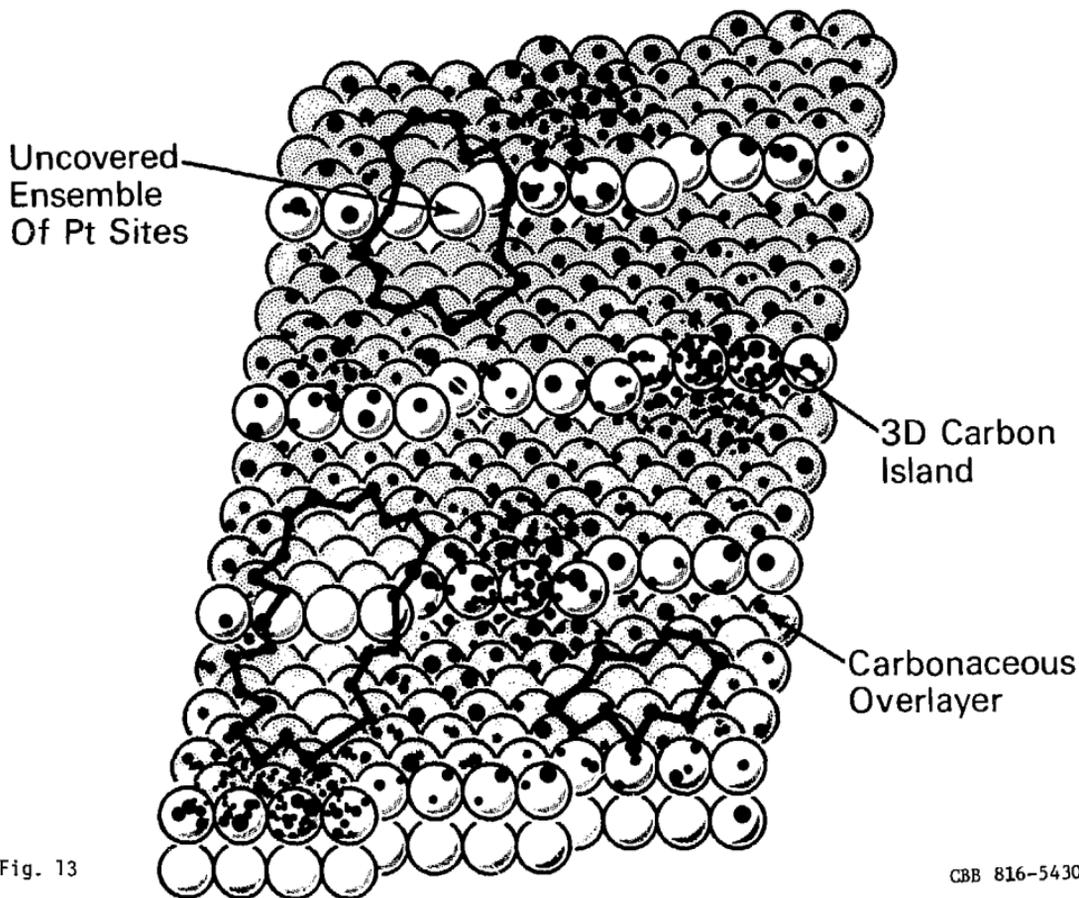


Fig. 13

CBB 816-5430

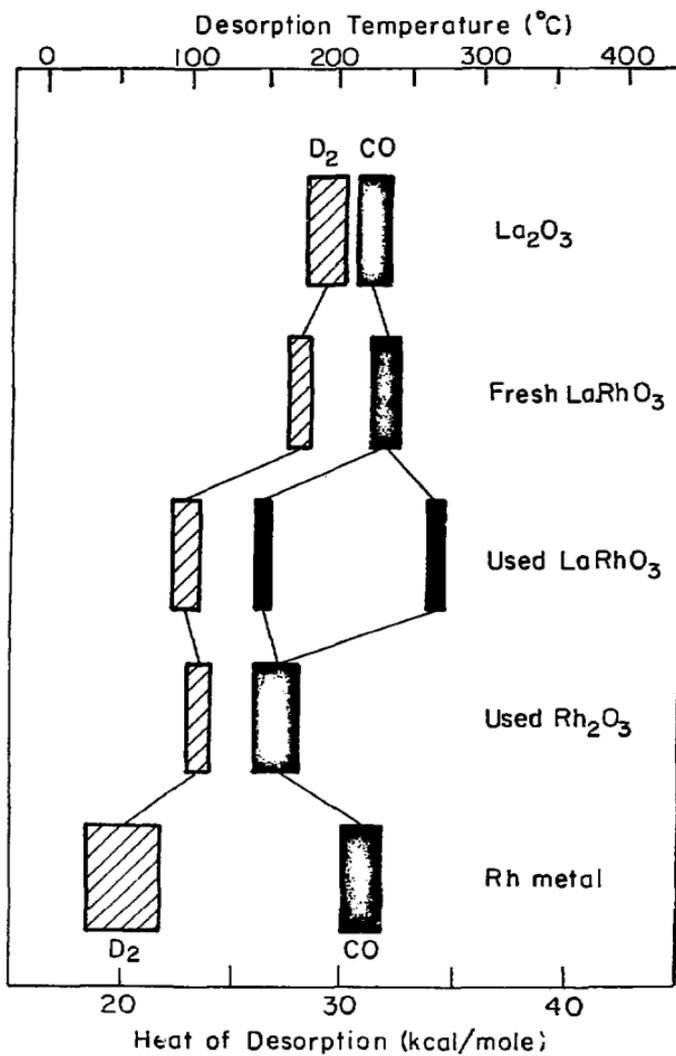
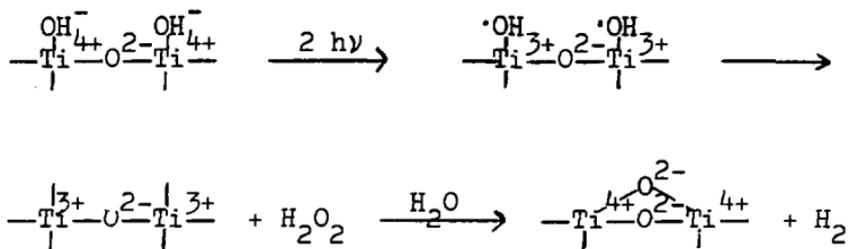


Fig. 14

XBL 817-6123



Van Damme and Hall, JACS 101 4373

Fig. 15

XBL 822-7B16

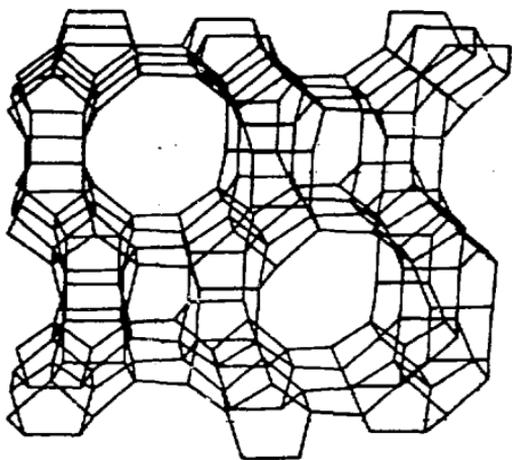


Fig. 16

XBL 7911-12828

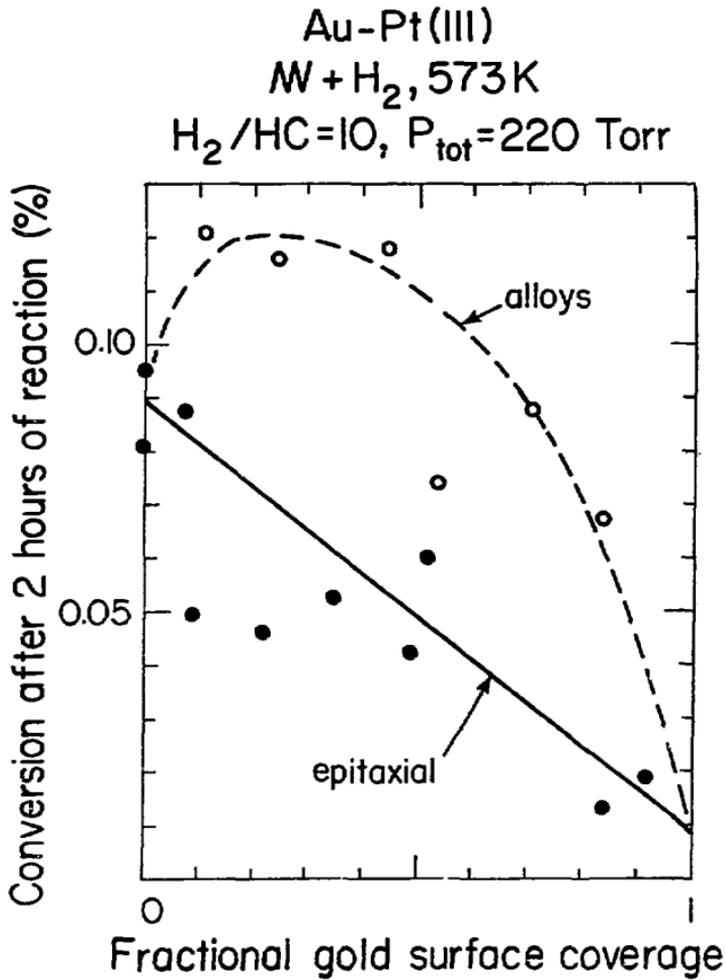


Fig. 17

XBL 819-1309

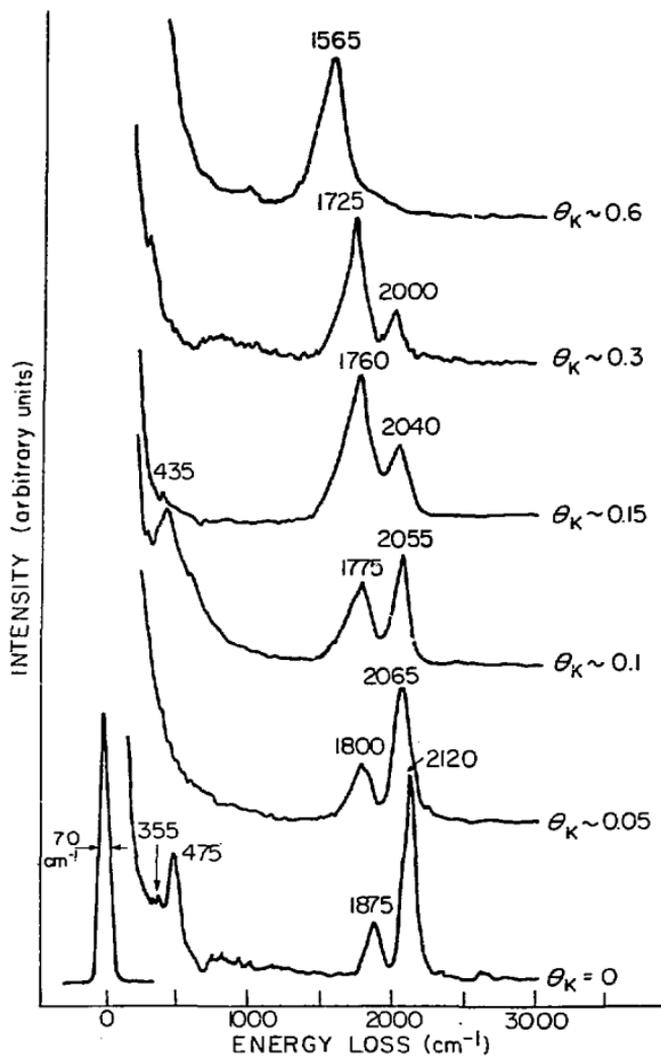
SATURATION CO COVERAGE ($T=300K$) ON Pt(III)/K

Fig. 18