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DIRECTIONS OF THEORETICAL AND EXPERIMENTAL INVESTIGATIONS INTO THE MECHANISMS OF HETEROGENEOUS CATALYSIS

G.A. SOMORJAI

Chemistry Department, University of California, Berkeley, CA 94720;
and Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, U.S.A.

The roles of the atomic structure and the electronic structure of the active surface sites in bonding of reactants and causing bond breaking or bond formation have been the focus of theoretical studies. In addition to calculations on static systems, usually clusters, modelling of the transition states and the dynamics of elementary reaction steps (adsorption, dissociation, surface diffusion, desorption) have been performed. Variations of electronic structure of elements across the periodic table have been shown to be responsible for the unique importance of transition metals in catalysis.

Experimental studies utilize catalysts with well-characterized structure (zeolites, crystal surfaces) and information about surface structure, composition and chemical bonding of adsorbates becomes available on the molecular level. Deliberate alteration of catalyst structure, surface composition by alloying and electronic structure by addition of electron donor and electron acceptor promoters have been utilized to modify reaction rates and selectivity. This way many of the molecular ingredients of heterogeneous catalytic reactions have been identified.

In recent years evidence has been accumulating that indicates periodic and long term restructuring of the catalyst surface as necessary for chemical change and reaction turnover. These findings point to the need of time resolved studies and in-situ investigations of both the substrate and the adsorbate sides of the surface chemical bonds simultaneously on a time scale shorter than the reaction turnover frequency.

Close collaboration between theorists and experimentalists is essential if we are to succeed in designing heterogeneous catalysts.

Keywords: Concepts of catalysis, activity trends, surface restructuring, cluster-like bonding, rough surface reactivity, building complex catalyst systems, bimetallic systems, oxide-metal interfaces

1. Introduction

The science of catalysis is built on concepts with firm foundations in experimental observations. The macroscopic studies of kinetics of catalytic reactions have in recent years been complimented with investigations that are carried out on the molecular scale. These molecular level studies permitted the definition of new concepts and the reinterpretation and broadening of more classical ideas.

Recently, theoretical studies provided us with physical models that explain some of the concepts based on experimental findings and help us to predict catalytic behavior and even aid the design of new catalysts.

Below I shall attempt to assess the directions of theoretical and experimental investigation into the mechanisms of heterogeneous catalysis. The field is rapidly moving as a result of pull by the needs of technologies and by the rapid advances or push in instrumentation that provide molecular level scrutiny of surfaces with atomic spatial resolution, ever improving energy resolution and on time scales that are shorter than catalytic turnover times (time resolved techniques). Studies in heterogeneous catalysis are carried out using both model single crystal catalyst systems and high surface area crystalline microporous catalysts like zeolites. In both types of systems knowledge of the atomic structure at the surface is the key ingredient on which understanding of the catalytic process is being built.

2. The classical concepts of heterogeneous catalysis

One of the well established phenomenon in heterogeneous catalysis is the key role d-transition metals play and how the catalytic activity for a given reaction varies by orders of magnitude from metal to metal. One such correlation, due to Sinfelt [1], depicts over 8 orders of magnitude variation of the rate of ethane hydrogenolysis to methane ($C_2H_6 + H_2 \rightarrow 2CH_4$) over transition metals is shown in fig. 1. Another concept is the need for bonding of intermediate strength during catalytic reactions. Fig. 2 shows a so called volcano plot for the decomposition of formic add due to Sachtler [2] and his coworkers. Here the temperature at which a given reaction rate is obtained is plotted as a function of the heat of formation

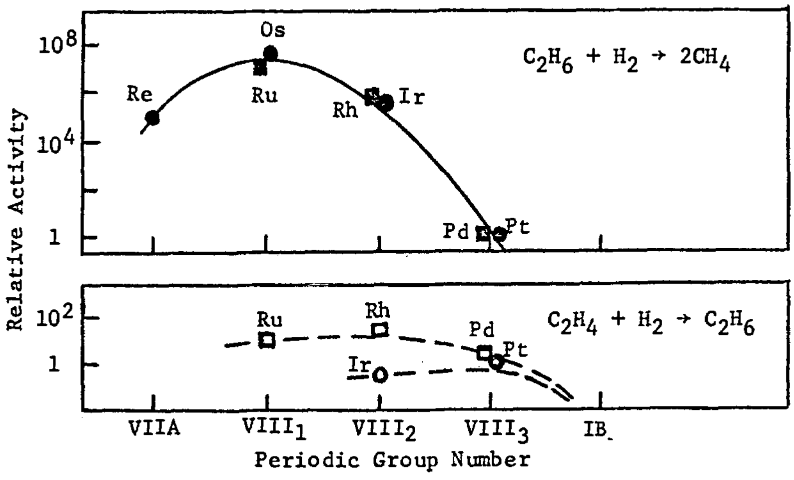


Fig. 1. Catalytic activity of transition metals for ethane hydrogenolysis.

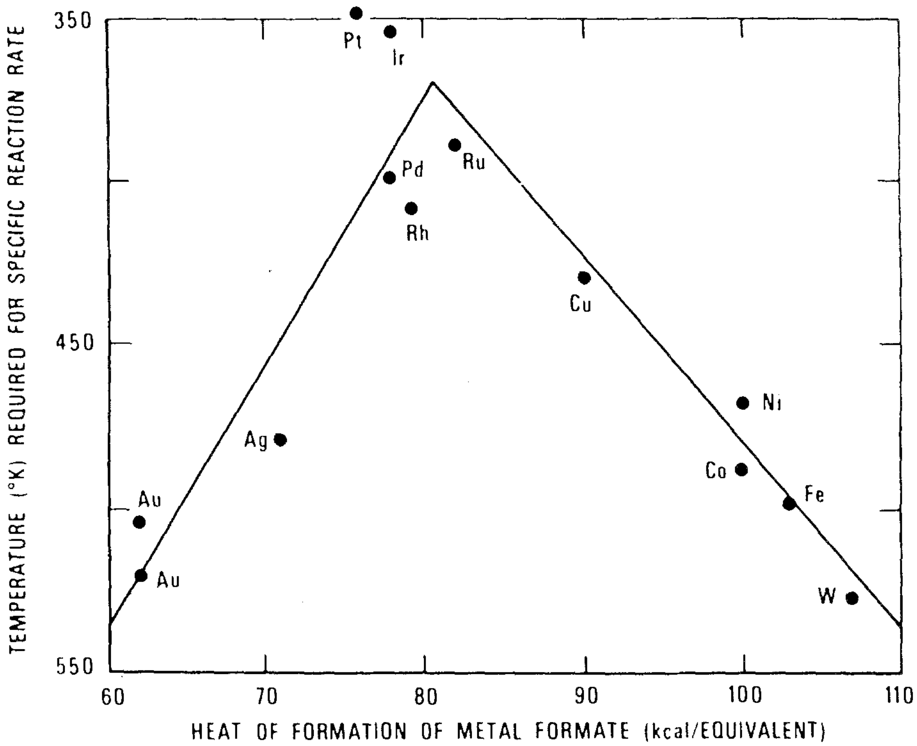


Fig. 2. Correlation between the catalytic activity of different metals for the decomposition of formic acid (HCOOH) and the corresponding heat of formation for the bulk metal formate. The temperature required for a specific rate of decomposition is plotted. Note the inverted temperature scale.

of the formate bond. Weak surface bonds do not permit reactions to occur while strong bonds form too stable reaction intermediate thereby slowing the turnover.

One dimensional potential energy diagrams [3] showing the existence of weakly adsorbing molecular precursor states and the need for a finite activation energy for bond dissociation to occur, indicated by curve crossings, are depicted in fig. 3. Curves of this type although lacking molecular details have been used to rationalize the need for thermal activation before bond breaking occurs and low reaction probabilities on many chemically active surfaces.

One of the most successful classifications of catalytic reactions is placing them into structure sensitive and structure insensitive groups [4]. Structure sensitive catalytic reaction change their rate markedly by changing the catalyst particle size (ammonia synthesis, hydrogenolysis) while the rates of other catalytic reactions remain independent of particle size (hydrogenation, carbonylation). Single crystal model catalytic studies that permitted controlled variation of surface structure confirmed the structure sensitivity or insensitivity of many of these reactions placed in these two categories based on studies using dispersed catalytic particles [5].

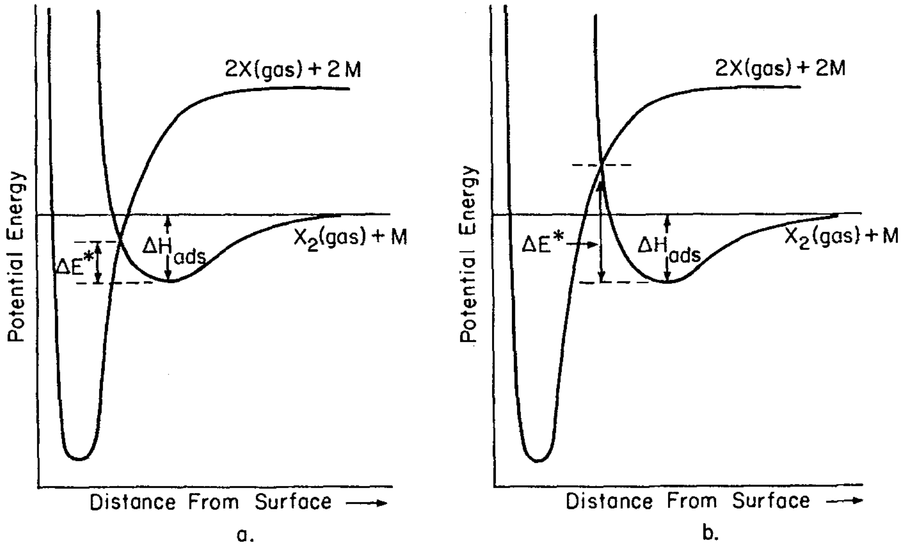


Fig. 3. One dimensional potential energy curves for adsorption in molecular and atomic states. The low activation energy permits the dissociation of the molecules adsorbed in a precursor or physisorbed state.

The experimental and theoretical challenges to understand these classical concepts of heterogeneous catalysis are formidable. We need time resolved spectroscopic techniques that monitor the bonding of surface reaction intermediates and their residence times. Simultaneously, we should be able to characterize the transition metal side of the surface chemical bond, how charges of the metal surface atoms are redistributed during the formation of the surface bond, the directionality of the bond and the possible periodic relocation of metal surface atoms during the reaction turnover. Thus we should monitor both sides of the surface chemical bond, the adsorbate and the metal side, on a time scale that is shorter than catalytic turnover times ($< 10^{-3}$ sec) under the conditions of the reaction, usually atmospheric pressure and elevated temperatures (300–700 K). Some experimental techniques can detect the structural changes that occur on both sides of the chemical bond (for example low energy electron diffraction - surface crystallography) [6]. However, most techniques are only capable of detecting the surface bond on the adsorbate side (infrared spectroscopy for example) or on the substrate side (the electron microscope for example). As a result, often only incomplete information about the surface chemical bond is obtained that leads to a one-sided molecule centric view or a surface centric view of the adsorbate surface system that is produced during the catalytic reaction. Many promising techniques require low pressures (electron spectroscopies or ion scattering). Extended X-ray fine structure *EXAFS* [7], scanning tunneling microscopy *STM* and atomic force microscopy *AFM* [8] appear promising along with sum frequency generation *SFG* [9] using non-linear laser optics although it is too early to evaluate their capabilities and limitations in studies under catalytic reaction conditions.

Theoretical approaches that are further developed by Nørskov [10] recently permit a quantum mechanical evaluation of the dominant roles of d-electrons in transition metals for dissociative chemisorption and in catalytic reactions. Salem [11], Hoffman [12] and Goddard [13] developed quantum mechanical models of surface bonding that have predictive value. Levine [14] proposed a molecular framework to understand the thermal activation of surface bonds and the coverage dependence of reactivity. Falicov [15] pointed out the variation of the local density of states from site to surface site that can be used to explain the surface structure sensitivity of bond dissociation. The recent contributions of Tully [16], Siegbahn [17], Sautet [18], Feibelman [19], Anderson [20], Schustorovich [21], Van Hove [22] and Pendry [23] are providing a molecular view of the surface bond under static as well as under dynamic conditions.

3. Concepts of heterogeneous catalysis that emerge from molecular level studies of surface reactions

Model systems often use single crystals with well defined structure and composition. Co-adsorbed additives can modify the structure of the surface or of

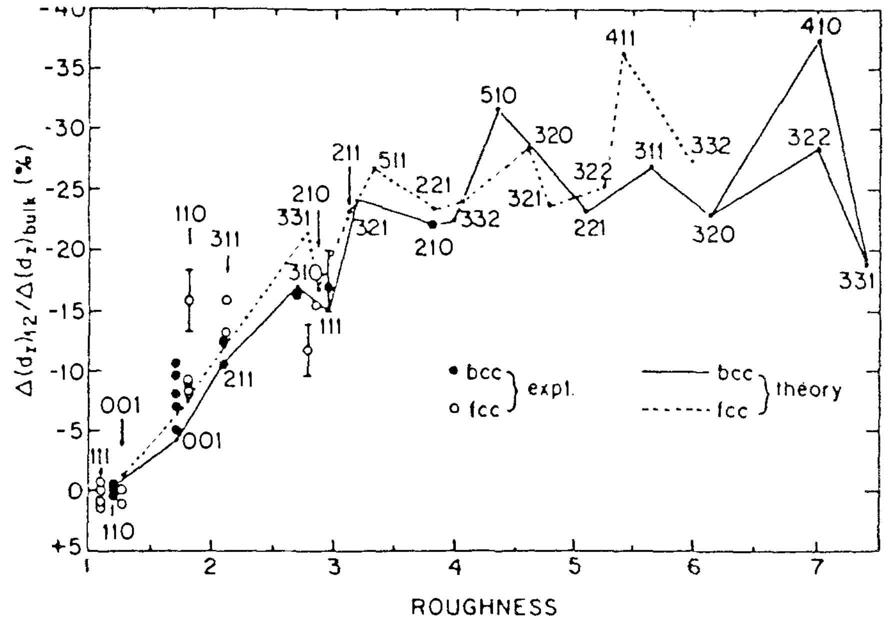
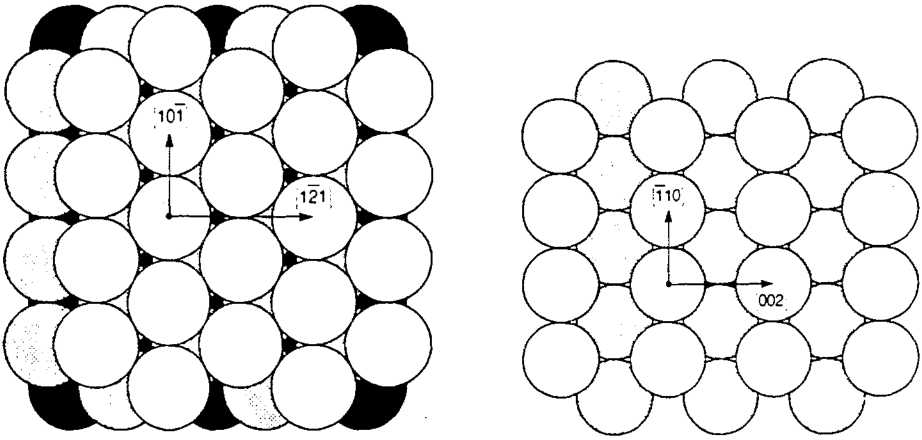


Fig. 4. The magnitude of inward relaxation as a function of surface roughness (defined as the reciprocal of the packing density; after Jona and Marcus [24]).

the adsorbates and the adsorbate bond. These studies uncovered several surface phenomena that are important during heterogeneous catalysis.

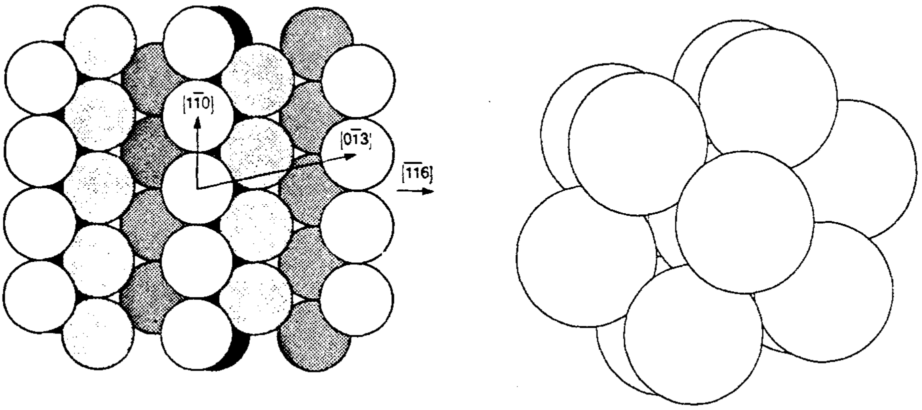
A. CLEAN SURFACES RESTRUCTURE, ROUGH SURFACES RESTRUCTURE MORE MARKEDLY

Low energy electron diffraction surface crystallography studies revealed large relaxations of atoms at surfaces. The surface atoms move inward toward the solid, thereby shortening the interlayer distances near the surface. Combined



fcc (111)
flat - most rigid

fcc (110)
open - less rigid



fcc (331)
stepped - less flexible

cluster - most flexible

Fig. 5. Four surfaces distinguishable by the coordination number of surface atoms. Atoms in the fcc(111) surface have the largest and atoms in the cluster have the smallest number of nearest neighbors.

perpendicular and lateral movements of surface atoms often lead to reconstruction, to the formation of new surface unit cells. Fig. 4 shows the magnitude of inward relaxation (denoted by a negative sign) as a function of surface roughness (defined as 1/packing density) [24]. The more open the surface, the larger is the relaxation. The relaxation can lead to extreme restructuring at stepped surfaces. The step edge atom may move 0.2 Å inward to smooth out the surface irregularity and the nearest neighbor atoms at the step restructure as well.

Rough surfaces that are also chemically active (as will be discussed later) appear to be flexible. The surface atoms move toward the bulk and to new equilibrium positions. The more open the surface, the larger the movement, the more flexible the surface atoms are. Upon chemisorption these surfaces restructure more readily. It is perhaps instructive to divide surfaces according to their flexibility as shown in fig. 5. Close packed surfaces, like the fcc(111) crystal faces are fairly rigid because of the large number of nearest neighbors (high coordination) the atoms stay close to their bulk-like equilibrium positions in spite of the anisotropy of the surface environment. Upon chemisorption these surfaces may restructure; however, the thermodynamic driving force for such restructuring is not too great. Clusters of atoms are perhaps the most flexible, the atoms ready to relocate because the low coordination of atoms at each surface site. Upon chemisorption massive restructuring of these clusters may occur.

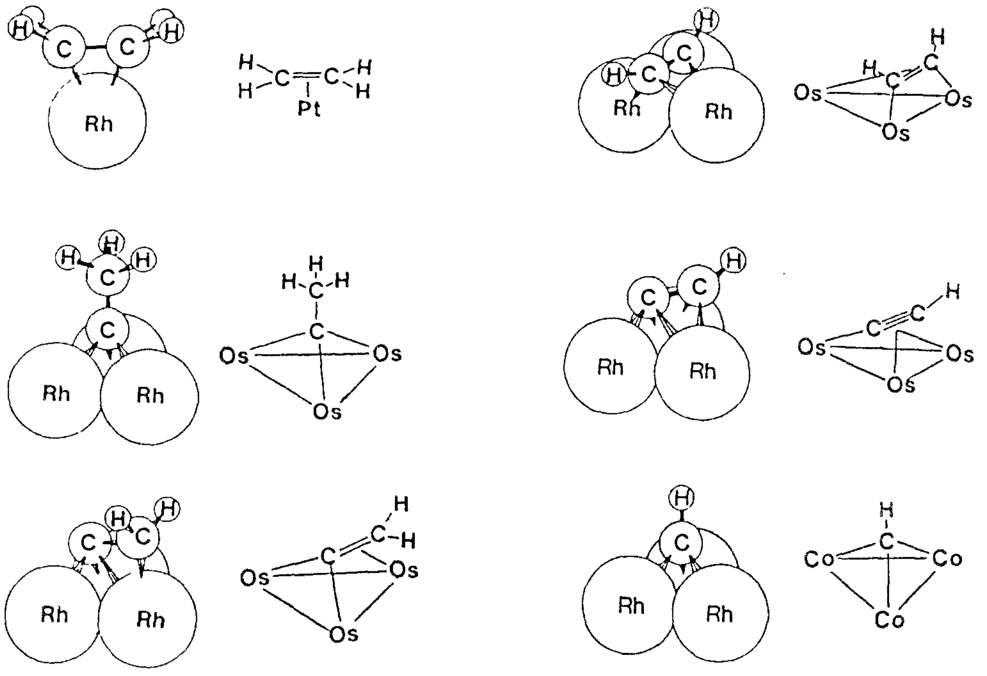


Fig. 6. Cluster-like adsorbed species on rhodium metal surfaces and structurally equivalent organometallic clusters.

B. THE CLUSTER-LIKE BONDING OF CHEMISORBED MOLECULES

The next concept of modern surface science to be described is that of surface chemical bond. The binding of surface species has been found to be cluster-like [25]. This is a particularly useful concept since it permits one to use localized bonding models in the study of surfaces. It is also an approach often adopted in theoretical calculations of molecular adsorption. Several organic molecules and molecular fragments that have been identified on metal surfaces by combination of vibrational spectroscopy and diffraction techniques exhibit the same local structure and similar chemistry to those found in multinuclear organometallic clusters for which good X-ray diffraction information is available (fig. 6). In fact for virtually every surface species found so far there is a cluster equivalent that has been synthesized by organometallic chemists.

These two concepts, the restructuring of clean surfaces and the cluster-like bonding of molecules, are good examples of the surface centric and molecule centric views of the surface chemical bond. The next concept unifies these two views of surface bonding.

4. Adsorbate induced restructuring

The restructuring of surfaces upon chemisorption of atoms and molecules has been described in detail recently [26]. When an atom or a molecule chemisorbs it usually forms chemical bonds with its nearest neighbor substrate atoms that are just as strong as the bonds between substrate atoms. Thus there is a thermodynamic driving force for restructuring upon adsorption. For example low coverages of hydrogen on W(100) induced a C(2 × 2) surface reconstruction at 300 K. Similarly the presence of a quarter monolayer of atomic carbon on nickel(100) induces a reconstruction of the topmost nickel atoms both parallel and perpendicular to the surface in such a manner that the 4 nickel atoms surround each carbon atom are rotated with regard to the underlying layers. The timescale for the restructuring may be much shorter than catalytic turnover times or in other cases may even be determined by the reaction mechanism [27]. There have been numerous investigations of kinetic oscillations in the catalytic oxidation of CO on platinum surfaces or the reduction of NO by ammonia. These self-sustained reaction rate oscillations may be accompanied by large temperature changes or the presence of reaction waves on surfaces that are described in this volume by Ertl. One of the mechanisms shown to operate under isothermal conditions involves the restructuring of the platinum(100) surface under the influence of various surface concentrations of oxygen or carbon monoxide. In the presence of high concentration of adsorbed carbon monoxide, the primitive (1 × 1) surface structure with a square unit cell is preferred, in the presence of atomic oxygen the reconstructed hexagonal surface structure is stable. Another reconstruction mechanism involves the periodic oxidation and reduction of transition metals during catalytic reactions. The rates of the oxidation and reduction controls the turnover period.

If restructuring occurs very slowly on a timescale that is much longer than that of the reaction, there may be long term changes in the catalytic reaction rate (either a gradual increase in activity or a slow poisoning of the catalytic reaction). This type of behavior is likely to be irreversible under reaction conditions but might be reversed by thermal restructuring upon desorption of the reaction intermediates. A related phenomenon is the changing structure and size of small supported metal particles upon oxidation or reduction. This effect is utilized in the regeneration of many aged catalysts where an oxydation-reduction cycle can result in an enhanced dispersion of the active phase. Oxidation of the large metal particles formed by sintering generally leads to better wetting of the underlying oxide surface. During subsequent low temperature reduction there is a tendency for the oxidized layer to break up into smaller metal particles. Hence, the increase in metal surface area and dispersion.

5. Rough surfaces do chemistry

Thermal desorption studies indicate that the chemisorption bonds of adsorbed atoms and molecules are stronger at surface defect sites at steps and kinks than on flat close-packed smooth surfaces [28]. The maximum rates of desorption shift to higher temperatures for species adsorbed at these more open surface sites. This is shown for CO chemisorbed on the platinum stepped (533) crystal face and for hydrogen adsorbed on the flat (111) stepped (557) and kinked (12, 9, 8) platinum surfaces (figs. 7a and 7b). Another example is the thermal decomposition of ethylene on the nickel(111) (110) and stepped 5(111) × (110) crystal faces (fig. 8). Bond breaking shifts to much lower temperature, below 150 K, at step sites. Molecular beam scattering studies of the catalytic H_2/D_2 exchange reaction clearly show that at low coverages the dissociation probability of H_2 at defect sites such as steps is near unity while at flat defect free (111) platinum surfaces have dissociation probability of less than 10^{-3}, below the detection limit. (table 1).

Table 1
Structure sensitivity of H_2/D_2 exchange at low pressures ($\approx 10^{-6}$ Torr)

	reaction probability
Stepped Pt(332)	0.9
Flat Pt(111)	$\approx 10^{-1}$
"Defect free" Pt(111)	$\leq 10^{-3}$

6. Adsorbate-adsorbate interactions

The pressure regime investigated by surface science is in the 10^{-9}–10^{-6} Torr range that permits studies of adsorbates with long surface residence times by electron and ion spectroscopies and gas surface interaction by molecular beam-surface scattering. Catalytic reactions are usually studied at high pressures ($1-10^2$ atm) where coverages are much higher and adsorbate-adsorbate interaction plays important roles in controlling bonding and reaction dynamics. Figs. 9a and 9b show the typical variation of the heat of chemisorption with coverage. It is generally thought that repulsive adsorbate-adsorbate interactions drastically weaken adsorbate-substrate bond strengths leading to the behavior exhibited in

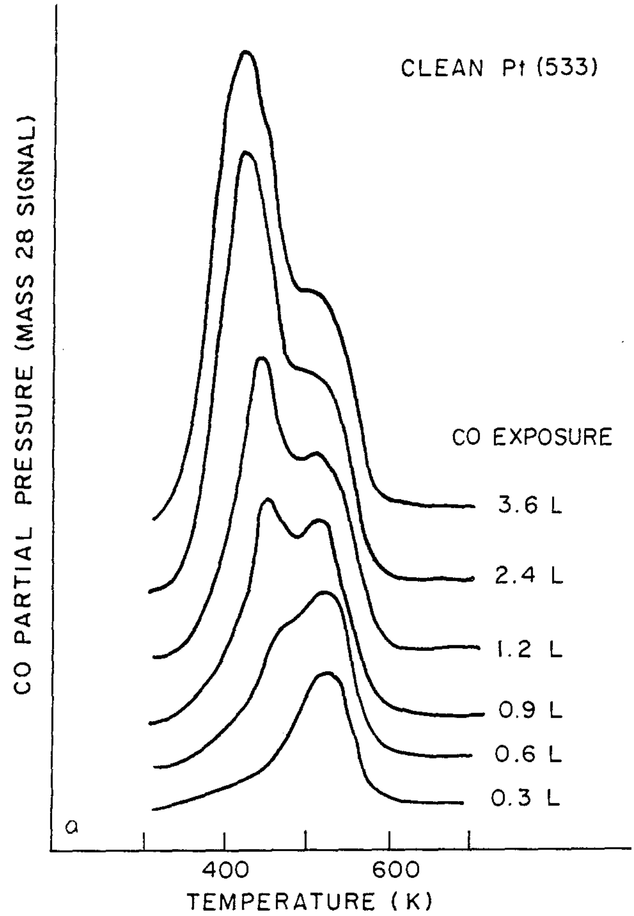


Fig. 7. a) Thermal desorption of CO from a stepped Pt(533) surface as a function of coverage. Note the sequential filling of sites. The step sites adsorb CO with higher binding energy and adsorb CO first. b) Thermal desorption of chemisorbed hydrogen from the flat (111), stepped (557) and kinked (12, 9, 8) crystal faces of platinum.

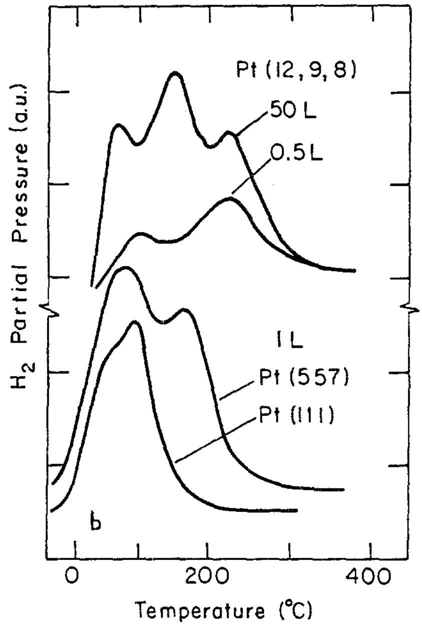


Fig. 7. (continued).

these figures. Relocation of CO molecules at high coverages [29] and neutralization of K ions with increasing coverage have been revealed [30].

Attractive adsorbate-adsorbate interactions have been found upon the coad-

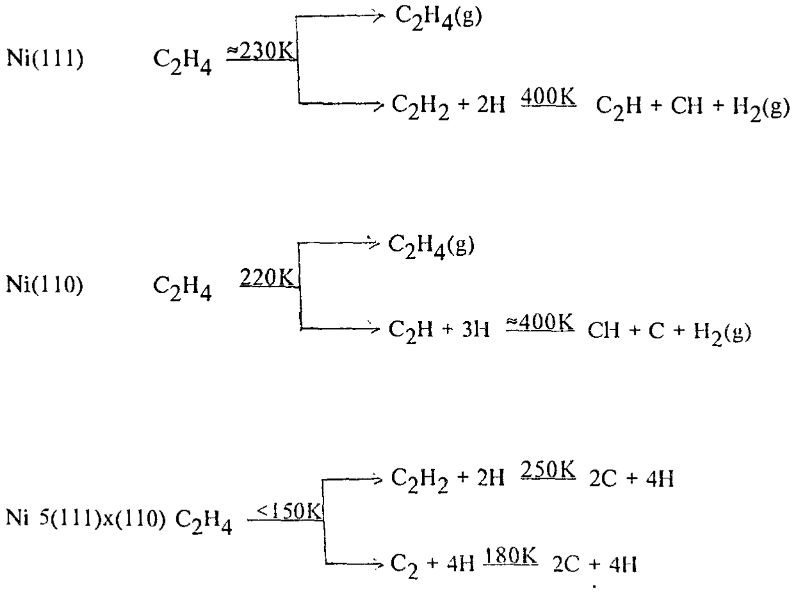


Fig. 8. Thermal decomposition of ethylene on the nickel(111), (110) and stepped nickel surface. Note the much lower temperature necessary for bond breaking on the stepped metal surface.

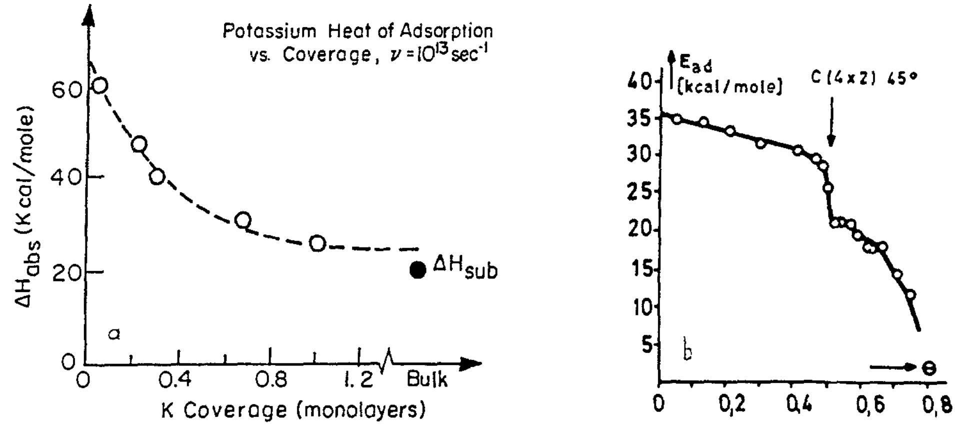
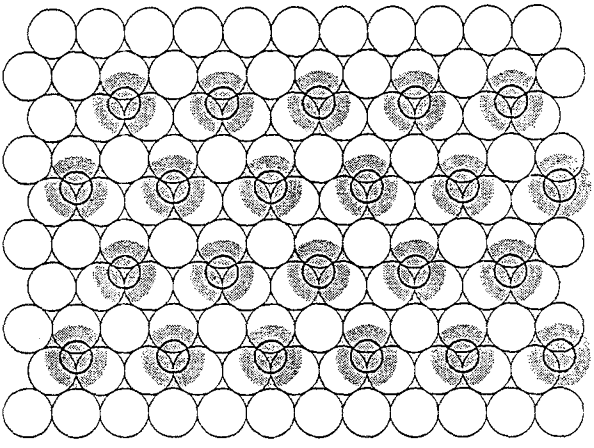


Fig. 9. a) The heat of adsorption of potassium as a function of coverage on the rhodium(111) crystal face. b) The heat of adsorption of CO as a function of coverage on the Pd(100) crystal face (after Ertl et al.).

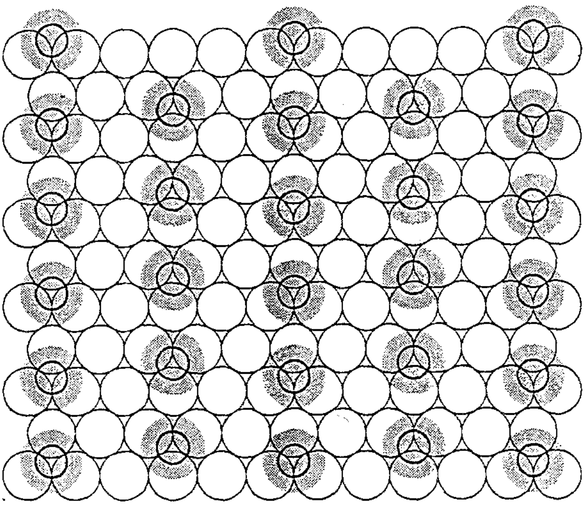
sorption of two different molecules, one a donor the other an acceptor, to metal surfaces. The coadsorption of CO, an electron acceptor on Rh with organic molecules (all of them donors to Rh) leads to the formation of ordered surface structures with both molecules as part of the unit cell [31]. When two acceptors or two donor molecules coadsorb disordered monolayers are produced. The coadsorption of potassium (donor) with CO (acceptor) on metal surfaces leads to higher heats of adsorption for CO and to a more facile CO bond dissociation [32]. Coadsorption of potassium (donor) with ammonia (donor) on iron surfaces leads to a reduction of the heat of adsorption of NH_3 because of repulsive K-NH_3 interaction [33]. As a result, K plays an important role as a catalyst "promoter" for CO hydrogenation as well as for ammonia synthesis on iron. In the former case, CO dissociates in an elementary reaction step that is aided by coadsorbing K on various transition metal surfaces. In the latter case the rapid desorption of NH_3 that is the product of the N_2/H_2 reaction is aided by coadsorption with K thereby increasing the turnover rate of ammonia synthesis. Potassium also affects the bonding of hydrogen and N_2, also important reactants in many catalytic processes.

It has been customary to separate adsorbate-substrate and adsorbate-adsorbate interactions as obtained from low pressure and high pressure surface studies. It has been assumed that the substrate remains unaltered as a function of coverage. Chemisorption induced restructuring clearly indicates that the substrate structure is altered during chemisorption and it is reasonable to assume that substrate restructuring can also be coverage dependent. In this circumstance unusual coverage dependent bonding and structure behavior is expected. One such a case appears to be sulfur chemisorption on Re(0001) [34]. Sulfur forms clusters, trimers, tetramers and hexamers with increasing sulfur coverage (fig. 10). The S–S



a

Sulfur 2 x 2 on Re(0001)

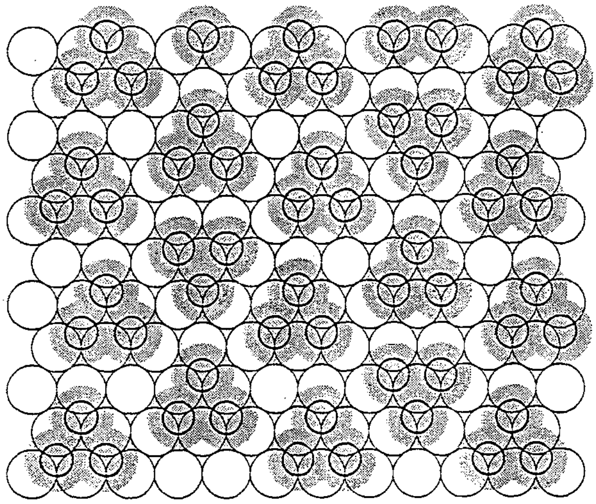


b

Sulfur c(√3 x 5)rect on Re(0001)

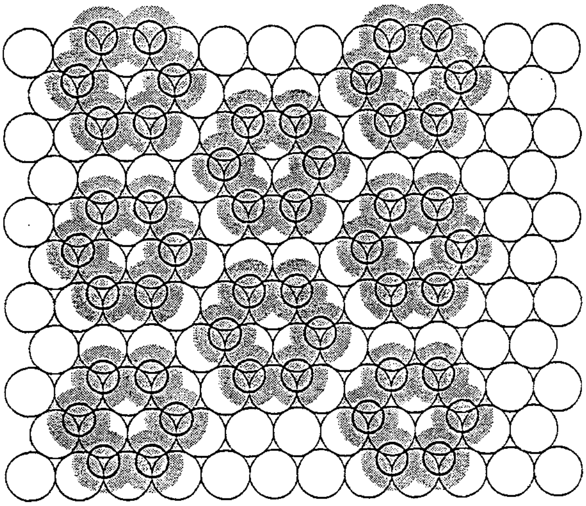
Fig. 10. a) A schematic diagram of the (2×2) structure of sulfur atoms on the Re(0001) crystal surface. The hatched circle indicates the sulfur Van der Waals radius of 1.80 Å and the smaller solid ring shows the 0.9 Å covalent radius of sulfur adsorbed on the metal surface. b) A schematic diagram of the $c(\sqrt{3} \times 5)$ rect. lattice showing sulfur adatoms on the Re(0001) substrate. c) A schematic diagram of the $(3\sqrt{3} \times 3\sqrt{3})$R30° sulfur lattice on Re(0001). d) A schematic diagram of the $(\begin{smallmatrix} 3 & 1 \\ 1 & 3 \end{smallmatrix})$ sulfur lattice on Re(0001).

bonds in the clusters are long, as long as the metal–metal bonds which is unexpected. In addition these clusters exhibit long range order and periodicity. The formation of these unique S surface structures that appear with increasing coverage must be due to subtle changes in the structure of the underlying



c

Sulfur (3√3 x 3√3)R30° on Re(0001)



d

Sulfur (2√3 x 2√3)R30° on Re(0001)

Fig. 10. (continued).

rhenium substrate that gives 'rise to an attractive S–S interaction even at high coverages leading to the periodic condensation of the clusters.

The adsorbate-adsorbate interaction whether it is repulsive or attractive, becomes complex when accompanied by the coverage dependent restructuring of the substrate. As a result, the adsorbate-substrate and adsorbate-adsorbate interactions are not likely to be separable.

7. Ingredients of complex catalytic systems: structure modifiers, bonding modifiers, bimetallic systems and oxide-metal interfaces

Heterogeneous catalyst systems are usually cluster-like and complex that include additives that modify the structure of the catalysts and the bonding of the reactants and products. The molecular phenomena discussed above highlights the importance of rough surfaces in breaking or rearranging chemical bonds, chemisorption induced restructuring that points to the dynamic behavior of surfaces on the time scale of chemisorption or catalytic reactions. Adsorbate-adsorbate interactions that modify surface bonding by charge transfer can also alter catalytic reaction rates and reaction paths leading to changes of product distribution. The modifying effects of additives on catalytic behavior can all be explained by these molecular phenomena as they are due to alterations of surface structure and adsorbate bonding. There are two other effects that modify catalytic behavior that could only be explained by the dynamic rearrangement of surfaces as it responds to the changing surface chemical environments. These are the unique catalytic activities of bimetallic systems and oxide metal interfaces.

The catalytic behavior of the Pt-Au system demonstrates the first effect [35] The addition of gold to Pd increases the rate of H_2O formation from H_2 and O_2

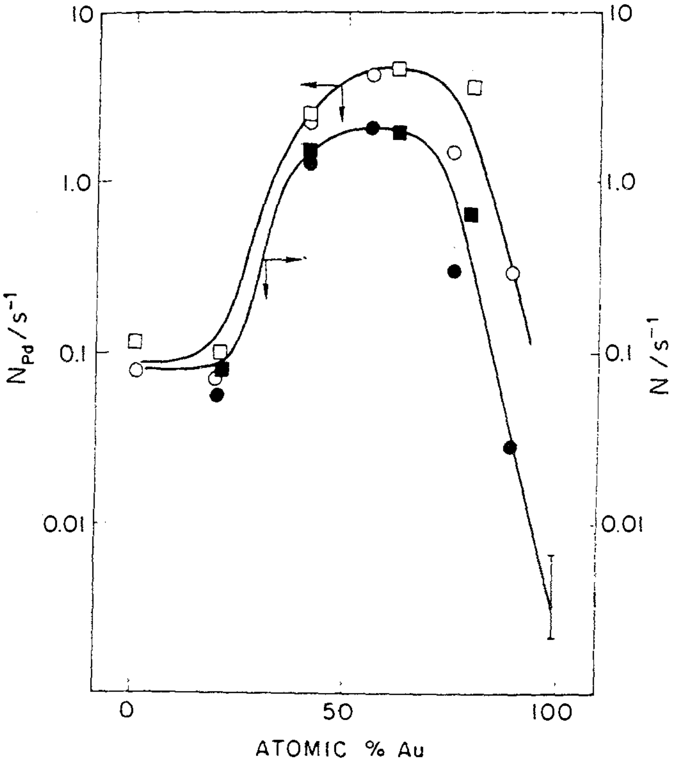


Fig. 11. The rate of formation of water as a function of gold addition to the palladium catalyst.

by 50 fold over that of pure Pd even though Au alone is a poor catalyst for this reaction. This is shown in fig. 11. The addition of Au also increases the rate of n-heptane isomerization over the Pt(111) crystal face.

A similar effect of very large reaction rate increases is found at oxide-metal interfaces. As TiO_2 is deposited on Rh, the rate of CO or CO_2 hydrogenation exhibits a maximum at about 0.5 monolayer coverage of the oxide as shown in fig. 12 [36]. The oxide alone does not catalyze the reaction to produce alkanes. The large enhancement of activity shown at metal-metal and oxide-metal interfaces can be explained if the dynamic restructuring rate is increased at these interfaces to enhance the turnover rates in proportion. A static picture of surfaces cannot rationalize the large rate enhancing effect of the addition of an inactive metal or an inactive oxide.

We can now build complex catalyst systems that include additives of various types on single crystal surfaces. Two of these are shown schematically in figs. 13a and 13b. We need techniques that can monitor the surface structure and bonding during the catalytic process and in a dynamic range that provides for detection of surface restructuring if it is indeed occurring during the reaction turnover time. STM appears to be a promising technique for this purpose. Studies of this type are in progress in our laboratory.

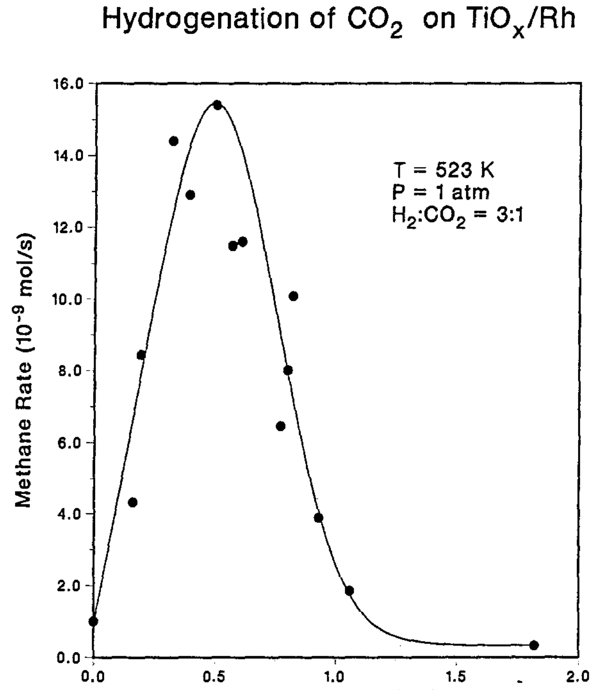


Fig. 12. The rate of CO_2 hydrogenation as a function of TiO_2 coverage deposited on rhodium.

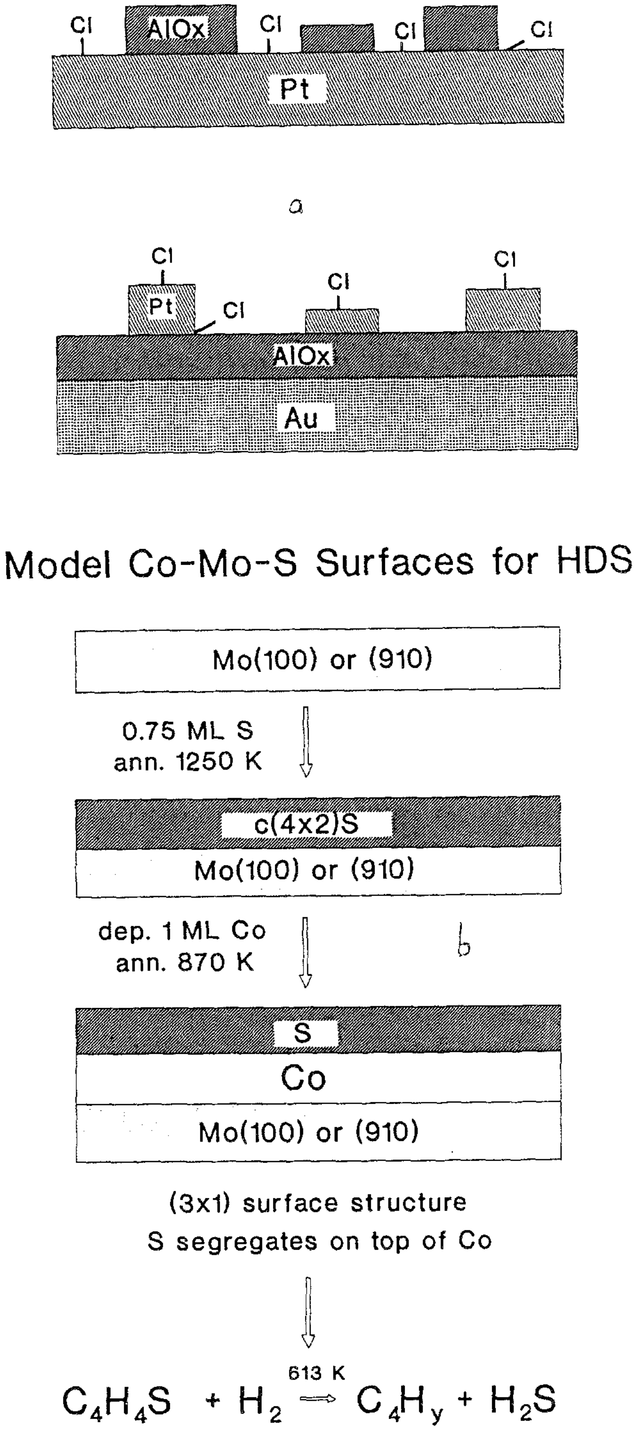


Fig. 13. Building of complex catalysts: a) The Pt/Al_2O_3/Cl model catalyst system for dehydrocyclization. b) The Mo/Co/S model catalyst system for hydrodesulfurization.

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