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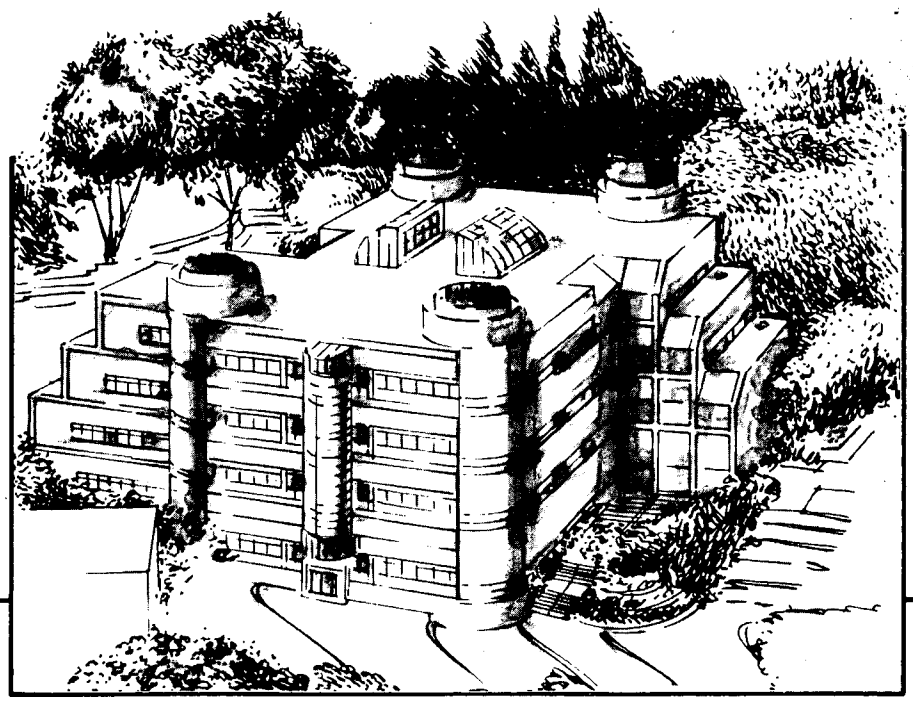
August 1987



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Classification of Catalytic Reactions Based on Molecular Surface Science

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INTRODUCTION

The methodology used in the study of heterogeneous catalysis has changed drastically over the past 15 years. Classical methods required high surface area samples (>10m^2) to generate measurable amounts of product. Presently, catalyst samples with surface areas as low as 1 cm^2 are sufficient for study by a number of techniques under ultra-high vacuum (UHV) conditions. Such small samples can have a high degree of homogeneity and can even be obtained in single crystal form. The use of such single crystals as model catalysts has greatly accelerated the rate of development of catalysis science.

Many techniques have been developed for the direct study of surfaces and have been applied to catalysis. A partial list of such techniques is presented in Table 1. Catalysts studied include platinum for hydrocarbon conversion (1), iron and rhenium for ammonia synthesis (2,3), and silver for the partial oxidation of ethylene (4). The hydrogenation of carbon monoxide has been studied over a large number of metal surfaces including iron (5), nickel (6), ruthenium (7) and molybdenum (8). The oxidation of carbon monoxide, shown to have oscillatory behavior, has been studied over platinum catalysts (9, 10). Finally, platinum and rhodium have been used to catalyze the hydrogenation of ethylene (11) and molybdenum to hydrodesulfurize thiophene to butenes (12). These investigations have lead to an increased understanding of catalytic mechanisms and the role of surface structure in catalysis.

The atomic scale characterization of catalytic surfaces has often been performed under UHV conditions (10^{-10} - 10^{-9} torr). These conditions are necessitated by the need to keep sample surfaces clean of contamination and the need to use electron or ion spectroscopies. At pressures of 10^{-6} torr a clean surface would be completely covered by an adsorbed monolayer of the background gas in a period of about 1 second. In order to keep surfaces clean for periods of hours UHV conditions are necessary. Ions and electrons interact strongly with condensed matter and thus are ideal for the study of surfaces because of their short penetration depths. The use of these probes also requires working in vacuum.

Much of the criticism of UHV techniques as viable tools for the study of catalysis has been based on the argument that chemisorbed species formed under these conditions may bear no relationship to those formed at industrial catalytic pressures. In order to overcome this difficulty, we

TABLE I

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

Surface Analysis Method	Acronym	Physical Basis	Type of Information Obtained
Low energy electron diffraction	LEED	Elastic backscattering of low energy electrons	Atomic surface structure of surfaces and of adsorbed gases
Auger electron Spectroscopy	AES	Electron emission from surface atoms excited by electron, x-ray or ion bombardment	Surface composition
High resolution electron energy loss spectroscopy	HREELS	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 adsorption of infrared radiation	Structure and bonding of adsorbed gases
x-ray and ultraviolet photoelectron spectroscopy	XPS UPS	Electron emission from atoms	Electronic structure and oxidation state of surface atoms and adsorbed species
Ion scattering spectroscopy	ISS	Inelastic reflection of inert gas ions	Atomic structure and composition of solid surfaces
Secondary ion mass spectroscopy	SIMS	Ion beam induced ejection of surface atoms as positive and negative ions	Surface composition
Extended x-ray absorption fine structure analysis	EXAFS	Electron Interference effects during x-ray adsorption	Atomic structure of surfaces and adsorbed gases
Thermal desorption spectroscopy	TDS	Thermally induced desorption or decomposition of adsorbed species	Adsorption energetics, composition of adsorbed species

have designed an apparatus for combined UHV surface analysis and high pressure catalytic reaction studies over small surface area samples (13). In addition to being equipped with a number of surface analytical techniques, this UHV chamber has an internal environmental cell that can enclose the sample, isolating it from vacuum and forming part of a closed loop batch reactor that can be pressurized to about 30 atm (Fig. 1). In this manner we can characterize the catalytic surface before and after exposure to reaction conditions and attempt to correlate surface characteristics with the kinetic parameters (rate, product distribution, activation energy) of the catalytic reaction.

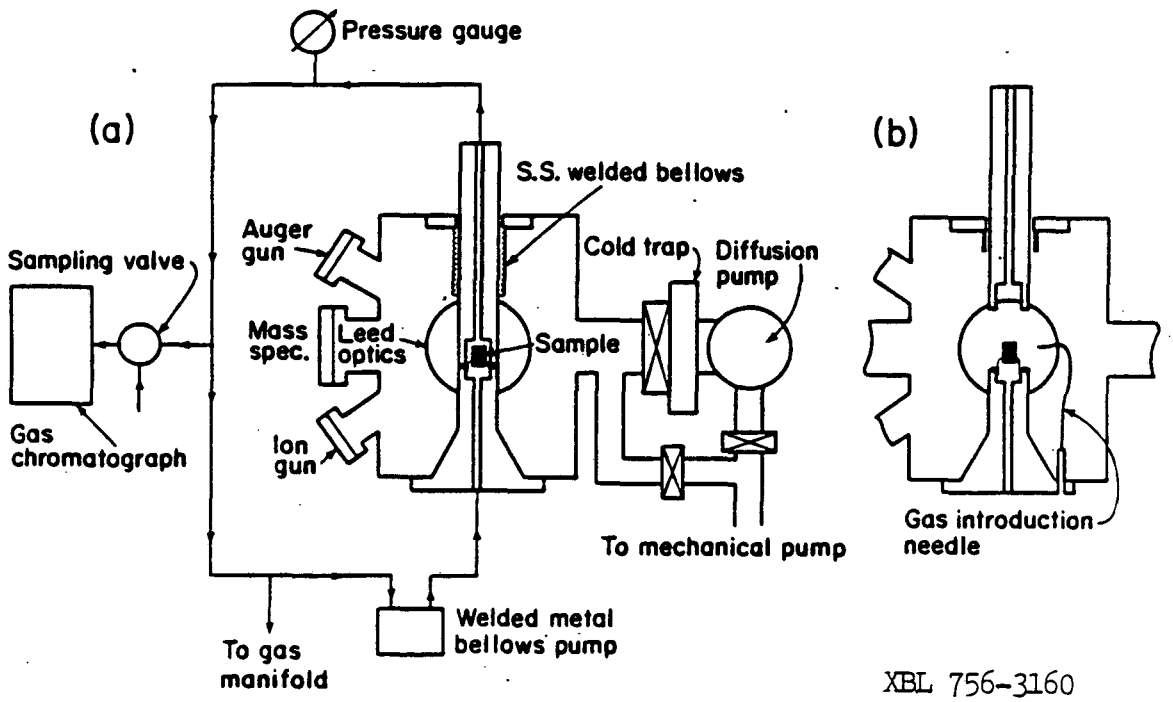

Fig. 1 (a) Schematic diagram of the high pressure/UHV apparatus with sample enclosed in the high pressure cell. (b) HP/UHV apparatus with cell open.

The surface science studies of catalytic reactions which have been performed to date indicate that there are three types of metal-based catalytic systems:

1. The first encompasses reactions that occur directly on a bare metal surface. These catalytic processes are characterized by their sensitivity to the atomic structure of the surface.

2. The second class includes reactions occurring on an overlayer that is irreversibly bound to the metal surface. Such reactions involve adsorbates that are weakly bound to this overlayer and, thus, are insensitive to the structure of the underlying metal surface.

3. Finally, reactions on coadsorbate modified surfaces fall into the third category. These catalysts contain additives that alter the bonding of reactants to the surface, or block specific reaction sites, altering reaction pathways. Most practical catalyst systems are formulated with additives (promoters and inhibitors) to optimize their activity, selectivity and life even if the reactions they catalyze belong to class (1) or class (2).

The following accounts present case histories of surface science studies of catalytic processes representing each of the three categories. We shall discuss ways in which these reaction types may be identified by experiments. Finally, some of the methods that could be employed to build catalysts with desirable properties will be reviewed.

Catalytic Reactions On Metal Surfaces.

These reactions usually involve strongly adsorbed intermediates and are surface structure sensitive. Atomically rough surfaces usually exhibit the highest turnover rates. The best example of this type of process is the synthesis of ammonia. Figure 2a shows the rates over three iron single crystal surfaces.[14] The (111) orientated crystal face is about 500 times as active as the (110) close packed surface. Adsorption studies by Ertl et al.[15] show equally large differences in the sticking probability of N_2 on these surfaces, confirming that the dissociation of N_2 is a rate limiting step in this reaction. The ammonia synthesis over rhenium crystal surfaces[16] shows even larger structure sensitivity as shown in Figure 2b. The $(11\bar{2}0)$ and the $(11\bar{2}1)$ crystal faces of this hexagonal close packed metal are over 1,000 times more active than the close packed (0001) crystal face. Figure 2c shows the three metal surfaces that are most active for ammonia synthesis. These surfaces are rough on the atomic scale and have open structures that expose high coordination sites especially in the second layer. These atoms with large numbers of nearest neighbors are accessible to the in-coming N_2 molecules and appear to be most active for their dissociation.

The ammonia synthesis may be viewed as an example of a reaction that obeys Langmuir-Hinschelwood kinetics, being dominated by the reactions between adsorbed species on the metal surface.

High coordination sites may be made available in catalytic reactions by using surfaces with open atomic structures so that atoms in the second layer become available to the incoming reactants. This is clearly the

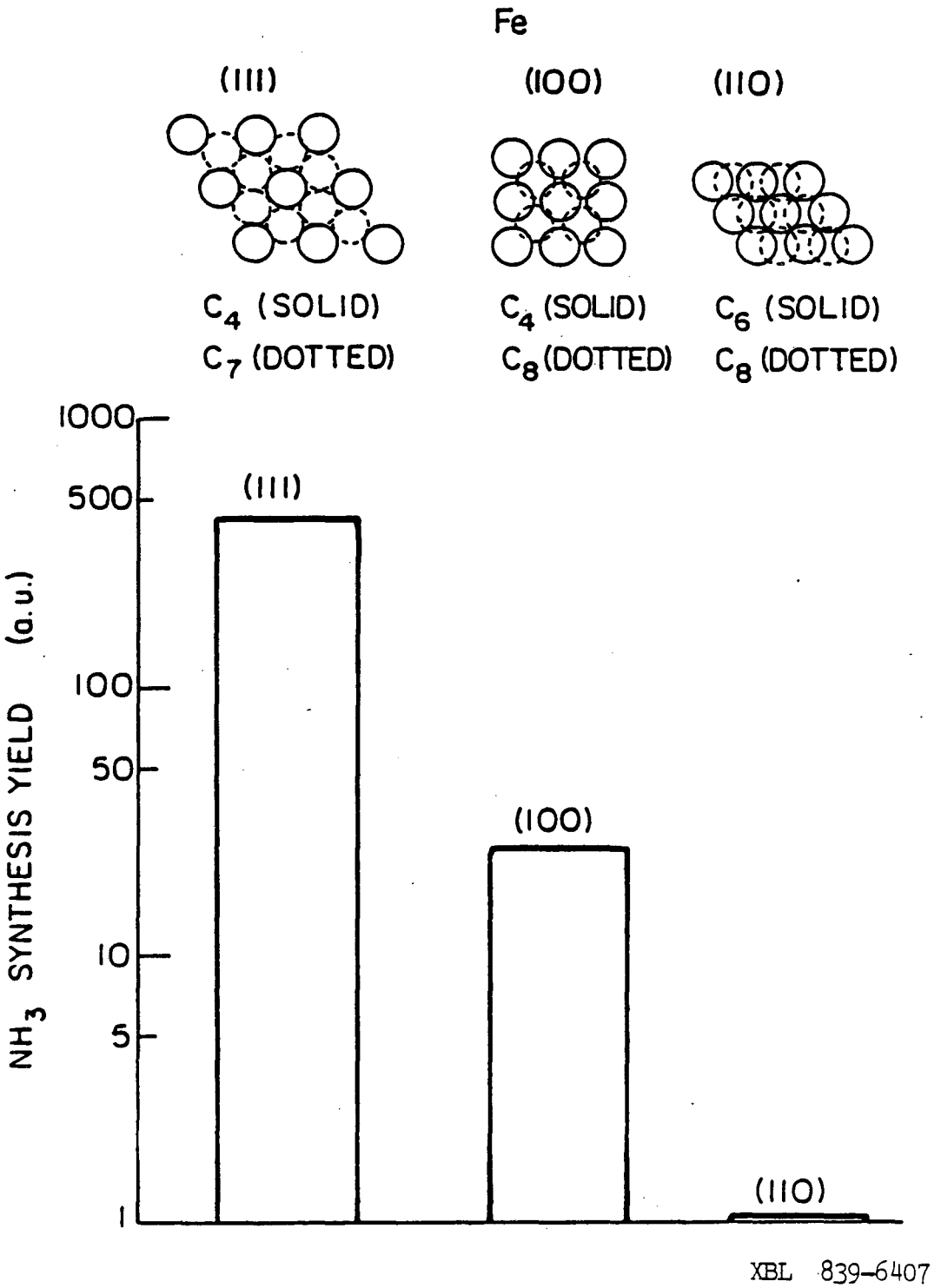

Fig. 2a Bar graph showing the profound influence of surface structure on the rates of ammonia synthesis over iron single-crystal surfaces at 20 atm and 700 K.

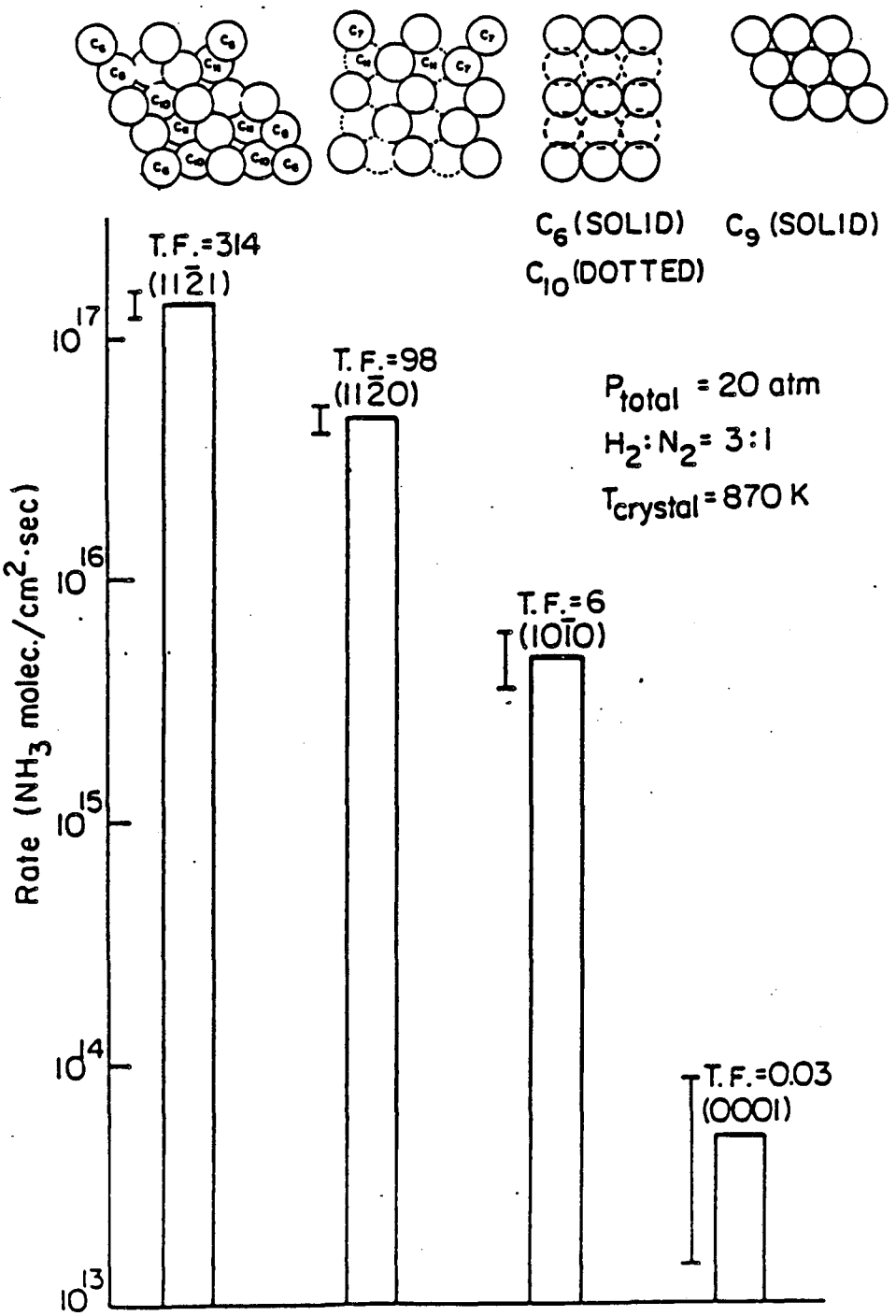

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Fig. 2b Rates of NH_3 synthesis over rhenium single-crystal surfaces at 20 atm and 870 K.

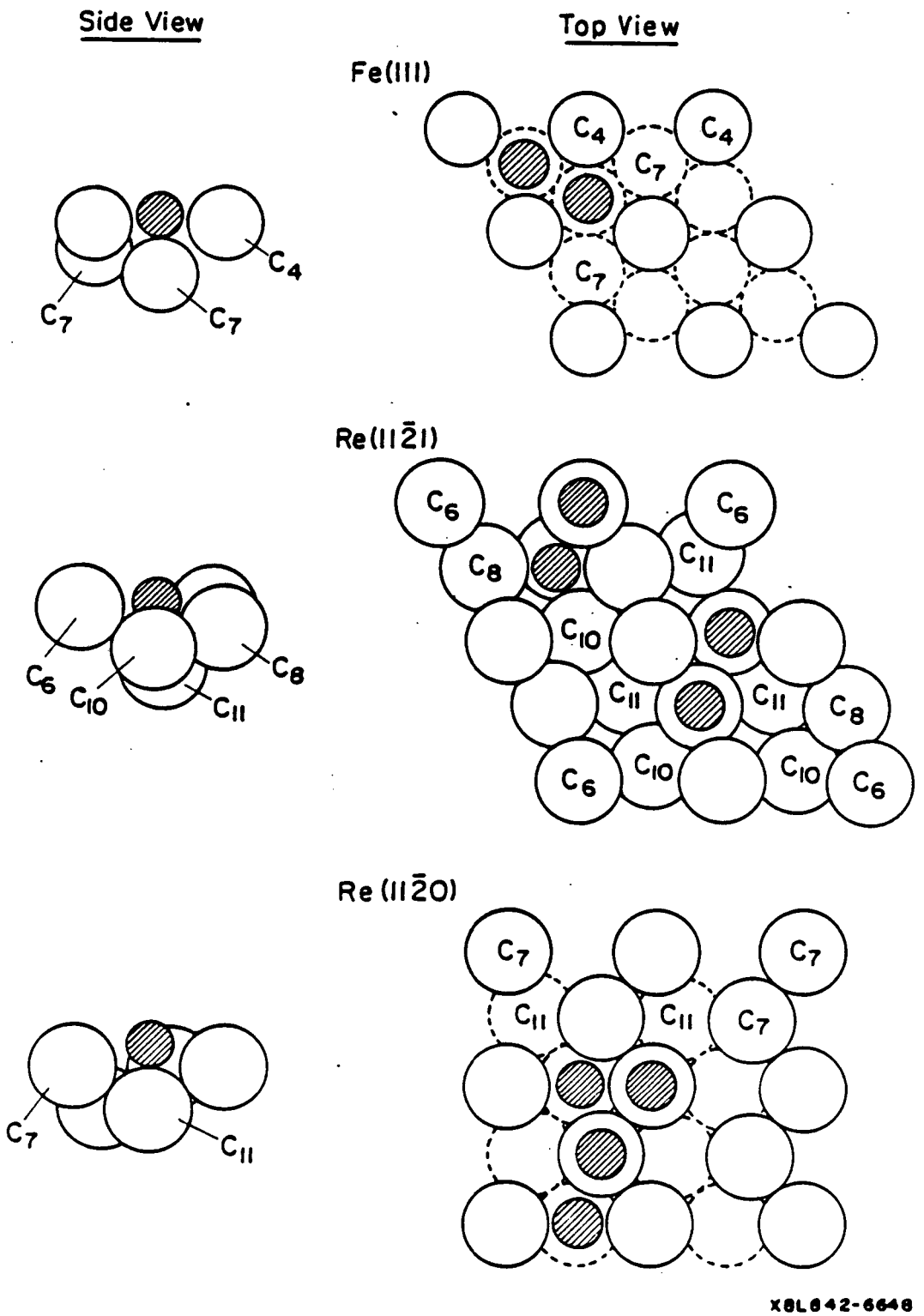

Fig. 2c The metal surfaces that are most active for ammonia synthesis, showing coordination numbers and adsorption sites (shaded atoms).

situation during ammonia synthesis where these open, high Miller index surfaces, which are most active for this reaction, are stabilized in the presence of nitrogen despite their high surface energy as compared to the close packed low Miller index surfaces, bcc(110) and hcp(0001). Another more frequent method of generating rough surfaces is through the creation of atomic steps and kinks.[17] Figure 3a exhibits different close packed surfaces with variable concentrations of steps. These are usually one atom in height and are separated by terraces of low Miller index orientations. There may be kinks in the steps (Figure 3b). The relative concentration of

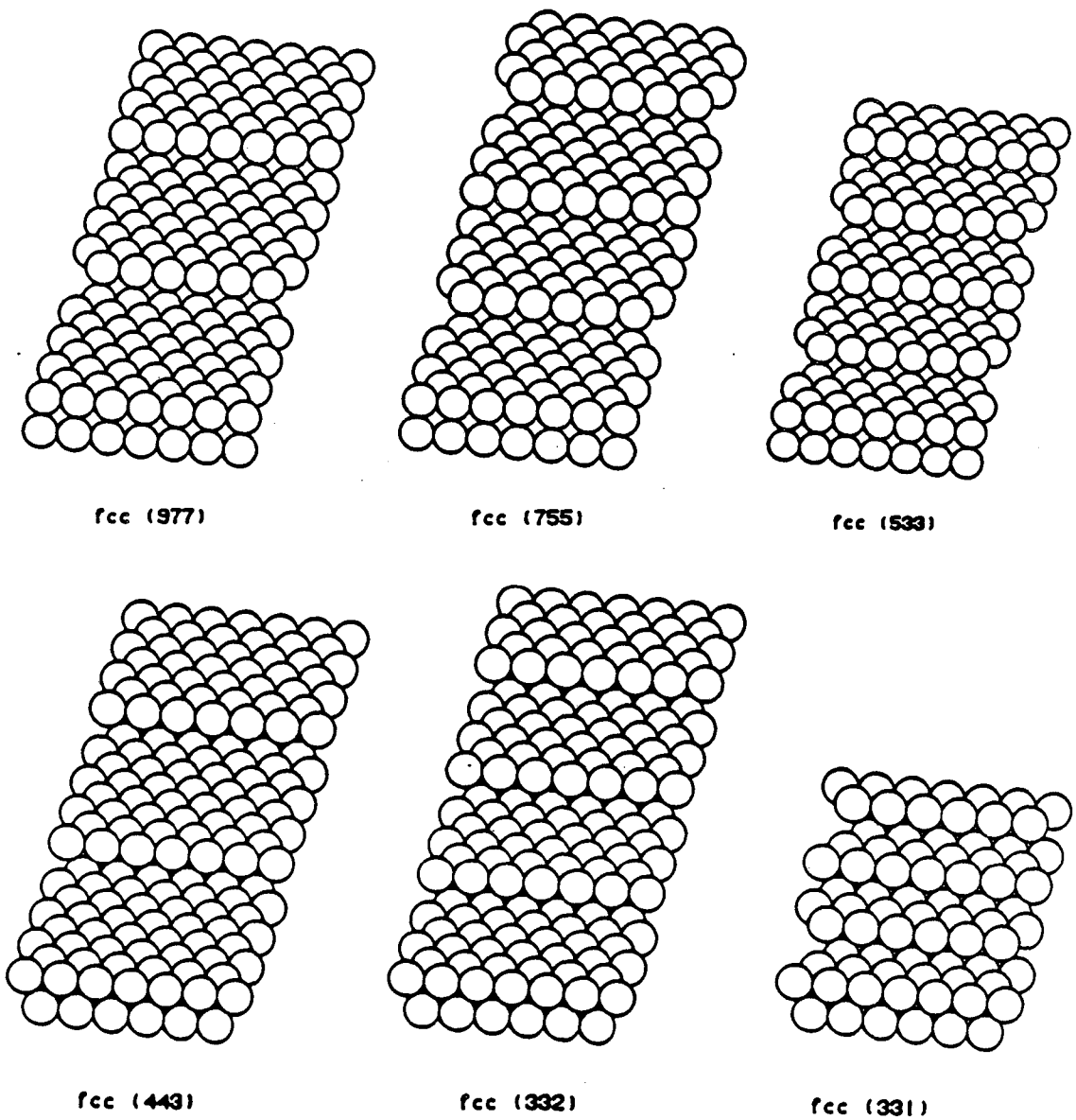

Fig. 3a Structure of several high-Miller index stepped surfaces with different terrace widths and step orientations.

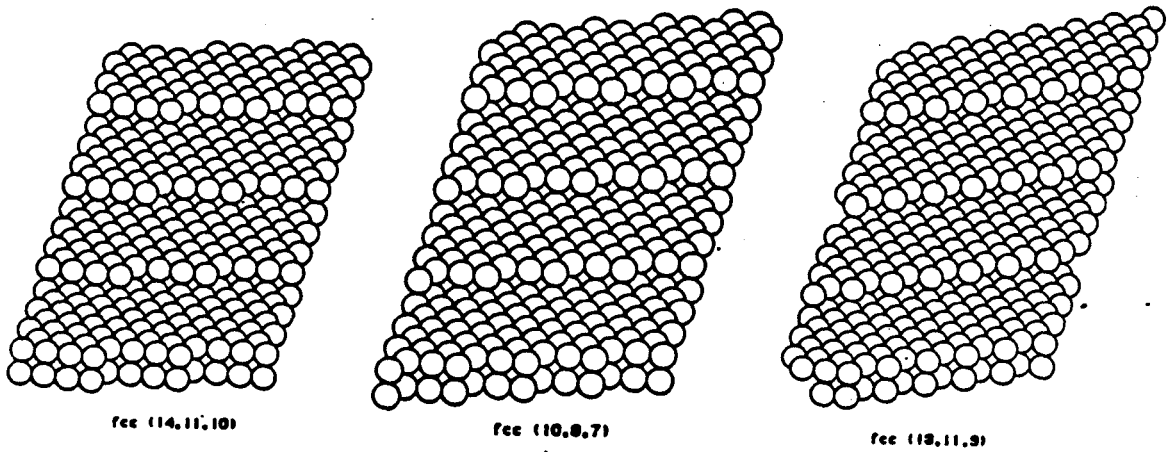

Fig. 3b Surface structures of several high-Miller index surfaces with different kink concentrations in the steps.

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atoms at steps, kinks and in terraces depends on the conditions of preparation. For single crystals, the direction of cut determines the surface structure. For small particles, the particle size and shape determine the concentrations of the various irregularities, steps and kinks. Usually the smaller the particle, the higher the concentration of steps and kinks.

The bottom of a step or kink exposes atoms of high coordination while the top consists of atoms with a smaller number of nearest neighbors. Kink sites in platinum single crystal studies proved to be centers of strong hydrogenolysis (C-C bond breaking) activity as shown in Figure 4.[18] The rates of hydrogenolysis of light molecules or n-heptane correlates well with increasing kink concentrations.

There is increasing evidence that while high coordination sites enhance the catalytic reaction rates for structure sensitive reactions, low coordination sites adsorb molecules strongly and hold them tenaciously. On a stepped or kinked surface, both high coordination and low coordination sites are present side by side. Therefore sites of increased turnover have neighboring sites where strongly adsorbed species exist with resident times that are over an order of magnitude greater than the turnover times for the catalytic reaction. ^{14}C and ^{35}S isotope labeling studies of reactants clearly indicate the presence of a strongly adsorbed overlayer that partially covers a catalytically active metal surface. It is one of the ironies of metal catalysis that the creation of active sites of high turnover brings about the production of other sites of strong bonding and thus minimal turnover, in equal numbers.

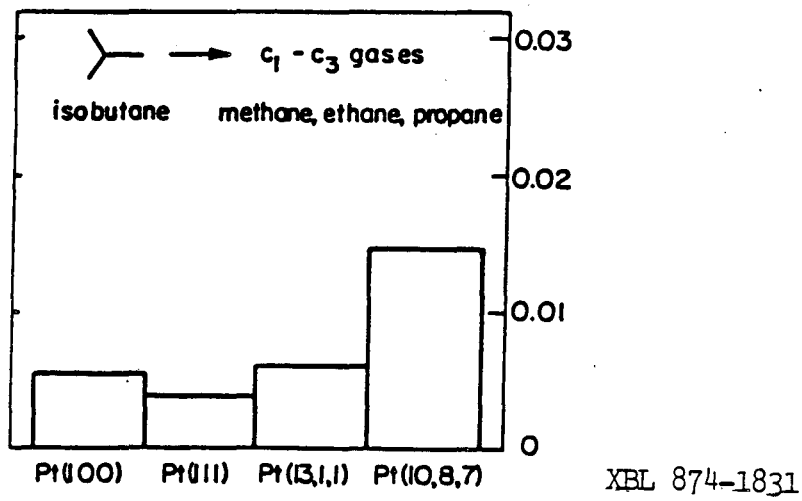


Fig. 4 Reaction rates shown as a function of surface structure for isobutane hydrogenolysis catalyzed at 570 K, at atmospheric pressure over four platinum surfaces. Hydrogenolysis rates are maximized when kink sites are present at high concentrations as in the platinum (10,8,7) crystal surface.

Catalysis On Top Of A Strongly Adsorbed Overlayer.

Reactions of this type do not occur directly on the metal surface and therefore are usually structure insensitive.[19] In fact, the role of the metal is reduced to providing atoms, hydrogen for example, via the dissociation of diatomic molecules. The metal is usually covered by strongly adsorbed overlayers and thus the incoming reactants (other than hydrogen) cannot form strong metal-adsorbate bonds. An example of this type of reaction is the hydrogenation of ethylene.[20] This facile reaction occurs at 300°K and at atmospheric pressures on many transition metal surfaces. It has been the subject of investigations of many researchers including Farkas and Farkas,[21] Eley,[22] Beek,[23] Twigg and Rideal,[24] Horiuti and Polanyi,[25] Roberts,[26] and many others.[27] I shall restrict my comments to platinum and rhodium which are among the most active catalysts for this process. Table II indicates that hydrogenation occurs equally well on platinum crystals, films, foils, and supported particles, indicating that the reaction is structure insensitive.[28] When the clean metal surfaces are exposed to ethylene, a strongly adsorbed overlayer of ethylidyne, C_2H_3, forms. This molecular specie is shown in Figure 5 along with its vibration spectrum, obtained by high resolution electron energy loss spectroscopy HREELS.[29] The kinetics of ethylene hydrogenation and those of ethylidyne formation have been studied extensively over the (111) faces of rhodium and

TABLE II

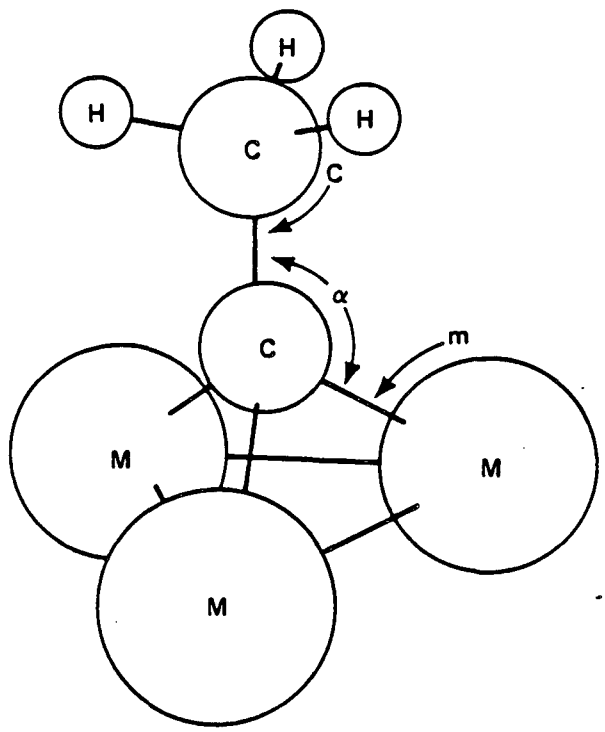
Comparison of ethylene hydrogenation kinetic parameters for different platinum catalysts.

Catalyst	Log Rate[a]	a[b]	b[b]	E_a(Kcal/mole)	Ref.
Platnized foil	1.9	-0.8	1.3	10	11
Platinum evaporated film	2.7	0	1.0	10.7	12
1% Pt/Al_2O_3	---	-0.5	1.2	9.9	5
Platinum wire	0.6	-0.5	1.2	10	13
3% Pt/SiO_2	1.0	----	---	10.5	14
0.05% Pt/SiO_2	1.0	0	---	9.1	15
Pt (111)	1.4	-0.6	1.3	10.8	Our work

a) Rate in molec/Pt atom.sec, corrected for the following conditions: T = 323K, $P_{C_2H_4}$ = 20 torr, P_{H_2} = 100 torr.

b) Orders in ethylene (a) and hydrogen (b) partial pressures.

Different ethylidyne species: bond distances and angles
(r_C = carbon covalent radius; r_M = bulk metal atomic radius)



	C [Å]	m	r_M	r_C	α [°]
$Co_3(CO)_9CCH_3$	1.53 (3)	1.90 (2)	1.25	0.65	131.3
$H_3Ru_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.34	0.74	128.1
$H_3Os_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.35	0.73	128.1
Pt (111) + (2 X 2) CCH_3	1.50	2.00	1.39	0.61	127.0
Rh (111) + (2 X 2) CCH_3	1.45 (10)	2.03 (7)	1.34	0.69	130.2
$H_3C - CH_3$	1.54			0.77	109.5
$H_2C = CH_2$	1.33			0.68	122.3
$HC \equiv CH$	1.20			0.60	180.0

Fig. 5a Surface structure of ethylidyne. Bond distances and bond angles are compared with several trinuclear metal cluster compounds of similar structure.

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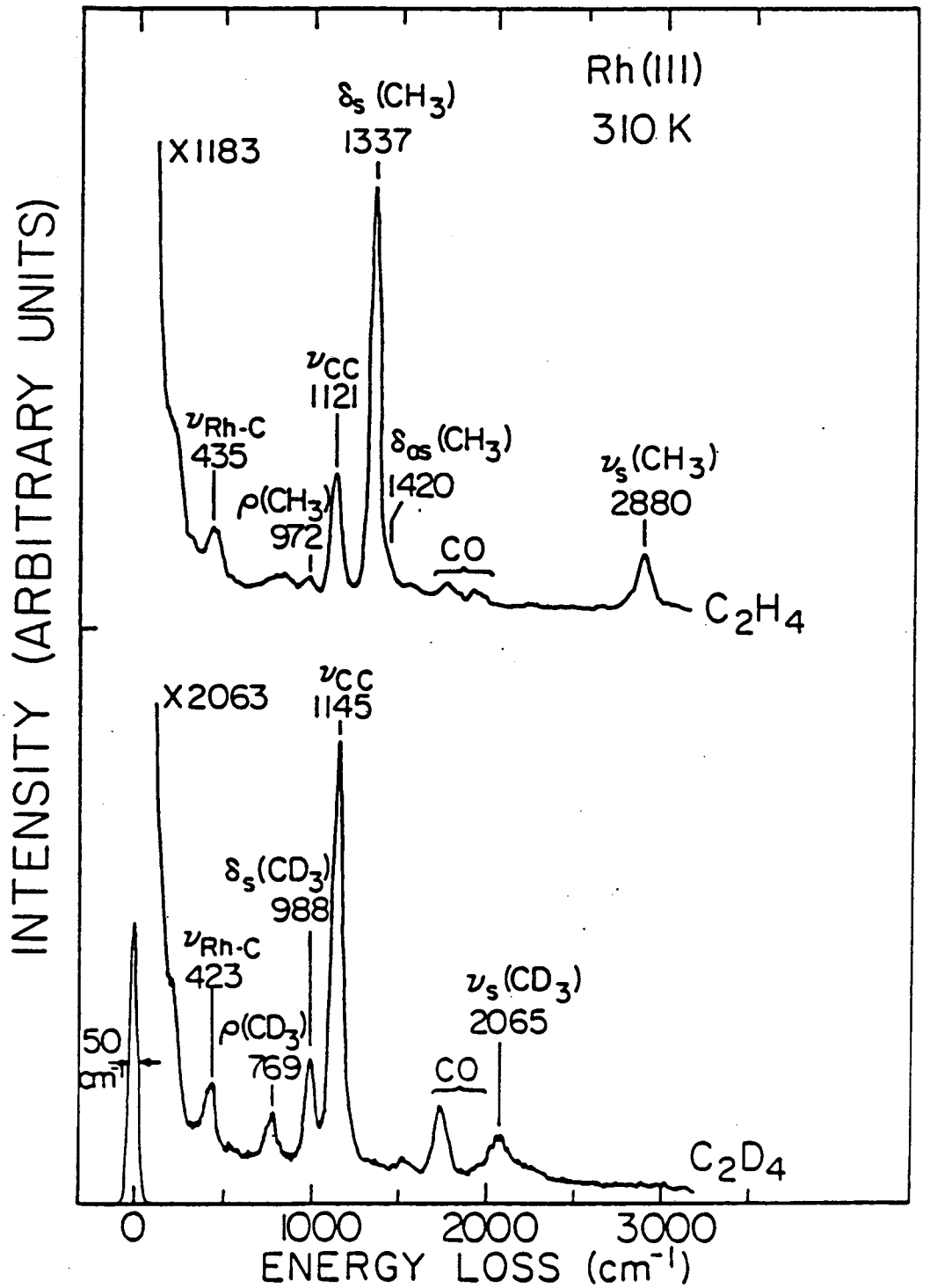

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Fig. 5b High-resolution electron-energy-loss vibrational spectrum of ethylidyne and deuterated ethylidyne on rhodium (111).

platinum and the rates of these processes are displayed in Figure 6. Ethylene hydrogenation occurs at a rate six orders of magnitude higher than the rehydrogenation of the strongly adsorbed ethylidyne.[20] Even the deuteration of the methyl group of ethylidyne occurs very slowly. ^{14}C labeling of ethylidyne and vibrational spectroscopy studies confirm these findings.

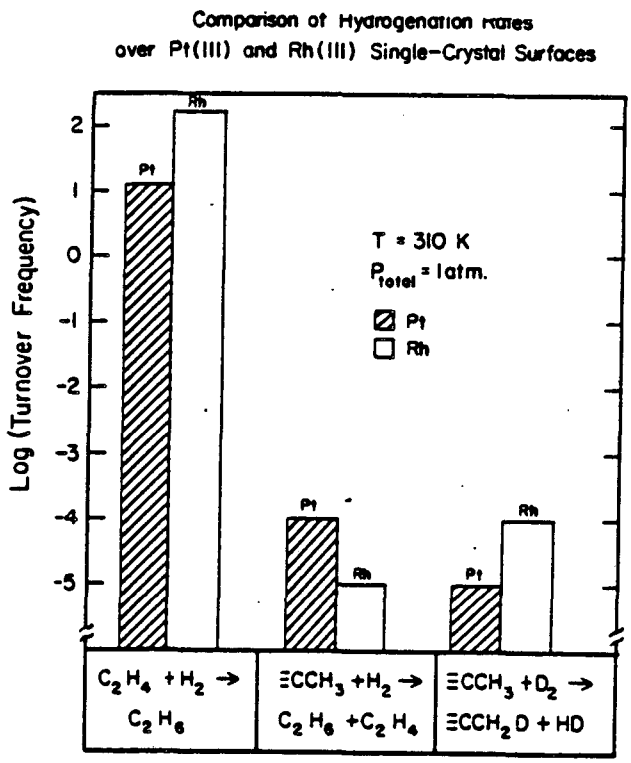

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Fig. 6 Turnover rates for ethylene hydrogenation, the rehydrogenation of ethylidyne, and the deuteration of the methyl group of ethylidyne on platinum and rhodium crystal surfaces.

The (111) faces of platinum and rhodium are covered with a monolayer of ethylidyne during ethylene hydrogenation since reaction rates are nearly identical over initially clean surfaces and surfaces pre-covered with ethylene. Vibrational spectroscopy studies confirm that the adsorbed monolayer structure on these surfaces after hydrogenation is ethylidyne. Thus ethylene hydrogenation occurs rapidly on the C_2H_3 covered surfaces. The packing of the ethylidyne on the overlayer does not permit C_2H_4 adsorption directly on the metal surface as proven by exchange studies with C_2H_4 on C_2D_4. On the other hand, thermal desorption studies show that $H_2(D_2)$ can be dissociated and readsorbed on the ethylidyne covered surfaces up to about one-quarter of a monolayer coverage.

A reaction model that explains these results is shown in Figure 7.[20] The hydrogen atom is transferred to the ethylene molecule that is weakly adsorbed on top of the ethylidyne and in the second layer perhaps by forming an ethylidene intermediate. Such model of hydrogen transfer from hydrocarbons to ethylene was first proposed by Thompson and Webb,[30] and our studies corroborate their findings. Our mechanism is of the Eley-Rideal type and is characterized by low-activation energy and structure insensitivity.

PROPOSED MECHANISM FOR ETHYLENE HYDROGENATION

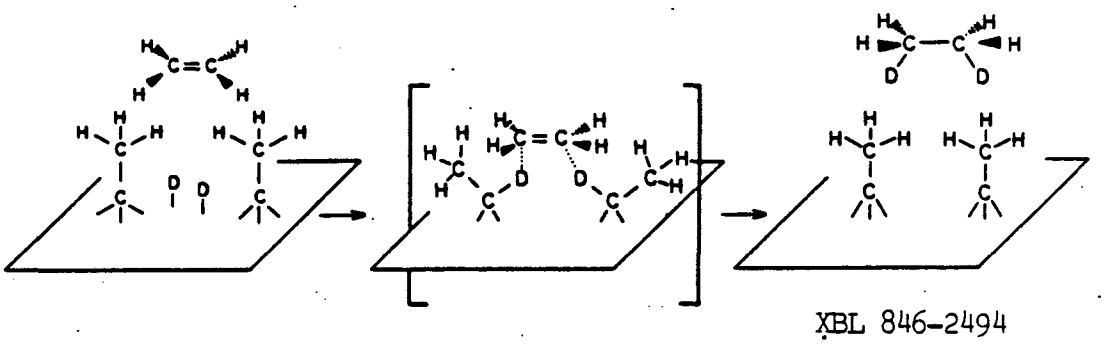

Fig. 7 Proposed mechanism for the rapid, structure-insensitive hydrogenation of ethylene.

However, there are other mechanisms of C_2H_4 hydrogenation that our studies and those of others have uncovered.[20] At higher temperatures, the rate of rehydrogenation of C_2H_3 is significant and the bare metal becomes available, in part, for C_2H_4 hydrogenation. During the electrochemical hydrogenation of C_2H_4, the platinum surface is covered with a layer of hydrogen atoms (hydride) that react rapidly with the approaching C_2H_4 and do not permit the formation of ethylidyne. The complexity of surface reactions cannot be underestimated.

Nevertheless, ethylene hydrogenation provides an example of reactions of weakly adsorbed molecules in the second layer, an important class of catalytic reactions that could occur at low temperatures or high pressures. The hydrogenation of CO over certain transition metals that exhibit positive order pressure dependence on both H_2 and CO pressures are thought to occur this way.

These types of structure insensitive reactions may be compared with homogeneous catalytic reactions which are facile, occuring at lower temperatures and include hyrogenation or hydroformylation. Since the metal

plays secondary roles in this process, high coordination sites are not needed to carry out the reaction. It is hoped that future studies will reveal the possible correlation between homogeneous catalytic reations and heterogeneous reactions of this type.

It is interesting to speculate how hydrogen transfer occurs that is mediated by the strongly adsorbed organic overlayer and the nature of bonding of the incoming reacting molecules in the presence of this overlayer. Rapid hydrogen transfer and weak bonding of the reactants are indicated by the low activation energy and the rapid turnover of these processes. These are the properties of enzyme catalyzed reactions as well, in addition to many homogeneous catalytic processes. If the mechanism of these reactions can be correlated with the mechanism of ethylene hydrogenation, it brings into focus the key role of the strongly adsorbed overlayer, both for hydrogen transfer and for acting as a template to the reactant molecules. Is it possible that direct bonding of reactants to metal sites is not necessary for the reaction to occur? Our data are consistent with such a model which should force a re-evaluation of many of the reaction mechanisms that are suggested for homogeneous catalytic processes.

The organic overlayer may also serve as a template to orient or align the reactants. LEED surface crystalography and HREELS studies of the structure of these monolayers indicate that their structural integrity is preserved up to 400 K, thus their presence may permit carrying out various specific reactions below this temperature. Above 400 K, fragmentation to small organic CH and C_2H groups occurs (Figure 8 shows this process). While at low temperatures,[31] benzene and ethylene maintain their molecular identity on the platinum and rhodium crystal surfaces, above 400 K, the fragments are the same small organic moieties. Thus enzyme-like catalysis that requires a template to line up the reactant molecules can only be carried out below 400 K.

REACTIONS OVER MODIFIED SURFACES

Let us consider how the location and bonding of an adsorbed molecule is altered when another molecule or atom coadsorbs with it. The relatively weak interactions of benzene and carbon monoxide when coadsorbed on platinum or rhodium illustrate this.[32] Benzene forms a disordered monolayer over platinum in the absence of carbon monoxide. When CO is introduced, several ordered structures form that are detectable by low

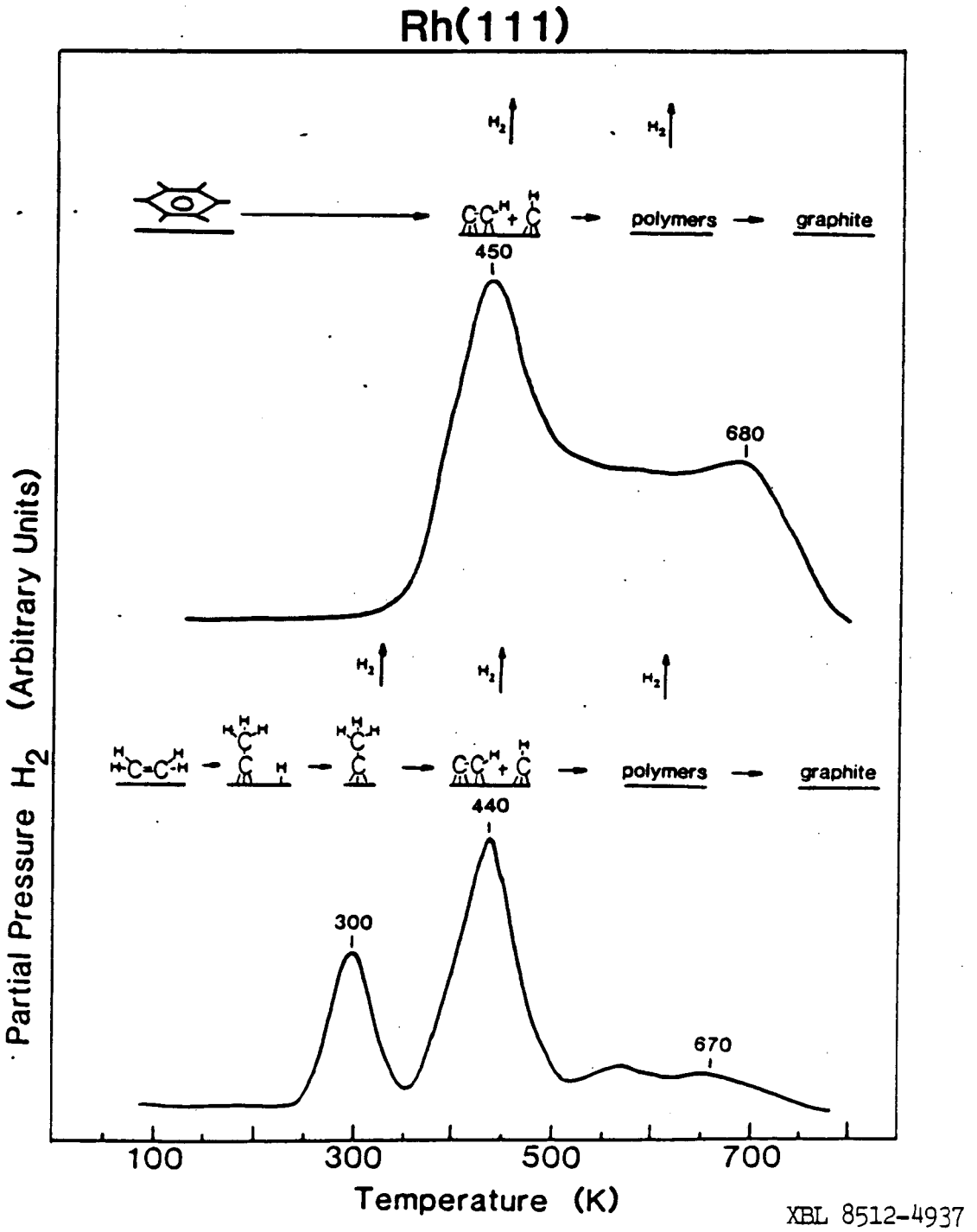

Fig. 8 Fragmentation of ethylene and benzene adsorbed on the rhodium (111) crystal surface as a function of temperature as determined by thermal desorption spectroscopy and high-resolution electron-energy-loss spectroscopy studies.

energy electron diffraction, LEED. These structures change depending on the carbon monoxide to benzene ratio on the Pt or Rh surfaces, which can be monitored by HREELS and thermal desorption spectroscopy, TDS. Figure 9 shows the various ordered structures that consist of mixed CO-benzene layers with one, two or three CO molecules per benzene. The ordering of benzene is facilitated by the weak attractive interaction with CO that also blocks certain alternative adsorption sites. It should be noted that, on Rh, CO is located in a three-fold site as determined by LEED surface crystallography and HREELS, a site that it would never occupy in the absence of benzene.[33]

The coadsorbed atoms or molecules may be viewed as surface modifiers and they have indeed profound influence on the structure and distribution of the bonding sites and also on the nature of the chemical bond that the reactants form with the catalyst surface. We shall arbitrarily divide the surface modifiers into two groups: 1) structure modifiers; and 2) bonding modifiers. It should be noted that often the modifier influences both the surface structure and the bonding of the reactants.

1. Structure Modifiers

a. Site Blocking By Sulfur. Let us consider the interaction of coadsorbed sulfur with thiophene that occurs during the hydrodesulfurization of thiophene on the molybdenum (100) crystal surface.[34] This gentle reaction removes the sulfur from the molecule as H_2S in the presence of hydrogen, leaving behind C_4 species that readily hydrogenate to butadiene, butenes, and butane without fragmentation. Molybdenum metal strongly adsorbs and decomposes thiophene and butenes as shown by surface studies, and thus, the clean surface cannot be an active catalyst. MoS_2 is a layer compound and its basal plane holds thiophene so weakly that its thermal desorption occurs at 165 K.[35] Thus this surface is not chemically active. The active molybdenum surface contains about one-half of a monolayer of strongly adsorbed sulfur. These atoms block the metal sites where thiophene decomposition would occur. ^{35}S labeling studies indicate that these sulfur atoms remain permanently on the metal surface during the catalytic reactions. The sulfur atom that is removed from the thiophene molecule occupies sites of weaker bonding where hydrogenation to H_2S and subsequent desorption occurs while the C_4 species partly hydrogenate as well and desorb.

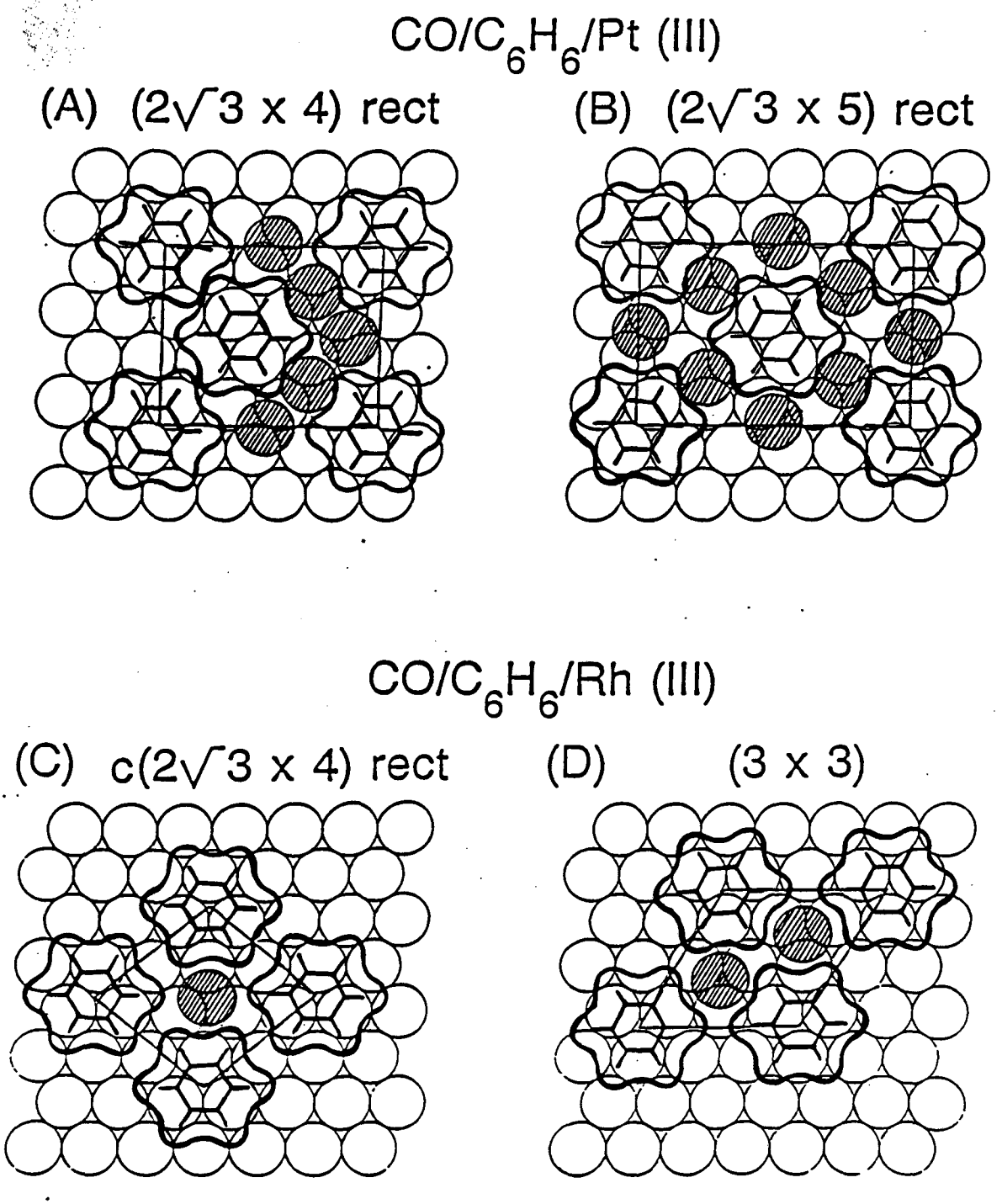

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Fig. 9 Coadsorbed surface structures of carbon monoxide and benzene on the platinum (111) and rhodium (111) single-crystal surfaces.

Thus the blockage of certain adsorption sites on the surface of early transition metals attenuates the strong bonding and permits the catalytic reaction to occur.

The hydrogenolysis of organic molecules is frequently an undesirable reaction that leads to the production of lower molecular weight products. Kink sites on transition metal surfaces are especially active for the C-C bond breaking reaction.[36] While their surface concentration is no more than about 5 percent of the total number of metal sites, they may account for 90 percent of hydrogenolysis activity. These hydrogenolysis sites can often be poisoned by the chemisorption of controlled amounts of sulfur (produced by H_2S decomposition) that binds more strongly to kink sites as compared to terrace sites. In this way, the hydrogenolysis reaction can be poisoned selectively as the kink sites are blocked and rendered inactive.

b. Ensemble Effect In Alloy Catalysis and the Creation of New Sites By Alloys. As compared to pure platinum, bimetallic alloys such as platinum rhenium and platinum gold frequently exhibit superior activity, selectivity, and deactivation resistance during catalyzing reforming reactions. The influence of gold on hydrocarbon conversion catalysis by platinum was recently studied by evaporating gold onto platinum single crystal surfaces.[37] At low temperatures, gold forms expitaxial overlayers on platinum but upon heating it dissolves to form an alloy in the near surface region. This Pt-Au alloy displays markedly different activity and selectivity for the conversion of n-hexane as shown in Figure 10a. Isomerization activities increase substantially as compared to that for clean platinum while the aromatization and hydrogenolysis rates decrease exponentially with increasing gold surface concentration. This remarkable change in catalytic behavior can be explained by a change in the geometric distribution of platinum sites that are present in the (111) alloy surface. Substitution of gold atoms dilutes the surface platinum atoms such that the high coordination three-fold platinum sites are eliminated much faster than the two-fold bridge and single atom top sites. This change in the size distribution of the available reaction sites is frequently called the ensemble effect.[37] As a result of this effect, catalyzed reactions that involve adsorption and rearrangement at three-fold sites are eliminated, while reactions that require one or two atom sites are attenuated to a much lesser extent. While minor changes in electronic structure may also occur at the alloy surface sites, most of the reaction results can be simple

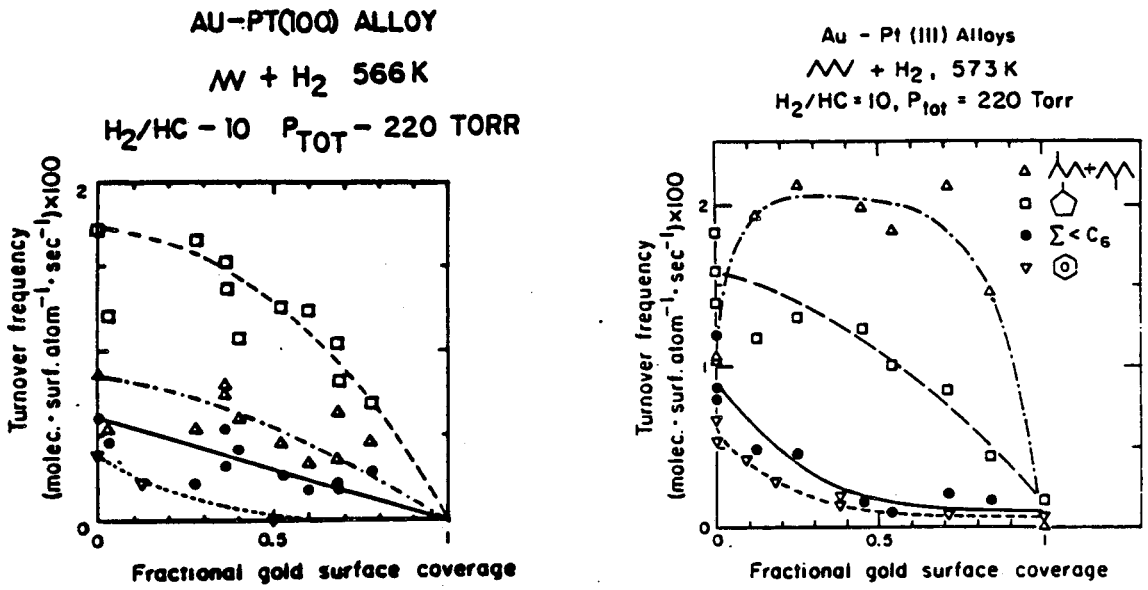

Fig. 10a and 10b Rates of formation of various products from n-hexane conversion as a function of fractional gold coverage for gold-platinum alloys that were prepared by vaporizing gold onto (a) platinum (111) and (b) platinum (100) crystal surfaces, respectively.

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explained by this high coordination site elimination model. Similar results revealing pronounced changes in catalytic behavior with alloy composition were recently reviewed by Ponec[38] and Sinfelt.[39] For a variety of hydrocarbon reactions, catalyzed over metal films and high area supported catalysts, in most cases, the geometrical ensemble effect is decisive in controling the reaction selectivity.

The effect of alloying is also surface structure sensitive as shown by recent studies where gold was the alloying constitutent in the Pt(100) crystal face instead of the Pt(111) surface.[40] The (100) surface has a square unit cell that contains four-fold, bridge and top sites and unlike the (111) surface it does not have three-fold sites. When this surface is alloyed with gold, all reaction rates decline in proportion to the concentration of inactive gold on the Pt(100) surface when n-hexane was used as a reactant. This is shown in Figure 10b. Thus the enhancement of the isomerization activity requires a presence of three fold sites. When gold is used as an alloying agent, there are three types of three-fold sites available. One contains three platinum atoms while the other two are mixed Pt-Au sites and contain one and two Pt atoms, respectively (Figure 11). Thus, alloying produces new mixed metal sites with catalytic behavior that can modify the selectivity. Figure 10a clearly indicates that the high

isomerization rate of n-hexane is sustained until the surface was covered up to two-thirds of a monolayer of gold.[40] Thus all three three-fold sites, shown in Figure 11, are active for isomerization. The mixed platinum-gold sites are then responsible for the enhanced isomerization activity of the platinum-gold alloy that exhibits markedly higher rates than the pure platinum (111) crystal surface.

Boudart et al have shown a fifty-fold increase in the rate of the H_2/O_2 reaction to produce water over palladium-gold alloys.[41] Such large effects cannot be explained by site-blocking ensemble effects. The new sites that are created by alloying have unique structure and bonding. In fact, a new catalyst is created with structural and bonding properties that are not derived from the structural and bonding properties of the pure alloy constituents.

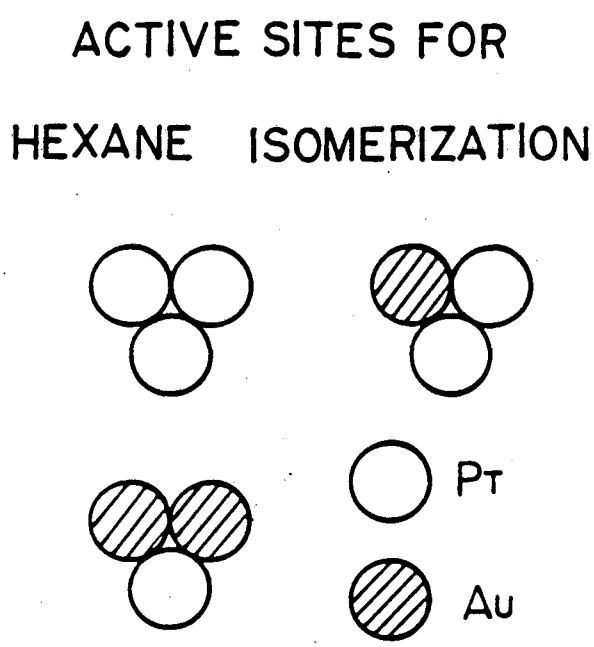

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Fig. 11 Platinum and mixed platinum-gold threefold sites that are active for hexane isomerization.

c. Modifiers That Cause Surface Restructuring. We have previously shown that the iron (111) crystal face is about 500 times more active for the synthesis of ammonia from nitrogen and hydrogen than the iron (110) crystal face. However, when alumina is present on the metal, which is then heated in a nitrogen or ammonia atmosphere, massive restructuring occurs. The iron (110) face recrystalizes into (111) orientation facets that become the predominant surface orientation after only one hour of heat treatment at 500°C in one atmosphere of nitrogen.[42] The restructured iron is now

as active for ammonia synthesis as is the clean iron (111) crystal face. Al_2O_3 is called a structural promoter of iron catalysts for good reason. The surface restructuring must occur through the formation of an iron-aluminate/iron-nitride phase as both the presence of alumina and nitrogen are needed for it to take place. While the close-packed (110) iron surface has a lower surface free energy than the (111) face when clean, in the presence of nitrogen, the (111) crystal face appears to be more stable as it forms stronger metal-nitrogen bonds. This provides the thermodynamic driving force for restructuring and the presence of alumina is needed for compound formation as it accelerates the kinetics of restructuring which would otherwise be much too slow under the available experimental conditions.

Nickel, an excellent hydrogenation catalyst, can be poisoned by sulfur that is present on the metal surface in concentrations amounting to a few percent of a monolayer. Surface science studies revealed that the adsorbed sulfur aids the reconstruction of the (111) crystal face to form the (100) face. The sulfur that is responsible for this restructuring produces an ordered overlayer on this reconstructed surface.[43] Again the stronger metal-sulfur bond on the (100) face as compared to the (111) face provides the thermodynamic driving force for this restructuring. In this circumstance, however, the reconstruction leads to poisoning of the catalytic activity and to chemical passivation of the metal surface.

Surface restructuring is important not only for structural promotion or poisoning, but also for catalyst aging and regeneration. A growth of catalyst particles often occurs in chemical environments that promote restructuring with a drastic loss of active surface area. Regeneration of catalysts using active redispersing agents that alter the surface structure and the surface free energies of the particles is an important area of catalysis science. It is hoped that correlations between changes of bonding and surface structure and the kinetics of restructuring will be established with beneficial effects on both catalyst life and chemical stability.

d. Mixed Reactions Requiring Both Metal Sites Of High Coordination And Strongly Adsorbed Overlayers. Dehydrocyclization, Isomerization, and Hydrogenolysis. There are many hydrocarbon conversion reactions that need strong metal-adsorbate bond breaking structure sensitive reaction steps that also require hydrogen transfer mediated by a strongly adsorbed organic overlayer. These reactions occur at high temperatures and have high

activation energies. Dehydrocyclization, hydrogenolysis, and isomerization are likely examples. These processes occur exceptionally well over platinum during reforming of low octane linear alkanes such as n-hexane or n-heptane to aromatics or branched isomers of high octane number. The complexity of hydrocarbon conversion reactions requires structure sensitive bond scissions and rearrangements, as well as hydrogen transfer and desorption via weak adsorption sites over the strongly adsorbed overlayer. Therefore, while the structure sensitivity is clearly present, it is less pronounced than in the case of ammonia senthesis (a factor of 5 instead of 500 difference in rates from crystal face to crystal face).[44] As a consequence of surface structure sensitivity and strong metal carbon bonding with reaction intermediates, these processes have high activation energies and therefore are carried out at high temperatures to obtain suitable turnover rates. Nevertheless, the active surface must also be covered by organic fragments that contain hydrogen for the necessary hydrogen transfer and desorption reaction steps. The upper temperature limit of these reactions is determined by the complete loss of hydrogen from these fragments, leading to graphitization of the organic overlayer that renders the catalyst inactive.

Figure 12 illustrates the rates of benzene production fron n-hexane near atmospheric pressure and at 573 K over the various platinum single crystal surfaces that were shown earlier. Also shown are turnover rates for a competing cyclization reaction that produces methylcyclopentane. Platinum surfaces with hexagonal (111) terrace structure display superior activity and selectivity for the more important aromatization reaction. In this case, the hexagonal surface is 3--5 times more active than the square (100) surface. Similar results were also obtained for n-heptane aromatization.[45] Steps and kinks promote the aromatization reaction,[45] although their influence appears to be less important than the terrace structure. By contrast, the rate of methylcyclopentane formation appears to show little dependence on platinum surface structure.

The production of both methylcyclopentane and benzene over platinum catalysts illustrates that cyclization may occur by two mechanisms involving either 1,5- or 1,6-ring closure. Our studies show that 1,5-ring closure predominates under mild conditions, whereas the structure sensitive aromatization reaction via 1,6-ring closure becomes strongly favored at high temperatures. The temperature range where this change in selectivity

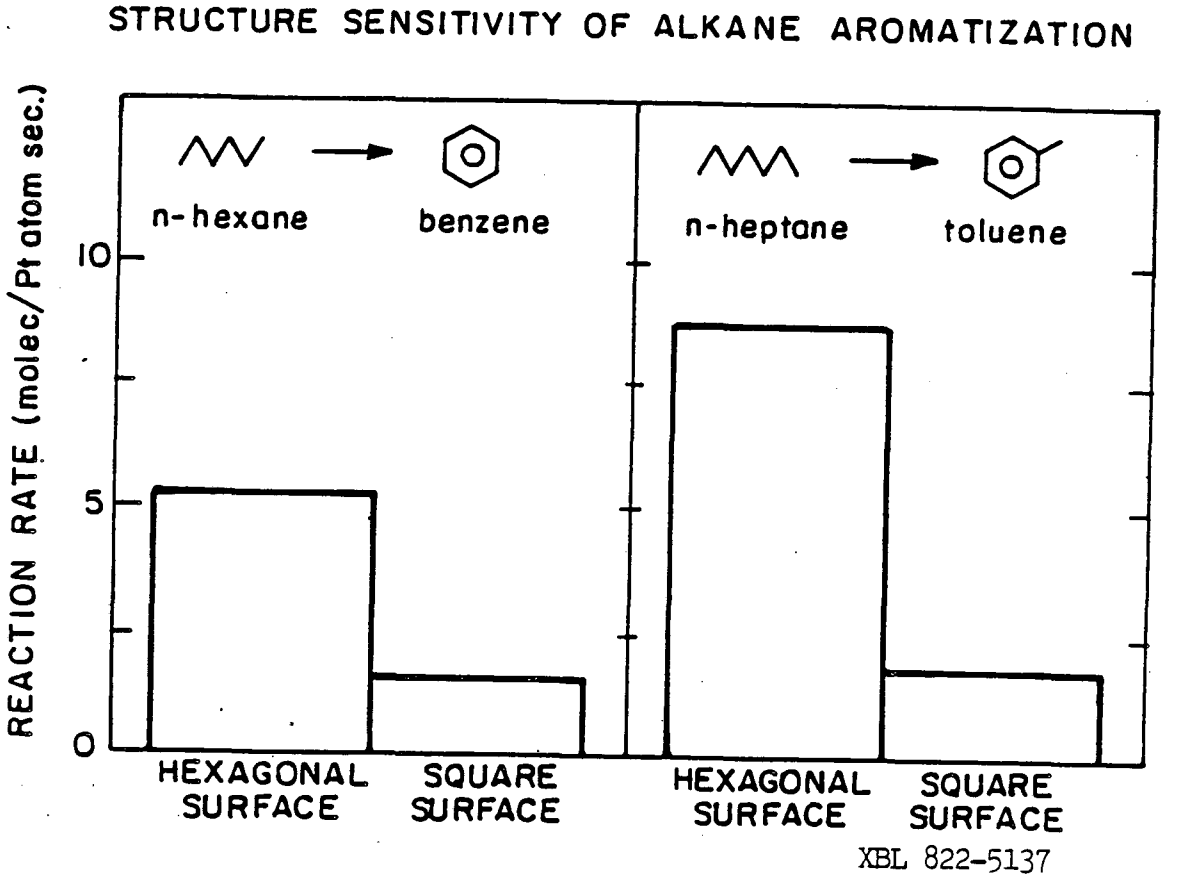

Fig. 12 Dehydrocyclization of alkanes to aromatic hydrocarbons is one of the most important petroleum reforming reactions. The bar graphs shown here compare the reaction rates for n-hexane and n-heptane aromatization catalyzed at 573 K and atmospheric pressures over the two flat platinum single-crystal 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.

occurs increases with increasing hydrogen pressure.[46] Figure 13 summarizes the selectivities for producing benzene over methylcyclopentane that were measured as a function of temperature. It can be seen that the hexagonal platinum surfaces exhibit superior aromatization selectivity over a wide range of conditions.

Conversely, the flat (100) platinum surfaces with square atomic arrangement are often much better isomerization catalysts as compared to the hexagonal platinum surfaces.[46] This is shown in Figure 14 where reaction rates are compared for isobutane isomerization and hydrogenolysis catalyzed over four platinum surfaces with different atomic structure. Depending on the catalyst preparation (structure), it is clear that one may obtain superior aromatization or isomerization activity that is also well documented in the literature for practical catalysts.[47,48] The hydro-

genolysis reaction that is also illustrated in Figure 14 proceeds with maximum rates on surfaces that contain large concentrations of kink sites during reforming. It is frequently desirable to poison the hydrogenolysis sites by chemisorbing controlled amounts of H_2S or other strongly bound additives that bind more strongly at step and kink sites as compared to the terrace sites. In this way, the hyperactive kink sites can be selectively poisoned and rendered inactive for the undesirable hydrogenolysis reaction. Because isomerization accounts for over 90% of the isobutane conversion over clean platinum,[46,49] it is clear from Figure 14 that the (100) surface is several times more active than Pt(111) for this small-alkane reaction.

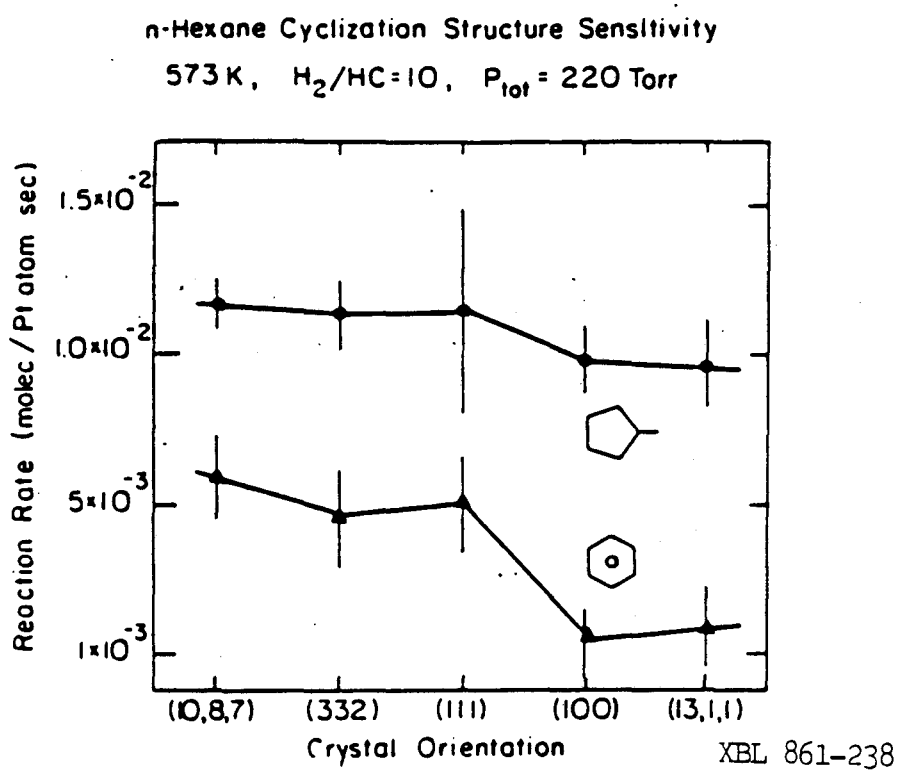

Fig. 13 Reaction rates for n-hexane dehydrocyclization to benzene and methylyclopentane catalyzed at 573 K over platinum single crystal surfaces with different atomic structure.

Similar results revealing marked structure sensitivity for simple hydrocarbon reactions catalyzed over clean metal surfaces were also obtained by Goodman[50,51] in studies of ethane and butane hydrogenolysis catalyzed over Ni (100) and Ni(111). Near atmospheric pressure and at 450-650K, the (100) surface with square atomic arrangement was several times more active than the hexagonal Ni(111) surface. The turnover rates, energetics and product distributions for alkane hydrogenolysis catalyzed over both platinum and nickel model catalysts were very similar to those frequently reported for high area supported catalysts.[52] Thus, it

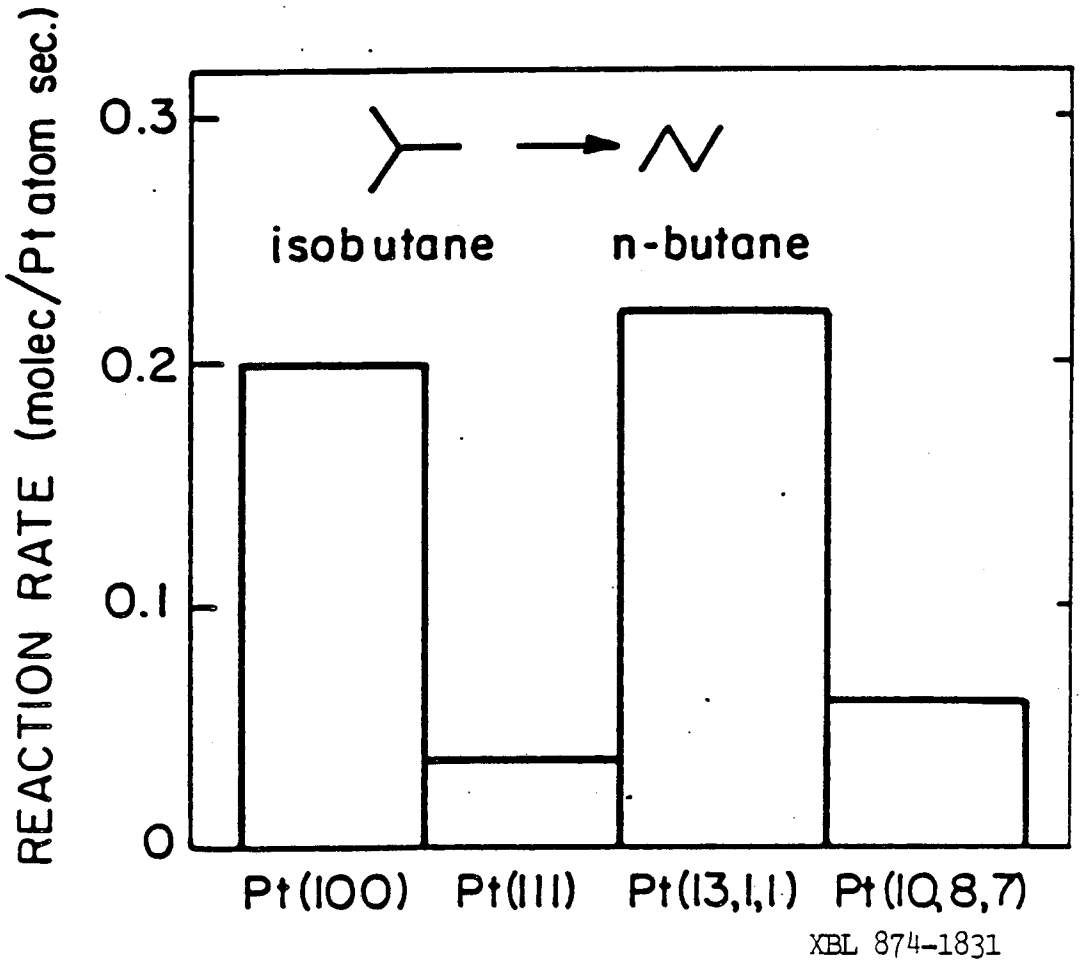

Fig. 14 Catalytic activity for isobutane isomerization at 573 K as a function of surface structure for four platinum surfaces. The (100) and (13,1,1) surfaces with square atomic arrangement exhibit maximum isomerization rates.

appears clear that the square (100) atomic arrangement leads to enhanced chemical activity for small hydrocarbon conversion reactions over both platinum and nickel. With platinum skeletal rearrangement is favored over hydrogenolysis, whereas with nickel hydrogenolysis is the exclusive reaction pathway.

In addition to altered reaction rates, the distribution of hydrogenolysis products also varies sharply over the (111) and (100) platinum surfaces. The hexagonal surface displays high selectivity for scission of the terminal C-C bond, whereas the (100) surface with the square unit cell prefers cleavage of C-C bonds located near the center of the reactant molecule as indicated by studies[46,47] of a variety of C_4-C_7 alkane reactions. Consecutive rearrangements during a single residence on the catalyst also occur more readily on the Pt(100) surface.[47]

The Carbonaceous Deposit. Perhaps the most general feature of hydrocarbon catalysis over platinum is the rapid and unavoidable build-up of one or more monolayer equivalents of strongly bound carbonaceous deposit. The formation of this deposit, its rehydrogenation dynamics, and the nature of its participation in the catalytic cycle for hydrocarbon skeletal rearrangement was revealed in detailed studies[53] correlating the rates and selectivities with the deposit surface coverage, composition, and structure. Carbon-14 labeled deposits were used to ascertain the residence time of the strongly bound carbon, while thermal desorption of hydrogen and CO were applied to monitor the deposit composition and the concentration of platinum sites that remain uncovered during the catalytic reactions, respectively. As a result of these studies a molecular model of the working platinum reforming catalyst[53] was developed that is shown in Figure 15. During skeletal rearrangement, most of the surface remains continuously covered by a disordered polymeric residue. The amount of deposit increases with increasing time and temperature, and the morphology gradually changes from 2-dimensional at low temperatures to 3-dimensional deposit increases with increasing time and temperature, and the morphology gradually changes from 2-dimensional at low temperatures to 3-dimensional for temperatures above

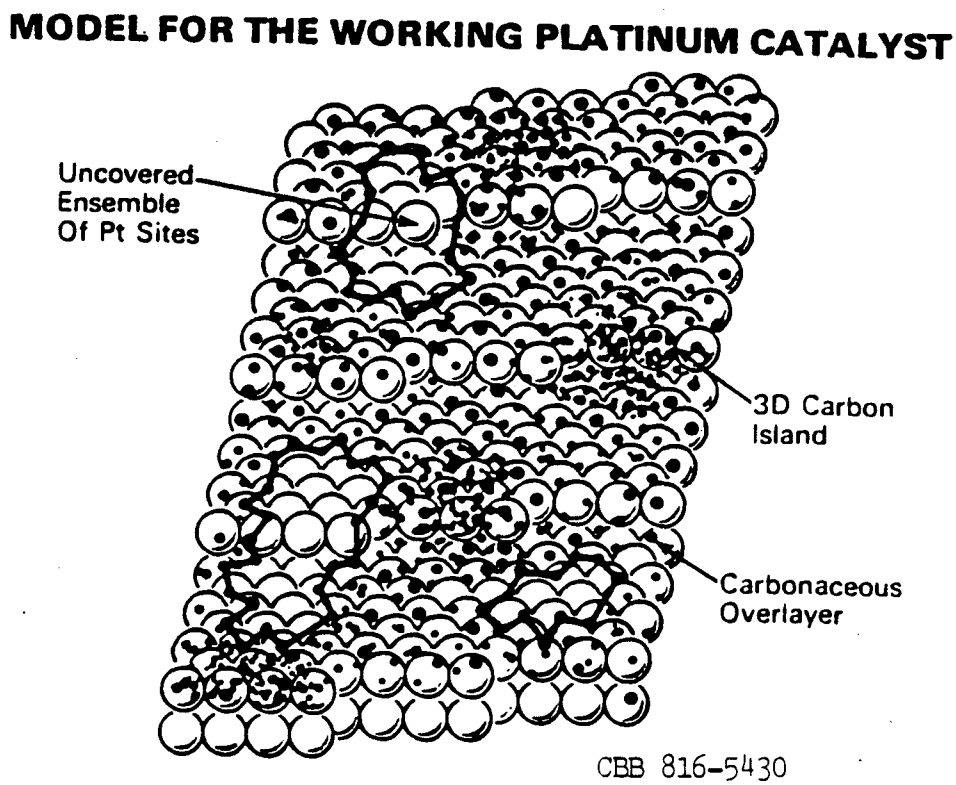

Fig. 15 Molecular model of the working platinum reforming catalyst.

about 625 K. These changes are accompanied by a decrease in the hydrogen content of the deposit with increasing temperature. This is shown in Figure 16 where hydrogen thermal desorption results are shown illustrating the sequential dehydrogenation of deposits prepared at several temperatures.[53] Also shown is the temperature dependence of the amount of deposit and its average (H/C) composition. As long as the reaction temperature is below about 800 K, the deposit contains hydrogen, and the catalyst remains active. At higher temperatures, the deposit completely dehydrogenates, condenses into graphitic structures, and all catalytic activity vanishes.

Radiotracer studies[54] showed that under typical reforming conditions, hydrogen transfer between this deposit and reacting molecules occurs easily. Deuterium exchange also occured readily,[55,56,57] although the residence time of the deposit was very long compared to the turnover period for skeletal rearrangement.[58,59] Furthermore, the presence of this deposit appears to provide weak adsorption sites that facilitate the release of

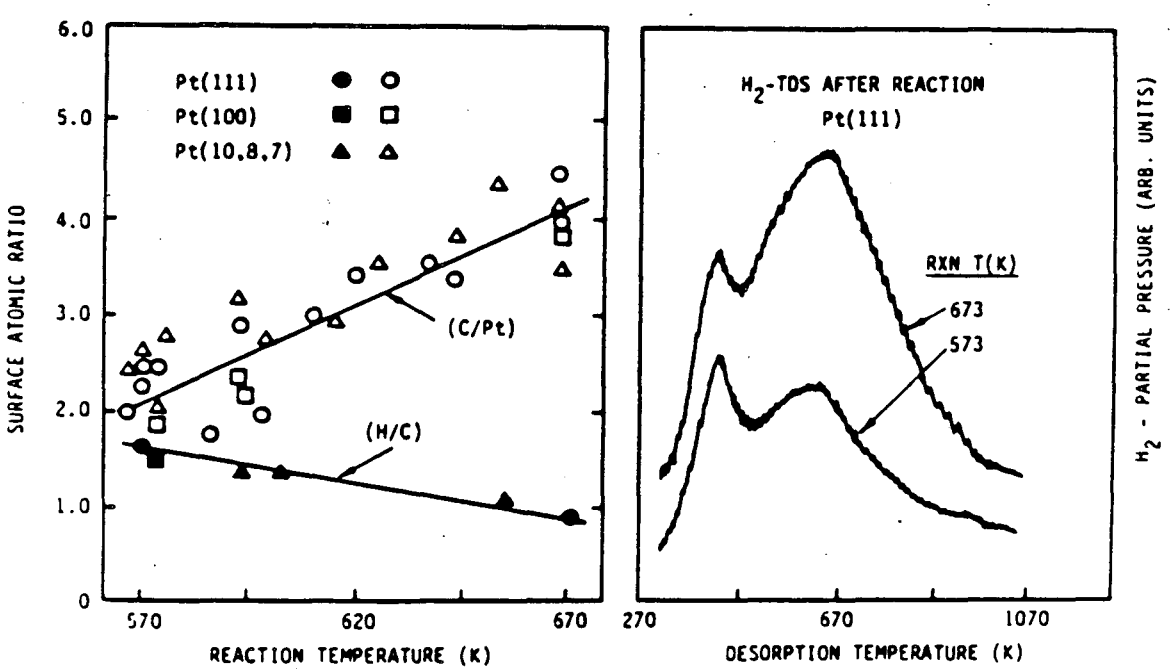

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Fig. 16 Important properties of the carbonaceous deposits produced during n-hexane reforming over platinum single-crystal surfaces shown as a function of reaction temperature. The left frame shows the amount of deposit expressed as carbon atoms per surface platinum atom as measured by AES and the H/C stoichiometry of the deposit as measured by H_2 TDS. The right frame illustrates the sequential dehydrogenation of deposits produced during n-hexane reaction studies using platinum (111) at the indicated temperatures.

product molecules from the catalyst surface. Thus, the presence of the carbonaceous deposit makes a catalyst out of platinum that readily exchanges hydrogen with reacting species and facilitates the release of product molecules.

Another ingredient of paramount importance is the presence of a small (5-30%) concentration of uncovered platinum surface sites that always persist in the presence of the active carbonaceous deposit. These sites mostly exist as patches or ensembles which contain several contiguous surface atoms.[53] In the steady state, these sites are responsible for the initial dissociative chemisorption and subsequent rearrangement of incident reactant molecules. The presence of these sites accounts for the structure sensitivities frequently observed for important aromatization and isomerization reactions. The dependence of the vacant site concentration on reaction temperature as measured by CO adsorption-thermal desorption following n-hexane reaction studies were monitored over the (100), (111) and (13,1,1) platinum surfaces.[53] The concentration of vacant sites approaches zero only at high temperatures (≈800K) where complete dehydrogenation also takes place. Also measured was the ratio of the steady state reaction rate to the initial rate over clean platinum as a function of vacant site concentration. The deviation from first order behavior appears to result from the participation of the carbonaceous deposit as a hydrogen transfer agent.

2. Bonding Modifiers

a. The Role of Potassium During Ammonia Synthesis and CO Hydrogenation. Potassium is frequently used as a promoter in many catalytic reactions. The hydrogenation of CO and the synthesis of NH_3 are perhaps the best known examples of potassium promotion. Potassium has a very high heat of adsorption at low coverages, about 60 kcal per mole on most transition metal surfaces indicating complete ionization of the atom. At high coverages, however, mutual depolarization of the charged potassium species leads to neutralization. When about 50 percent coverage is reached, the heat of adsorption equals the heat of sublimation of metallic potassium, about 23 kcal per mole, indicating that the adsorbed atoms are no longer ionized.[60]

During CO hydrogenation over transition metal surfaces, the presence of potassium usually increases the rates and also selectivities for C_2^+ hydrocarbon production as expected if the CO dissociation rate is

increased. As noted earlier, potassium adsorbed on transition metals exists in largely ionic states which result from the transfer of valence charge density into the metal d-band that reduces the metal work function. This charge transfer has a profound influence on the adsorption behavior of CO as revealed by thermal desorption and vibrational spectroscopy studies using platinum, nickel and ruthenium single crystal surfaces. In all cases, the CO desorption temperature is increased by 100 to 200K in the presence of potassium[61] reflecting a 5 to 12 kcal per mole increase in the heat of molecular CO chemisorption. In addition, the CO bond is weakened substantially as compared to adsorption on clean metal surfaces. Figure 17 illustrates the HREELS spectrum for CO coadsorbed with potassium at several coverages on the hexagonal (111) platinum surface.[62] With increasing coverage, there is a continued shift of the CO stretching frequencies from 1875 and 2120cm^{-1} to 1565cm^{-1}. These shifts correlate with a change in bonding from mostly top sites to bridge sites and a decrease in CO bond order from 2.0 to 1.5. This dramatic bond weakening reflects enhanced population of the CO $2\pi^*$ antibonding orbital as a result of the increased density of metal electronic states in the presence of potassium. One should anticipate that the weakened CO bond and strengthened metal carbon bond would facilitate CO dissociation. This was demonstrated by Goodman[63] using nickel (100) where the CO dissociation rate was increased four-fold at a potassium coverage of 10 percent of a monolayer. The activation energy for CO dissociation was also lowered from about 23 to 10 kilocalorie per mole.

It is now clearly established that potassium chemisorbed on transition metals functions as an unusually powerful donor thereby increasing the density of surface electron states available for back-bonding with certain adsorbates that possess orbitals with energy and symmetry that correlate near the Fermi energy of the metal such as the $2\pi^*$ orbitals of CO and N_2. The important general consequences of this interaction include increased heat of molecular adsorption and increased dissociation probability. Commercial fused iron catalysts normally contain about 1.8 percent potassium per mole which greatly accelerates the rate of ammonia synthesis over this high surface area material. The role of potassium in ammonia synthesis was revealed by our recent studies that indicate the weakening of the ammonia adsorption bond by the co-adsorbed alkali atoms. Thus, the ammonia surface concentration decreases and this in turn eliminates poisoning of the N_2 dissociation sites by the ammonia product molecules. The ammonia pressure dependence of the reaction rate also changes, indicating that ammonia

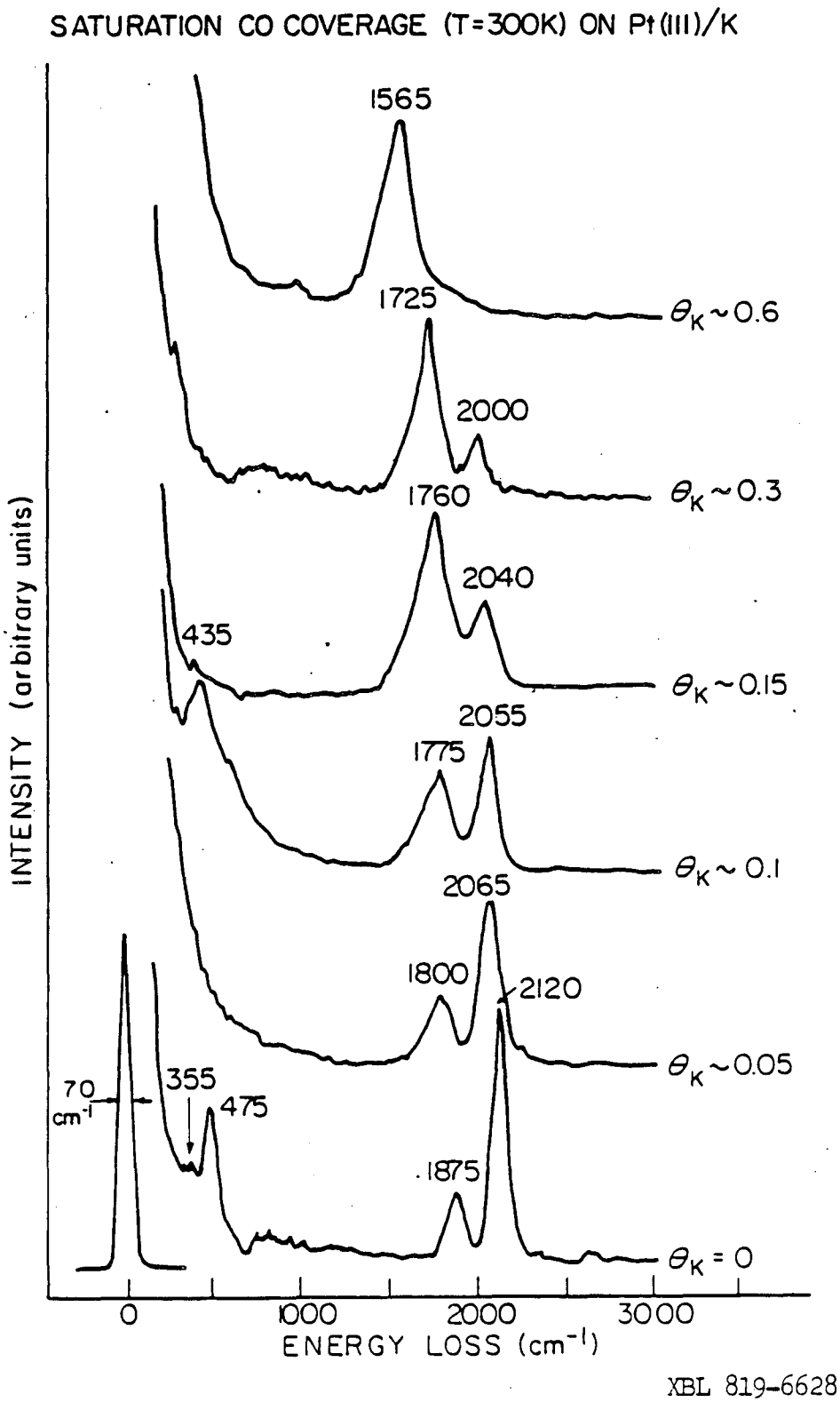

Fig. 17 Vibrational spectra of CO at the saturation coverage when chemisorbed on Pt(111) at 300 K as a function of preadsorbed potassium coverage.

inhibits the reaction rate in the presence of potassium to a lesser extent than on the clean iron surface.

On the clean rhodium (111) surface, CO stays molecularly adsorbed at low pressures while it dissociates in the presence of potassium.[64] This can be studied by the adsorption of a mixture of $^{12}C^{18}O$ and $^{13}C^{16}O$ and detecting $^{13}C^{18}O$, the products of scrambling, which clearly identify the dissociation of molecular CO on the metal surface. In Figure 18, we show that three CO molecules may dissociate per potassium atom at a potassium coverage where maximum charge transfer to the transition metal occurs.

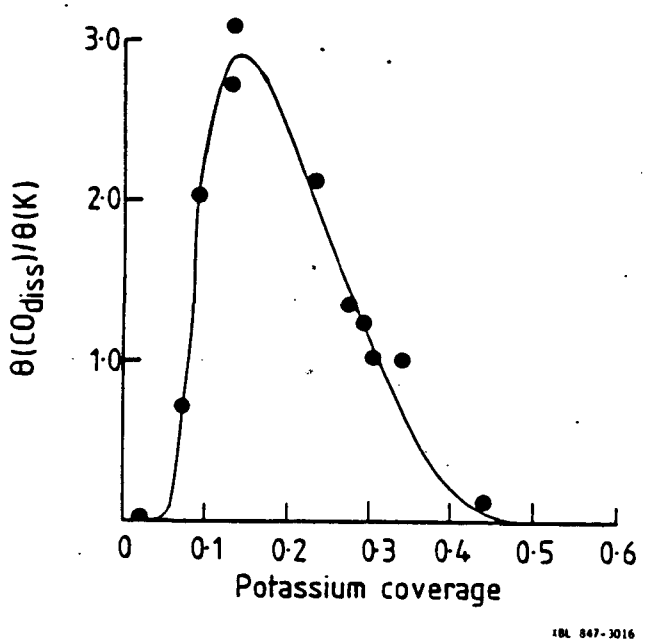

Fig. 18 Amount of dissociated carbon monoxide per potassium atom as a function of potassium coverage on the rhodium (111) single-crystal surface.

<u>b. The Role of Oxide Supports To Stabilize Different Oxidation States Of Transition Metal Catalysts</u>. Studies of carbon monoxide hydrogenation over initially clean rhodium foil and rhodium (111) single crystals at 6 atmospheres and at 500 to 600K showed high selectivities for methane production along with small yields of ethylene and propylene.[65] By contrast, when rhodium oxide, Rh_2O_3, was investigated for synthesis activity, high yields of C_2 and C_3 oxygenated hydrocarbons were produced. Ethylene addition to the CO/H_2 mixture produced propionaldehyde with high selectivity indicating the exceptional carbonylation activity of

oxydized rhodium species.[66] Under similar conditions, carbonylation activity was totally absent with rhodium metal. Thus it appears that higher oxydation state rhodium ions, Rh^{+} and Rh^{3+}, are essential for chemical activity in reactions that produce oxygenated products. Photoemission studies confirm that a combination of rhodium metal and rhodium cations is probably needed for maximum activity.

Unfortunately, rhodium oxide gradually reduces under typical synthesis conditions, resulting in unfavorable changes in reaction selectivity. Higher oxidation state rhodium ions were stabilized under synthesis conditions by reacting Rh_2O_3 with La_2O_3[66] in the presence of oxygen to produce the perovskite compound lanthanum rhodate, $LaRhO_3$. With this material, catalytic activity for producing oxygenated products was stable over long periods. Figure 19 shows the dependence of the synthesis selectivity on reaction temperature at 6 atmospheres total pressure.

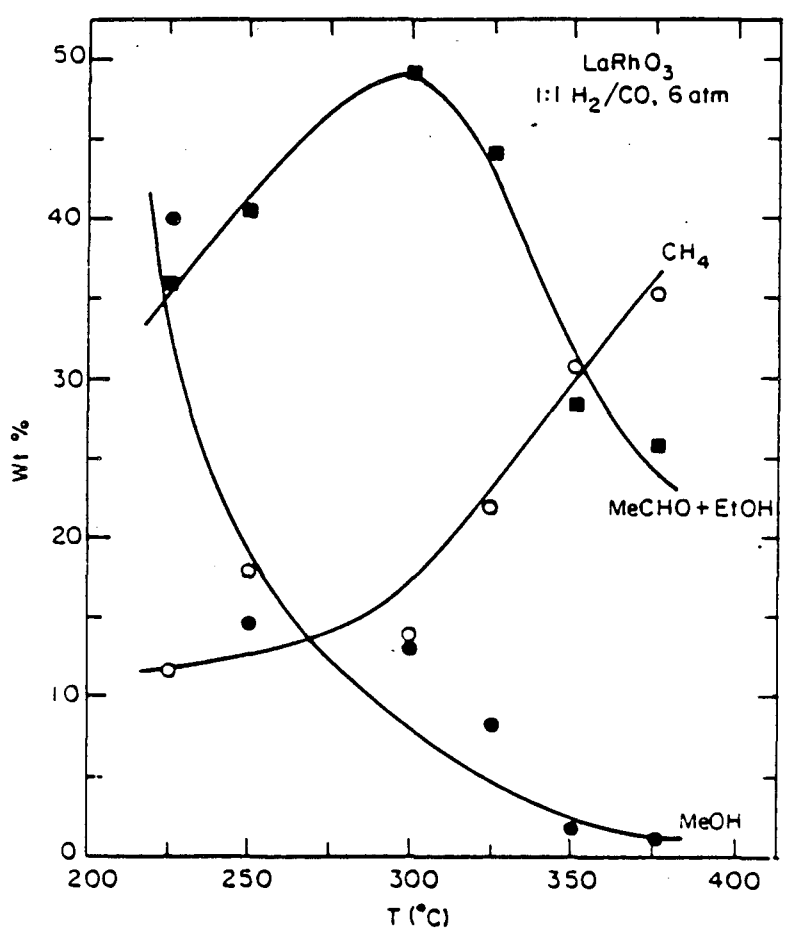

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Fig. 19 Temperature dependence and selectivities for producing methane, methanol, and C_2-oxygenated products over $LaRhO_3$ at 6 atm and 1:1 H_2/CO ratios.

Remarkably the selectivity for oxygenate synthesis was greater than 80 mole percent over a wide range of conditions. At low temperatures, methanol was formed with maximum selectivity and at low activation energy of 16 kcal per mole. At intermediate temperatures of 520 to 600K, carbonylation activity was accentuated, resulting in high selectivities for the synthesis of C_2 and C_3 aldehydes and alcohols. Under these conditions, it appears that activities for CO dissociation, carbon monoxide hydrogenation, and hydrogenation of carbon fragments as well as carbonylation all become comparable.

The unique selectivity of oxidized rhodium species for producing oxygenated products results largely from the altered strength of CO and H_2 chemisorption as the metal oxidation state is varied. Thermal desorption studies showed that the CO adsorption strength is decreased whereas the heat of hydrogen chemisorption is increased by 3-8 kcal per mole upon oxidation. These changes can be correlated with the elimination of high coordination bonding sites and the formation of surface hydroxyl groups, respectively. The combination of metallic and ionic sites provides the catalyst with high hydrogen storage capacity and bifunctional activity for carbonylation and hydrogenation.

The importance of higher oxydation state metal ions during hydrocarbon synthesis was further delineated in model studies using iron catalysts.[67] In addition to linear alkanes, olefins, and small alcohols, the water-gas shift reaction also accounts for a significant fraction of the CO conversion. The evolution of the active surface composition was investigated in extensive studies by Dwyer et al using single crystals, foils, and medium area powders.[67] At low CO conversions, photoelectron spectroscopy studies clearly showed that carbides were formed in the near surface region with compositions similar to bulk iron carbides. As the carbides formed, catalytic activity increased markedly, small alcohols were formed selectively, and the hydrocarbon products became heavier and more olefinic. These results are in good agreement with earlier Mossbauer emission spectroscopy studies by Raup and Delgass[68] which showed that catalytic activity correlates well with the extent of carbide formation. Fe_2C carbide formed with small iron particles whereas Fe_5C_2 carbide was favored in larger particles. When dispersed on carbon or MgO supports the larger particles give rise to maximum turnover frequencies. While the catalytic activity of carbided iron powders was stable for many hours, low area foils and single crystals deactivated quickly due to the formation of an unreactive surface carbon phase with properties similar to graphite.

The Strong Metal-Support Interaction.

Evidence For Surface Compound Formation.

The properties of titania-supported metal catalysts have been the subject of many studies since it was first reported that such catalysts can exhibit specific activities for CO hydrogenation which are substantially larger than those for silica- or alumina-supported metals.[69-72] More recently, similar increases in activity have been observed for NO reduction by CO and H_2 over TiO_2-supported Rh, Pd, and Pt.[73,74] Studies of H_2 and CO adsorption have demonstrated that the chemisorption of these gases decreases with increasing catalyst reduction temperature.[75,76] TEM observations[77,78] have established that this loss of adsorption capacity is not due to sintering and that the only change occuring upon high-temperature reduction is a flattening of the particle shape due to an improved setting of the support surface. Evidence for an interaction between the metal and the support has also been inferred from XPS observations. It has been proposed[79-82] that a shift in the core-level binding energy of a metal support on TiO_2 relative to that for bulk metal is eartly due to charge transfer from the support to the metal. The fact that the effects of using TiO_2 as the support can be evidenced for large (~50Å) metal particles as well as very small particles (~20Å) has led to the suggestion that the observed modifications in adsorption and catalytic properties may be due to the decoration of the metal particle surface by TiO_x moieties.[83-86]

The idea that the metal-support effects may be due to the decoration of the metal surface by TiO_x moieties has generated an interest in studying the effect of TiO_x deposited on metal foils and single crystals. Chung et al.[87] have observed that the deposition of TiO_x on Ni (111) results in a maximum methanation rate at a Ti coverage of $1.5 \times 10^{14} cm^{-2}$. The effects of TiO_x surface species on the chemisorption of CO and H_2 on polycrystalline Ni have been examined by Raupp and Dumesic.[88] These authors noted that TiO_x moieties caused a significant reduction in the activation energy for CO desorption, relative to clean Ni.

In studies by Levin et al.,[89] overlayers of TiO_x on Rh foil have been grown by Ti evaporation in vacuo followed by oxidation in 100 torr of O_2 at 420K. Auger electron spectra taken as a function of Ti dosing show a two-dimensional growth of TiO_x until completion of one monolayer; thereafter, growth is three-dimensional. The decrease in CO chemisorption

capacity of the foil is substantially greater than that expected for physical blockage of adsorption sites by TiO_x. This behavior is enhanced by H_2 reduction at 770K. Temperature-programmed desorption of CO shows a weakening in the strength of CO adsorption on Rh for TiO_x coverages exceeding 0.5 monolayer. The data can be interpreted in terms of a model in which CO chemisorption is inhibited at Rh sites adjacent to TiO_x species in addition to the Rh sites covered by TiO_x. This model is shown by Figure 20.

SCHEMATIC MODEL FOR TITANIA OVERLAYERS ON RHODIUM

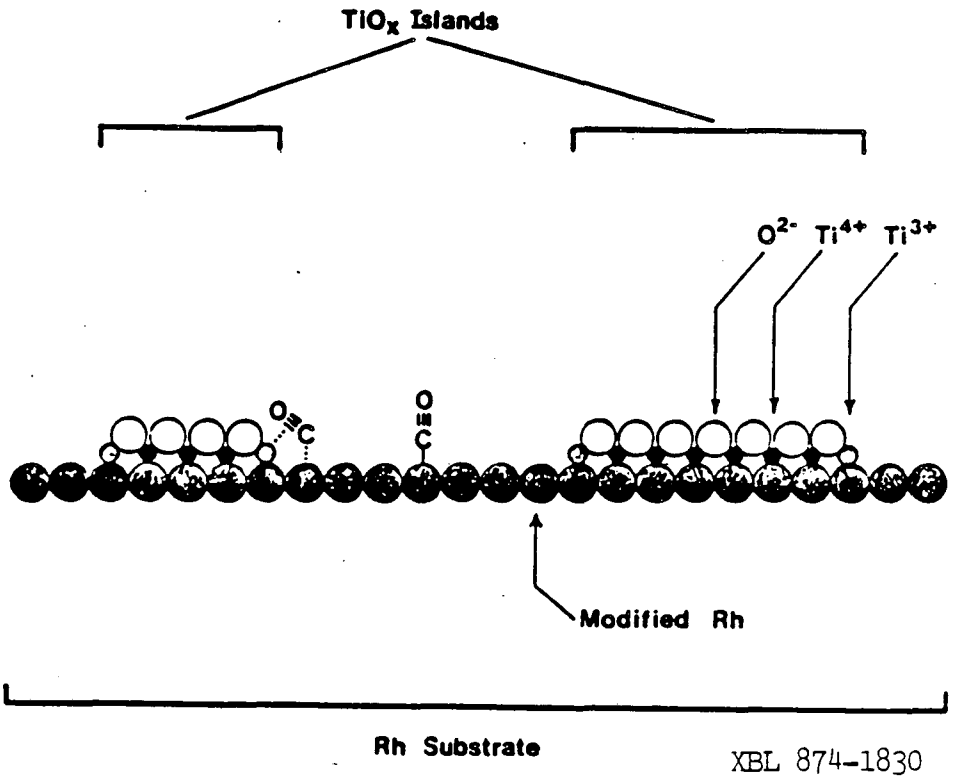

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Fig. 20 A model of the titanium oxide-rhodium oxide-metal interface system CO chemisorption showing inhibition at rhodium sites adjacent to TiO_x species, in addition to rhodium sites covered by TiO_x.

Oxide-metal interfaces show unique chemical composition and charge distribution that can have marked effects on the catalytic and chemisorption properties. Indeed, we may view these interfaces as surface compounds, since bulk, three-dimensional compounds with similar properties do not appear to exist. Bimetallic clusters[90] that form at high dispersions are another example of surface compounds as the miscibility of metals is only exhibited at high dispersions when most of the metal atoms are on the surface. Thus, the surface environment promotes unique interactions at the

oxide-metal interface and for bimetallic systems that can greatly modify the catalytic and chemisorption properties.

IDENTIFICATION OF TYPE OF CATALYZED REACTION

Building of new selective catalyst systems that perform superior activity requires detailed knowledge, on the molecular level, of the existing catalyst system. Several of the surface analytical techniques that are listed in Table 1 provide means to determine the chemical composition of the catalyst surface. This should be determined when the catalyst is clean as well as when the catalyst is covered with the reactant mixture. The chemical analytical techniques are of two types: those that can be used with microporous high internal surface area catalysts and those that can be used only with the external surfaces of model catalysts. X-ray photoelectron spectroscopy can be used for surface chemical analysis on both types of catalyst. In addition, this technique can determine the oxidation states of surface atoms as well. Solid state NMR is extremely useful for determining the chemical composition of microporous solids but it is not sensitive at present for surface areas of less than one square meter. Ion scattering techniques are most sensitive for the chemical analysis of external surfaces but can also be utilized for the analysis of internal surfaces.

Surface area determination is one of the most important and well-developed techniques. Total areas may be determined by physical adsorption of nitrogen or argon at low temperatures. Metal surface areas can be established by chemisorption of hydrogen, carbon monoxide, or oxygen molecules that would not readily chemisorb on the oxide supports under conditions of the adsorption experiments. Without knowledge of the surface area, one cannot determine specific reaction rates and other kinetic parameters. Variations of active surface areas are often responsible for catalyst degradation or regeneration. Thus, it is important to monitor catalyst surface areas under all conditions of the experiments.

The structure sensitivity of the reaction is determined by studies of the variations of specific reactions rates (molecules per area per second) with particle size or dispersion (concentration of surface atoms divided by concentration of total number of atoms) for high surface area catalyst systems. The reaction is considered structure sensitive if the specific turnover rates vary with particle size by more than the uncertainty of the

other experimental variables (surface area, temperature, etc). Conversely, the reaction is structure insensitive if its turnover rate shows no variation with particle size. Single crystal model catalyst studies provide excellent evidence of structure sensitivity if they exhibit variation of turnover rates and selectivities from one crystal face to another.

The interpretation of these studies is made difficult by structure sensitive side reactions that can give rise to apparent structure sensitivity. For example, the hydrogenolysis of organic molecules, a structure sensitive reaction, can often produce a carbonaceous deposit which renders part of the catalyst surface inactive. Thus, structure sensitivity of turnover rates may be caused by the varying amounts of inactive deposits with alteration of particle size. The active surface area, therefore, must be determined by selective chemisorption or some other appropriate techniques for precise determination of turnover rates.

It is of importance to determine the atomic surface structure of small particles that exhibit structure sensitive behavior in catalytic reactions to identify the surface sites that are responsible for observed structure sensitivity. Unfortunately, this is an arduous and difficult task. Electron microscopy techniques and extended x-ray absorption fine structure (EXAFS) techniques, at present, appear to be the most promising to obtain this information.

Temperature programmed thermal desorption measurements provide significant information about the bonding of molecules adsorbed on the catalyst under reaction conditions. Upon heating with a rate of 1 to 10 degrees per second, the adsorbed molecules desorb intact or undergo sequential bond breaking with increasing temperature to release hydrogen or other gaseous molecules. Desorption peaks appear at well-defined temperatures as detected by gas chromatography mass spectroscopy where the adsorbed species have maximum desorption rates. Since the adsorbate bond depends on the surface structure and the chemical environment on the surface in the proximity of the adsorption site, the thermal desorption spectrum yields a fingerprint of the catalyst surface, its structure and bonding characteristics. While the interpretation of the thermal desorption spectrum on the molecular level needs complementary studies using other techniques, the simplicity of thermal desorption experiments can be readily used to compare catalysts that are prepared differently or show different chemical behavior for the same reaction.

Pressure dependence measurements that determine how the rates and product distributions are changed with the partial pressures of the reactants permits the establishment of macroscopic rate equations in a wide range of applicable, experimental circumstances. This type of study is clearly necessary to predict how the catalyst is to behave with changing experimental conditions. The wider the pressure range of the investigation, the better, as the reaction mechanism often changes with pressure. As the pressure is increased, weakly adsorbed molecules are tabilized on the catalyst surface under the reaction conditions that may participate in chemical reactions of different types that nevertheless have high turnovers.

Temperature dependence studies of the total rates and the rates of each product leads to the determination of the apparent activation energies of the reactions. While the interpretation of their value, in terms of the rate determining elementary reaction steps, is difficult, it is often possible to give a sound physical interpretation by comparing these values with the results of theoretical calculations.

Identification of secondary reactions requires carrying out of the catalytic process both at low and high conversions. As long as the product concentration is low, secondary reactions are less likely to be important. This may be accomplished by variation of the flow rates that control the contact time of the reactants with the catalyst or by injection of the product along with the reactant into the catalytic reactor.

Determination of the surface residence times of reaction intermediates can often be accomplished by isotopic labeling of the reacting molecules. ^{14}C, ^{35}S are excellent long life beta-emitter isotopes whose concentrations can readily be monitored in the catalyst bed by the use of sensitive semiconductor detectors that have one percent of a monolayer sensitivity. Tritium labeling can also be used although hydrogen-deuterium exchange studies are more frequently employed to monitor the hydrogen exchange process.

Pulse studies that perturb the surface steady state have been useful to obtain valuable kinetic information about the catalytic process including surface resident times or retention times of molecules in the catalyst bed. A pulse of labeled reactant is introduced into the catalytic reactor and its reappearance at the outlet is monitored as a function of time along with the distribution of the product mixture. If the labelled species stay on the surface much longer than the turnover time, their role in the

catalytic reaction is indirect, while they are participating directly if their rate of reappearance is similar to the rate of catalytic reaction.

The role of the catalyst support must be determined by appropriate experiments. The support is usually a high surface area microporous oxide. It may act solely as a dispersing agent of the active metal catalyst. In this circumstance, exchanging it with another support or removing it altogether from the reaction mixture should have minimal impact on the kinetics of the reaction. The support may be an oxidation state modifier or, on the other hand, it may be a catalyst component. In these circumstances, it is a vital catalyst ingredient and its removal would greatly alter the reaction rates and the product distribution. It is then important to determine the type of reaction that cannot be carried without the presence of the support and the conditions of catalyst preparation that by a solid state reaction between oxide and metal will optimize the reaction conditions.

BUILDING OF IMPROVED CATALYSTS

The task ahead is to utilize our knowledge of the necessary molecular ingredients of the complex catalytic system presently employed and the information available on the thermodynamics and the kinetics of the reactions to be catalyzed to design a superior catalyst system. One of the first challenges is the synthesis of microporous catalysts and materials of high surface area that they to remain stable under the reaction conditions. Most of the synthetic methods at present use solutions and the solid precipitate from a colloid phase. There are other synthetic routes that may be explored. One could utilize the controlled decomposition of vapor phase molecules, for example. Both the active catalyst and the catalyst support must be available in high surface area forms. The use of cystalline microporous solids as supports has the advantage of structural uniformity. This, in turn, allows a better definition of how the atomic structure influences the catalytic chemistry as the ordered structure is available to scrutiny by diffraction experiments and determination by crystallography. For structure sensitive reactions, such a support can provide a template to produce the desired catalyst surface structure. The control of the catalyst structure is often the key to the actual selectivity. Where metal sites are deposited on oxide supports, the conditions of reduction often determine the surface structure of metal

particles that form. When the rate of reduction is slow surface structures of low surface energy are produced. These are the (111) faces of face centered cubic metals, the (110) face of body centered cubic metals and the (0001) face for hexagonal close-packed materials. When the rate of reduction is rapid, higher-Miller index, rougher or more open surfaces will form. Additives that are structural promoters can change the surface structure. Just as aluminum oxide facilitates the restructuring of iron in the presence of nitrogen, other additives might play the same role for other catalyst materials. Alloy components that may not participate in the reaction chemistry, but modify the structure and site distribution on the catalyst surface, should be explored utilizing the knowledge accumulated from the working alloy systems.

Site blocking could improve selectivity as has been proven for many working catalyst systems. Sulfur or silicon or other strongly adsorbed atoms that seek out the active site responsible for the undesirable side reaction could improve the selectivity. Well-chosen alloy constituents can act the same way, blocking low coordination sites, kinks, or steps that may be desirable in some circumstances, just as in the case of sulfur on platinum. Blocking of high coordination sites may profoundly alter the selectivity as in the case of sulfur on the nickel (100) face or gold on platinum (111).

Bonding modifiers may be employed to weaken or strengthen the chemical bonds. Strong electron donors, like potassium, or electron acceptors, like chlorine, may be used for this purpose. Alloying may create new active sites in addition to providing an ensemble effect that can greatly modify reactivity and selectivity. Many more alloy systems must be explored systematically to be able to predict the effects of alloying on catalytic behavior.

Perhaps the most promising area of new catalyst preparation lies in the combined use of metal and ion (acid) catalysis by building a system that contains both the oxide and metal. Multi-functional catalysts may lead to entirely new reaction schemes as shown by the production of gasoline from carbon monoxide and hydrogen over mixed metal-zeolite catalysts. Surface compounds that exhibit unique chemistry can form at the metal oxide interface. Spillover of reactants and reaction intermediates from the metal through the metal oxide compound interface to the oxide can lead to consecutive reactions that will occur with high selectivity and can lead to the formation of complex products. Crystalline micropores of molecular

dimensions can lead to shape selectivity that can enhance the formation of stereospecific products.

Our knowledge of the possibly in catalyst design provides only a guidance to the research path to take that has proven successful in the past. There is no substitute for the dreams and imagination of creative researchers who try new ideas that have not been explored much before. The use of molecules that are excited vibrationally or electronically, of new materials, carbides, nitrides, sulfides, unique reaction conditions, i.e. low temperature liquid phase enzyme-like catalysis, and the exploration of catalysis of new reactions will keep the field of catalysis an exciting frontier area of research for many generations of scientists to come. New instrumentation will be developed that permits closer scrutiny of the catalysts and the molecules adsorbed on the catalyst surface on the molecular level. Theory is providing more information that is useful to the practical catalyst researcher. Not only bonding information is becoming available, but calculations are possible of the reaction path that can help to at least rule out some of the many reaction mechanisms.

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