Surface Science Studies of Catalysis: Classification of Reactions

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Many of the processes used in the chemical and petroleum industries require the use of a catalyst. As originally defined by Berzelius, a catalyst is a material that increases the rate of a chemical reaction without itself being either consumed or changed.[1] While the increase of reaction rates is often desirable, control of reaction selectivity or product distribution is also a key ingredient in a successful catalytic process. The catalyst selects among available reaction channels (thermodynamically allowed) to yield desirable products while blocking the formation of undesirable species. In many cases involving solid catalysts these pathways consist of an adsorption step, followed by a surface reaction and finally desorption of the product. The understanding of such processes rests upon our molecular level understanding of the adsorption/desorption reactions, the structure of catalytic surfaces, and the bonding and coordination of reaction intermediates to these surfaces.

The methodology used in the study of catalysis has changed drastically over the past 15 years. Classical methods required high surface area samples (>10 m²) to generate measurable amounts of product. Presently, catalyst samples with surface areas as low as 1 cm² 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 I. Catalysts studied include platinum for hydrocarbon conversion,[2] iron and rhenium for ammonia synthesis,[3,4] and silver for the partial oxidation of ethylene.[5] The hydrogenation of carbon monoxide has been studied over a large number of metal surfaces including iron,[6] nickel,[7] ruthenium,[8] and molybdenum.[9] The oxidation of carbon monoxide, shown to have oscillatory behavior, has been studied over platinum catalysts.[10,11] Finally,

platinum and rhodium have been used to catalyze the hydrogenation of ethylene[12] and molybdenum to hydrodesulfurize thiophene to butenes.[13] These investigations have led 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 pressure 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 s. 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 under 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 have designed an apparatus for combined UHV surface analysis and high-pressure catalytic reaction studies over small surface area samples.[14] 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 (Figure 1). In this manner we can characterize the catalytic surface before and after exposure to reaction

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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 anal. method	acronym	physical basis	type of information obtained
low-energy electron diffraction	LEED	elastic back-scattering 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 of 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
IR spectroscopy	IRS	vibrational excitation of surface atoms by absorption of IR radiation	structure and bonding of adsorbed gases
X-ray and UV 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	interference effects during X-ray emission	atomic structure of surfaces and adsorbed gases
thermal desorption spectroscopy	TDS	thermally induced desorption or decomposition of adsorbed species	adsorption energetics composition of adsorbed species
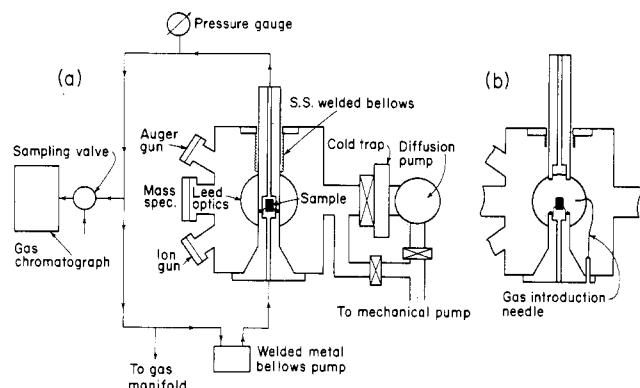
Figure 1. (a) Schematic diagram of the high-pressure/UHV apparatus with sample enclosed in the high-pressure cell. (b) HP/UHV apparatus with cell open.

conditions and attempt to correlate surface characteristics with the kinetic parameters (rate, product distribution, activation energy) of the catalytic reaction. Admittedly, some of the adsorbates may be modified or are removed when the surface is examined under vacuum. Nevertheless, most of the species that are present during the catalytic reaction in the surface monolayer of the active catalyst can be identified.

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

1. The first encompases reactions that occur directly on a 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.

The following accounts present case histories of surface science studies of catalytic processes repre-senting each of the three categories. Following these we shall indicate directions of future investigation.

Catalysis on a Metal Surface: The Ammonia Synthesis Reaction

The synthesis of ammonia from stoichiometric mixtures of H_2 and N_2 has been studied over clean iron and rhenium single-crystal surfaces having a variety of crystallographic orientations. The reactions were performed at temperatures between 500 and 800 K and at total pressures of 20 atm. The surfaces were fully characterized by LEED and AES to ensure cleanliness and to determine atomic surface structure.

Ammonia synthesis has also been studied extensively over high surface area catalysts. The conclusions drawn from these studies are that the rate-determining step of this reaction is the dissociative adsorption of N_2 and that the activity of the catalyst is strongly dependent on its atomic structure. The proposal has been made that iron surface atoms having sevenfold coordination are an important component of the active site.[15]

Studies of the chemisorption of nitrogen on the low Miller index planes of iron single crystals show dramatic variations with crystallographic orientation.[16] Initial sticking coefficients vary in the ratio 60:3:1 on the Fe-(111), Fe (100), and Fe (110) surfaces, respectively. We have studied the synthesis of ammonia over these surfaces (Figure 2) and found that the activity follows the same trend as the sticking coefficient, the relative rates being 418:25:1. The similarity between the dependences of the sticking coefficients and reaction rates on surface structure is a good indication that N_2 chemisorption is the rate-limiting step for this reaction. Examination of the sketches of the surface structures in Figure 2 shows that activity depends upon the atomic scale roughness of the surface. The Fe (111) surface, being the most open and corrugated, is also the most active, while the Fe (110) surface, the most closely packed, is much less active. Roughening of the two least active surfaces by argon ion bombardment increased their catalytic activity by a factor of 6.[17] It should also

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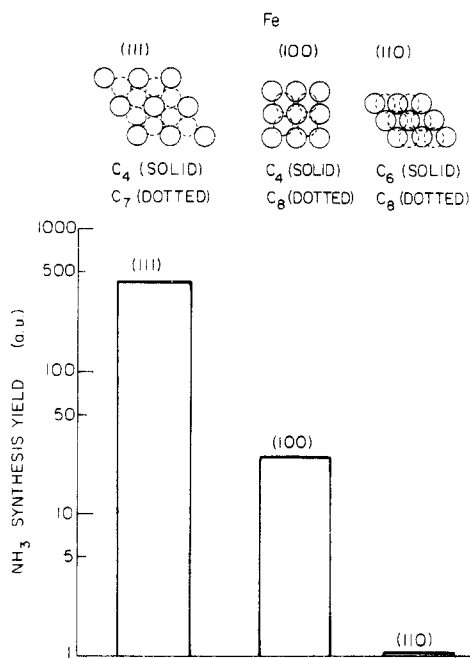(16) G. Ertl, *Catal. Rev. Sci. Eng.*, **21** 201 (1980).

Figure 2. Rates of NH_3 synthesis over three low Miller index Fe surfaces.
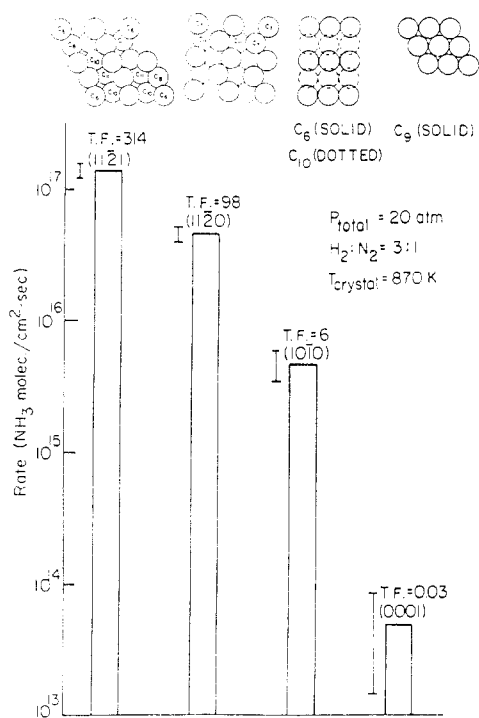

Figure 3. Rate of NH_3 synthesis over four Re surfaces.

be noted that the most active surface, Fe (111), contains atoms that have C_7 coordination.

The ammonia synthesis reaction was also studied over rhenium single-crystal surfaces.[4] Once again, the reactivity varies drastically with surface structure, ranging over more than 3 orders of magnitude among the surfaces studied (Figure 3). Higher activity was associated with surfaces having open topography. It is apparent that surface roughness is requisite for the dissociative chemisorption of N_2; however, the detailed geometry of the active sites cannot be uniquely determined from our results. Although both the Fe (111) and Re ($11\bar{2}0$)

(17) N. D. Spencer, R. C. Schoonmaker, and G. A. Somorjai, *J. Catal.*, **74** 129 (1982).

**Table II.
Comparison of the Kinetic Parameters for Ethylene
Hydrogenation over Different Platinum Catalysts**

catalyst	log rate[a]	a^b	b^b	E_a, kcal/mol	ref
platinized foil	1.9	−0.8	1.3	10	30
platinum evaporated film	2.7	0	1.0	10.7	31
1% Pt/Al_2O_3		−0.5	1.2	9.9	32
platinum wire	0.6	−0.5	1.2	10	33
3% Pt/SiO_2	1.0			10.5	34
0.05% Pt/SiO_2	1.0	0		9.1	35
Pt (111)	1.4	−0.6	1.3	10.8	12

[a] Rate in molecule/(Pt atom s), corrected for the following conditions: T = 323 K, $P_{C_2H_4}$ = 20 torr, P_{H_2} = 100 torr. [b] Orders in ethylene (a) and hydrogen (b) partial pressures.

surfaces contain atoms having sevenfold coordination, the most active Re surface, Re ($11\bar{2}1$), does not. Atomically rough surfaces, having high coordination hollows, seem to be a general requirement for the dissociative adsorption of N_2.

It appears that reactions occurring directly on metal surfaces are sensitive to the local surface structure. Open or rough surfaces that expose sites of high coordination in either the first or second atomic layer of the surface show especially high catalytic activity. Surface roughening can be introduced by using high Miller index surfaces with high densities of steps and kinks. The bottoms of the steps expose sites of high coordination to the reactant molecules. In addition to the ammonia synthesis reaction, H_2/D_2 exchange at low pressures[36] and the hydrogenolysis of *n*-hexane and lighter alkanes[37,43] have shown similar structure sensitivity. Recent theoretical studies have related the electronic structure of high coordination sites with observed catalytic activity. These show an interesting correlation; however, the detailed theoretical understanding of the surface structure dependence of such catalytic reactions is still in its initial stages.[18]

Catalysis on an Active Overlayer: The Hydrogenation of Ethylene

Platinum and rhodium single crystals are good catalysts for the hydrogenation of ethylene at temperatures of 300–400 K and atmospheric pressures. The surfaces were analyzed before and after reaction using AES, LEED, TDS, HREELS, and a ^{14}C radiotracer technique that monitors the rate of removal of labeled carbon from the surface. Kinetic parameters for ethylene hydrogenation over a Pt (111) surface compare well with those found using other forms of platinum (films, small particles), as can be seen from Table II. Activation energies for the reaction are all between 9 and 11 kcal/mol, and the rates all have close to −0.5 and 1.0 order dependence on ethylene and hydrogen pressures, respectively. Furthermore, the absolute values of the reaction rates, expressed as turnover frequencies (ethane molecules former per surface Pt atom per second), are all within the same order of magnitude, a clear indication that the reaction is not strongly affected by the structural details of the catalyst surface.

Extensive studies of the chemisorption of ethylene on single-crystal metal surfaces have been performed.[19]

(18) L. M. Falicov and G. A. Somorjai, submitted for publication in *Proc. Natl. Acad. Sci. U.S.A.*
(19) R. J. Koestner, M. A. Van Hove, and G. A. Somorjai, *J. Phys. Chem.*, **87** 203 (1983).
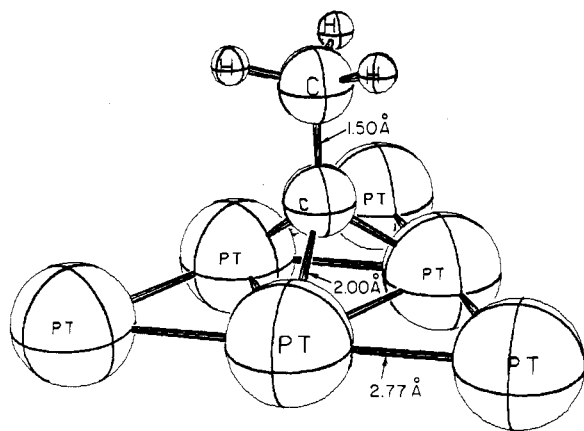
Figure 4. Ethylidyne moiety adsorbed on the Pt (111) surface.

Over Pt (111) and Rh (111) surfaces, ethylene undergoes a series of structural and chemical transformations as the temperature is increased. At low temperatures, the molecule adsorbs undistorted parallel to the surface. At about 300 K, a complete structural rearrangement occurs and a new surface moiety, ethylidyne (CCH_3), is formed. During the conversion of ethylene to ethylidyne a hydrogen atom from ethylene bonds to the surface and subsequently recombines with another H atom to desorb as H_2. A hydrogen atom shift occurs within the remaining C_2H_3 species, to produce a methyl group bonded to the second carbon in such a way that the carbon–carbon bond is perpendicular to the surface and the whole moiety sits on a threefold hollow site (Figure 4). This structure has been characterized by a wide variety of techniques.[20-23] Ethylidyne is stable up to temperatures of 400 K at which point further decomposition leads to the formation of CH and C_2H fragments and, ultimately, to the creation of a graphitic overlayer.

One of the most important results of our studies is the observation that ethylidyne fragments are present on the metal surface even after the ethylene hydrogenation reaction. The results of TDS, LEED, and HREELS experiments on a Pt (111) surface after ethylene hydrogenation are compared with similar data from ethylidyne in Figure 5. The LEED pattern after the reaction reveals a p(2 × 2) ordered overlayer, similar to that obtained for ethylidyne, although the extra spots are more diffuse (an indication of partial disorder). The TD and HREEL spectra after reactions show peaks that are primarily attributable to ethylidyne. The extra features are most probably due to minority CH_x fragments.

The stability of ethylidyne in the presence of high pressures of hydrogen and ethylene has been studied by using HREELS and radiation techniques with deuterated and ^{14}C-labeled ethylidyne, respectively.[24-26]

Figure 6 compares the rates of ethylene hydrogenation over Pt and Rh surfaces with rates for ethylidyne hydrogenation and the rate of incorporation of surface hydrogen into the methyl group of ethylidyne. It is clear that both processes are orders of magnitude slower than the overall rate of ethylene hydrogenation and, thus, that neither can be an intermediate step in the reaction pathway.

From our results it is apparent that ethylidyne forms and that it is permanently present on the metal surface during ethylene hydrogenation reactions. The stability of this species under reaction conditions suggests that it is not, in fact, a direct intermediate for the formation of ethane. Rather, we propose that it facilitates the transfer of hydrogen, dissociated by the metal surface, to ethylene that is weakly adsorbed to ethylidyne overlayer. Such a mechanism is illustrated in Figure 7. It is clear that olefin hydrogenation reactions occur on metal surfaces that are covered with a carbonaceous overlayer. With this in mind, it should be noted that alkylidyne moieties, analogous to ethylidyne, have been observed after propylene and butylene adsorption,[19] suggesting a similar mechanism for the hydrogenation of other olefins. Further studies are necessary to prove this proposition.

The ethylene hydrogenation reaction is probably the most distinctive example of a catalytic reaction occurring on an active overlayer rather than a metal surface. The role of the metal in this case is to dissociate hydrogen and to act as a template for the active ethylidyne species. Although it is quite likely that many examples of such catalysis exist, there are very few well-characterized cases. One similar case is the oxidation of CO on Pt surfaces at high pressures.[10,11] The reaction occurs over at platinum oxide layer that serves as an active source of oxygen and plays a dominant role in determining the reaction kinetics and mechanism.

Hydrodesulfurization of Thiophene over Sulfided Molybdenum Surfaces

The extraction of sulfur from sulfur-containing organic molecules is achieved by the hydrodesulfurization (HDS) process. We have recently studied the hydrodesulfurization of thiophene (C_4H_4S) over Mo (100) single-crystal surfaces. The reactions are performed at temperatures of 550–700 K on mixtures of 2.5 torr of thiophene in 1 atm of hydrogen. A typical product distribution is shown in Figure 8 compared with that from a high surface area MoS_2 catalyst.[27] The similarity between the two distributions suggests that the reaction mechanisms over the two catalysts are identical.

The chemisorption of sulfur on the Mo (100) surface has been studied in detail under UHV conditions.[28] At monolayer coverages sulfur is adsorbed atomically in a lattice with a p(2 × 1) structure with respect to the substrate. Heating the surface to temperatures between 1400 and 1800 K results in the desorption of sulfur and the formation of different overlayer structures as the coverage decreases. The LEED patterns, proposed real space structures, and coverages at which they occur are presented in Figure 9.

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EVIDENCE FOR THE PRESENCE OF ETHYLIDYNE AFTER
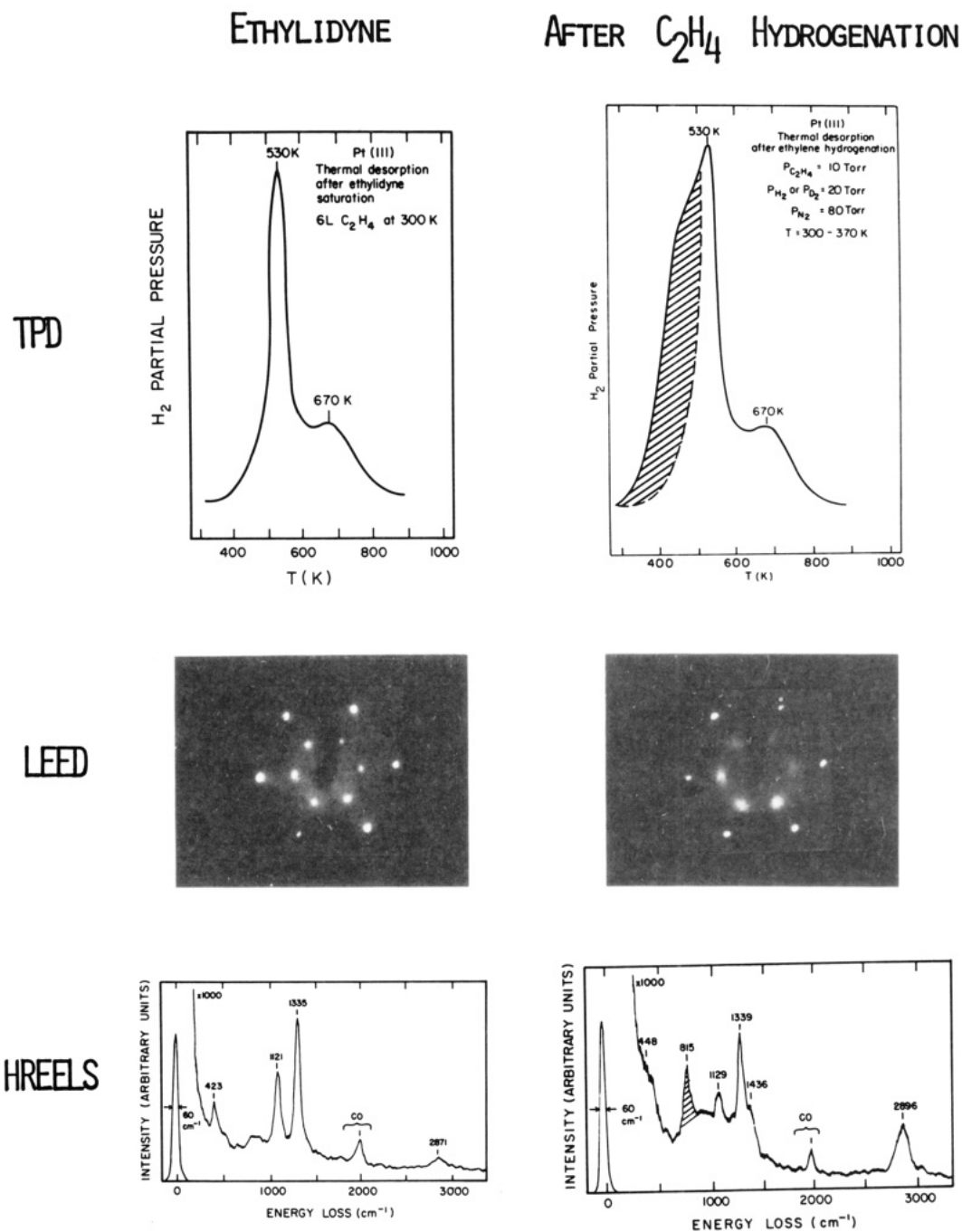# ATMOSPHERIC HYDROGENATION OF ETHYLENE OVER Pt (111)

Figure 5. Comparison of TPD, LEED, and HREELS measurements on a Pt (111) surface after C_2H_4 hydrogenation with those on an ethylidyne-covered surface.

At low coverages (≤0.5 monolayer) sulfur atoms adsorb on fourfold hollow sites.[29] The heat of desorption from this site, estimated from thermal desorption data, is about 110 kcal/mol. The appearance of a second peak in the TD spectra at higher coverages indicates

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(36) M. Salmeron, R. J. Gale, and G. A. Somorjai, *J. Chem. Phys.*, **67** 5324 (1977).
(37) S. M. Davis, F. Zaera, and G. A. Somorjai, *J. Catal.*, **85** 206 (1984).
(38) J. E. Crowell, E. L. Garfunkel, and G. A. Somorjai, *Surf. Sci.*, **121** 303 (1982).
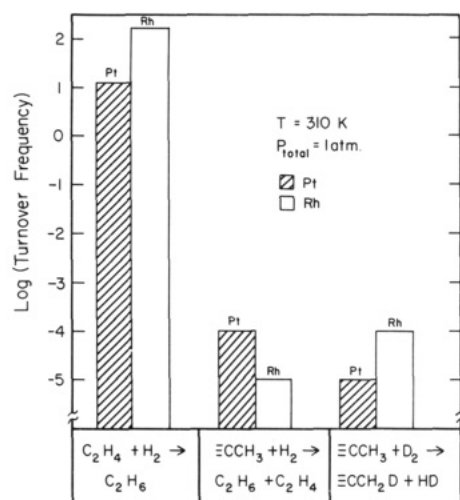(39) G. Blyholder, *J. Phys. Chem.*, **68** 2772 (1964).

Figure 6. Comparison of the rates of ethylene hydrogenation over Pt and Rh with those for ethylidyne hydrogenation and those for exchange of hydrogen between the metal surface and the methyl group of ethylidyne.
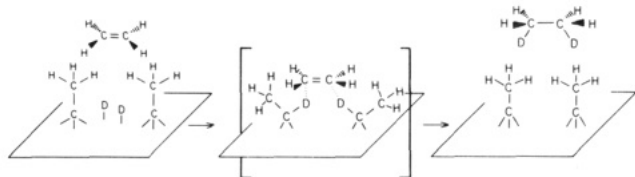

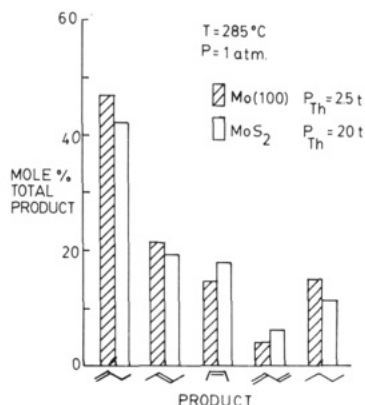**Figure 7.** Proposed model for ethylene hydrogenation mechanism over an ethylidyne-covered surface.

Figure 8. Comparison of thiophene HDS product distributions over Mo (100) and MoS$_2$ catalysts.

Figure 9. LEED patterns and proposed real space structures for sulfur on the Mo (100) surface at various coverages.

THIOPHENE HDS on Mo(100) vs. θ_S
RATE RELATIVE to CLEAN SURFACE
T = 340 °C P_{H_2} = 780 t P_{Th} = 2.5 t

Figure 10. Initial rate of thiophene HDS va. initial sulfur coverage on the Mo (100) surface.

the creation of a second, more weakly bound, sulfur adsorption state. The formation of a p(2 × 1) lattice at monolayer coverages suggests that the additional sulfur atoms are in fact bound to a different site, possibly in a bridged configuration (Figure 8). Structures composed of both hollow site and bridge-bonded sulfur can be proposed to account for the LEED patterns observed for coverages between 0.5 and 1.0 monolayer.

Studies of the rate of HDS of thiophene over clean and sulfided surfaces show that sulfur coverages that are produced before the reaction commences result in a decrease in reaction rates (Figure 10). The molybdenum surface is always covered with sulfur after reaction, and thus, the fact that the rate is affected by initial sulfiding of the surface indicates that the sulfur present on the surface during reactions is chemically different from that deposited beforehand. Isotope-labeling studies using ^{35}S indicate that the sulfur de-
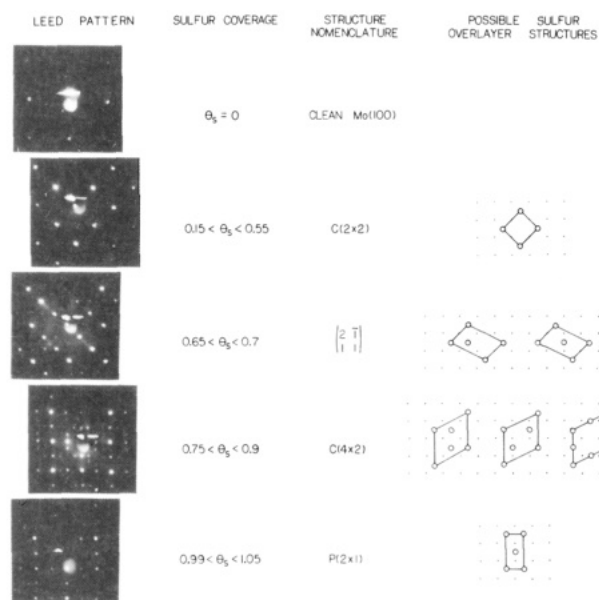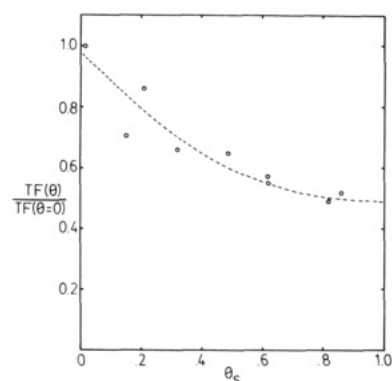
posited under UHV conditions remains on the surface during the reaction, retarding the reaction rate, while sulfur atom thiophene is removed from the surface as H$_2$S, without forming a strong surface bond. Sulfiding of the Mo surface to coverages greater than ~0.6 monolayer does not result in significant further reduction in the HDS rate. This observation is directly related to the formation of a weakly bound sulfur species at high coverages. This sulfur species is removed from the surface under reaction conditions desorbing as H$_2$S and, thus, does not have any effect on the reaction rate. Although the effect of sulfiding the catalyst is primarily one of site blocking, reducing overall activity, it also induces a change in the product selectivities. The adsorbed sulfur selectively blocks sites for hydrocarbon hydrogenation and thus reduces the rates of butane and butene production without affecting the rate of butadiene production. As a result, the presence of sulfur shifts the selectivity of the reaction toward the production of butadiene.

Finally, it appears that the HDS of thiophene occurs either via direct, concerted hydrogenation of C–S bonds, producing H$_2$S, or through some weakly bound, easily
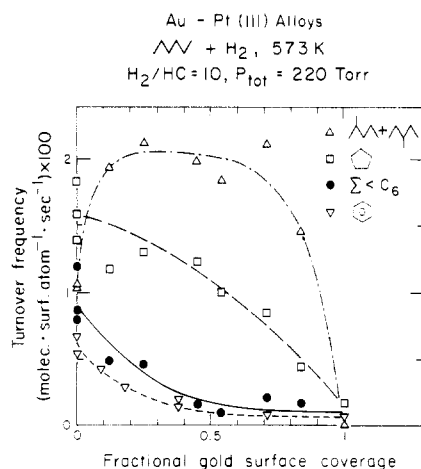
Figure 11. Dependence of the initial rates of product formation from *n*-hexane conversion on gold coverage over Au–Pt alloys: △, isomerization; □, cyclization; ●, hydrogenolysis; ▽, dehydrocyclization.

reduced Mo–S intermediate. In either case the process does not proceed via deposition of sulfur into the fourfold hollow site, from which it cannot be reduced under our reaction conditions. This sulfur species, bound in fourfold hollow sites, blocks hydrocarbon hydrogenation, modifying the HDS product distribution.

Conversion of *n*-Hexane over Gold-Modified Platinum Surfaces

The reforming of *n*-hexane over platinum catalysts occurs via a number of reactions including isomerization, cyclization, dehydrocyclization, and hydrogenolysis. Most of these are structure sensitive and have been studied in detail because of their importance as models for the processes used to produce high-octane gasoline.[40] Gold itself is inactive as a catalyst for these molecular rearrangements. However, when added to a Pt single-crystal surface it will alter the product distribution markedly. This is shown for the Pt (111) face as a function of gold coverage in Figure 11. The rate of isomerization increases while the rates of dehydrocyclization and hydrogenolysis drop quickly with gold coverage. Thus, low concentrations of gold drastically change the product distribution.[41]

This observation is usually explained by pointing out the important role that the high-symmetry threefold platinum sites play in the dehydrocyclization and hydrogenolysis reactions. The addition of gold to the surface decreases the concentration of these sites more rapidly than the low-symmetry bridging and top sites. Thus, the rates of reactions requiring high-symmetry sites (dehydrocyclization, hydrogenolysis) are reduced more rapidly than those needing the low-symmetry sites. This phenomenon is often called the ensemble effect.

In order to explain the large increase in the rate of isomerization, one must invoke the formation of mixed Pt–Au sites that are more active than the pure Pt. Such sites may be ensembles having Pt_2Au or $PtAu_2$ stoichiometry. Thus, alloying of gold with Pt can change

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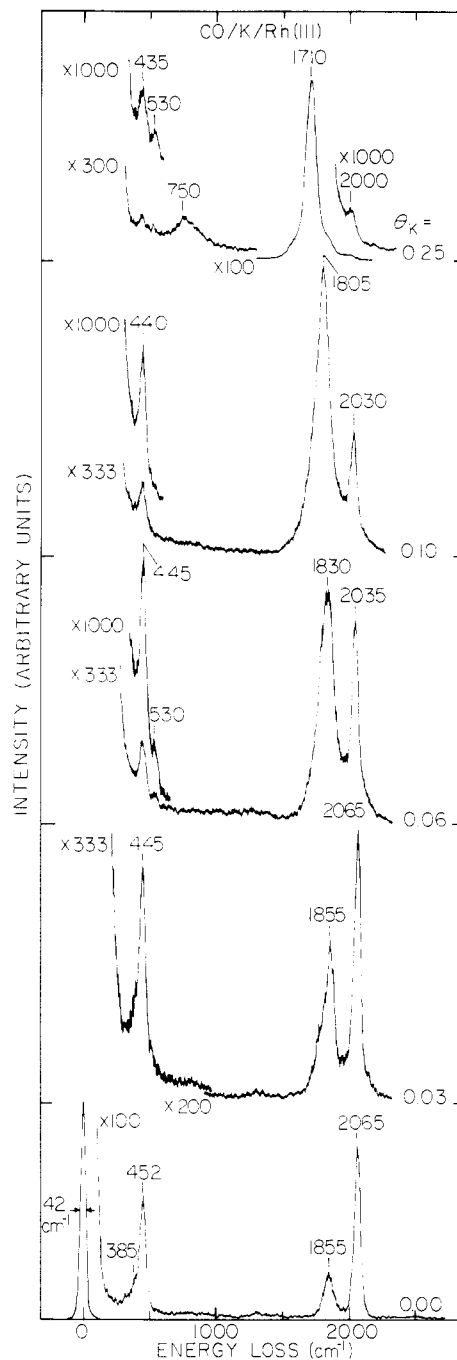

Figure 12. HREELS spectra of CO coadsorbed with K on the Rh (111) surface at various Θ_K. The two high-frequency peaks are the CO stretching frequencies.

reaction selectivity both by site blocking and by producing new catalytic sites.

Hydrogenation of Carbon Monoxide over Potassium-Doped Transition-Metal Surfaces

The hydrogenation of carbon monoxide produces alkanes, alkenes, and alcohols selectively or in a mixture over many transition-metal surfaces. Potassium is used as an additive in many catalysts for this reaction to increase activity and modify product distributions. These promoters increase the molecular weights of the products and increase the selectivity toward alkanes and unsaturates. The first explanation of this phenomenon in terms of an electronic effect was given by Blyholder[39] who suggested that potassium donates electrons to the metal that in turn increases the amount of back-dona-

tion to the CO molecules. Increased donation into the $2\pi^*$ orbital increases the metal–adsorbate bond strength while simultaneously weakening the C–O bond.

Surface science studies have shown that such effects are, in fact, observed. The heat of adsorption of CO on the Rh (111) surface is increased by 12 kcal/mol (from 25 to 37 kcal/mol) when coadsorbed with potassium. Vibrational studies using HREELS revealed a continuous decrease of the CO stretching frequency from 1850 to 1550 cm^{-1} with increasing potassium coverage[42] (Figure 12). Finally, isotope scrambling experiments using $^{13}C^{16}O$ and $^{12}C^{18}O$ indicate that potassium will induce molecular dissociation, unobserved in the absence of the alkali metal.[43] The enhanced ability to break CO bonds, induced by the presence of potassium, results in a higher surface carbon coverage and, as a result, a decrease in the hydrogen coverage. The decrease in the surface H to C ratio in turn favors carbon–carbon bond formation to produce higher molecular weight products. The reduced rate of C–H bond formation favors the production unsaturated hydrocarbons.

The modification of the catalytic properties of a metal surface by potassium differs from the previous cases in that it is an electronic effect. In the case of sulfur on the Mo (100) surface the modification is achieved by selective site blocking while the addition of gold to the platinum surface both blocks sites and creates new sites. An electronic effect that occurs through the metal substrate is expected to be more long range in nature. This has been observed to be the case using HREELS (Figure 12). The addition of potassium at low coverages induces a uniform and continuous shift in the CO stretching frequency. For such an effect to be observed at $\Theta_K \approx .05$, the influence of potassium cannot be highly localized.

Concluding Remarks

The combined use of UHV surface analytical tools and the ability to perform catalytic reactions over single-crystal surfaces under conditions that truly approach those of industrial processes have revealed detailed characteristics of these systems hitherto unobtainable. We may divide heterogeneous catalytic reactions into three classes. Catalysis of the ammonia synthesis reaction is clearly dependent upon the structural details of the metal surface. The need for atomically rough surfaces containing high-coordination hollowing sites where N_2 can dissociate has been revealed. Reactions of this type cannot occur on single transition-metal atom molecules that are utilized most frequently in homogeneous catalysis. The catalytic hydrogenation of ethylene by Pt and Rh has been shown to occur over an irreducible, carbonaceous overlayer primarily composed of adsorbed ethylidyne. It has been suggested that this overlayer serves as a medium through which atomic hydrogen, from H_2 dissociation by the metal, is transferred to ethylene, weakly adsorbed on the ethylidyne layer. This type of reaction may also occur over homogeneous catalysts.

Coadsorbates modify the rates and product distributions of catalytic reactions by blocking sites of high symmetry, by creating new sites, or by charge transfer that changes bonding of reaction intermediates. The examples that were presented include the hydrodesulfurization of thiophene over molybdenum (coadsorbed sulfur), the conversion of *n*-hexane over platinum (coadsorbed gold), and the hydrogenation of CO (coadsorbed potassium).

As the reaction to be catalyzed becomes more complex, characteristics that are associated with each of these reaction classes may all be needed simultaneously along with other features only found over oxides or other compound surfaces. Future work will expand to include non-metals (oxides, sulfides, carbides), catalyst deactivation and regeneration, and many other surface-related aspects of the catalytic process. Ultimately, the knowledge obtained will allow us to not only understand but also predict catalyst performance and design catalysts for new processes.

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(43) J. E. Crowell, W. T. Tysoe, and G. A. Somorjai, *J. Phys. Chem.*, **89** 1598 (1985).