Title
CATALYSIS

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CATALYSIS

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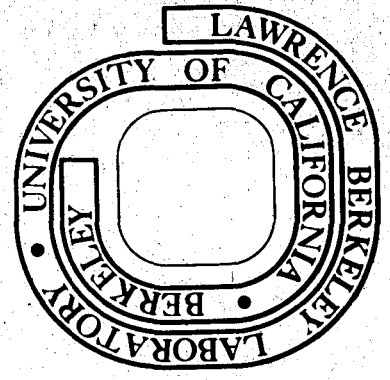

DISCLAIMER

Studies on the Atomic Scale. Perhaps the most significant achievement in the field of heterogeneous catalysis has been the development of techniques for investigating the catalytic surface on the atomic scale.[1] The atomic structure of clean catalyst surfaces and of adsorbates can be studied by low-energy electron diffraction if these structures are indeed ordered on the scale of 10^2 - 10^3 Å. In the absence of ordered domains of such sizes, electron spectroscopy techniques (ultraviolet photoelectron spectroscopy, X-ray photoelectron spectroscopy) are used to study the electronic structure of clean catalyst surfaces (electronic density of states, electron surface states) and of adsorbed molecules. The surface composition is also determined by electron spectroscopy (Auger electron spectroscopy and X-ray photoelectron spectroscopy) usually with the sensitivity of 1% of a monolayer. The atomic and electronic surface structure and the surface composition is then correlated with the rates of surface reactions and with the reaction paths that are determined by kinetic studies of catalytic reactions over these well-defined surfaces.

There are several transport techniques that have been developed for studies of catalytic surface reactions on an atomic scale.[2] In many of these investigations one face of a single crystal area, not larger than 1 cm^2, can be used to measure reaction rates and product

distributions. At low pressure (10^{-6} - 10^{-4} Torr) mass spectrometric detection of the reactant and product distributions while at high pressure (10^{2} - 10^{4} Torr) gas chromatography detection has been used.[3]

Using molecular beams as the incident gas flux, one can determine the reaction probabilities on single collision of the gas molecules with the surface, the surface residence time necessary to obtain the desired products, identify the atomic site where bond breaking occurs, and determine the energetics (rate constant, activation energies, pre-exponential factors) of the surface reaction.[4] Other steady state or batch reaction monitoring techniques yield similar information although with somewhat less atomic detail.

A scheme of a typical catalyst surface is shown below. There are several surface sites that are distinguishable by the number of nearest neighbors that surround them (coordination number). Molecular beam scattering of H_2 and D_2 from platinum crystal surfaces revealed atomic steps on the surface control the dissociation of these diatomic molecules.[4] The presence of large concentrations of atomic steps is necessary prerequisite to the formation of HD product. Studies of the dehydrogenation of cyclohexane (C_6H_{12}) or cyclohexene (C_6H_{10}) to benzene on platinum crystal surfaces showed that the C-H bondbreaking also occurs at atomic steps.[5] In the studies of hydrocarbon reactions on platinum crystal surfaces where several reaction paths

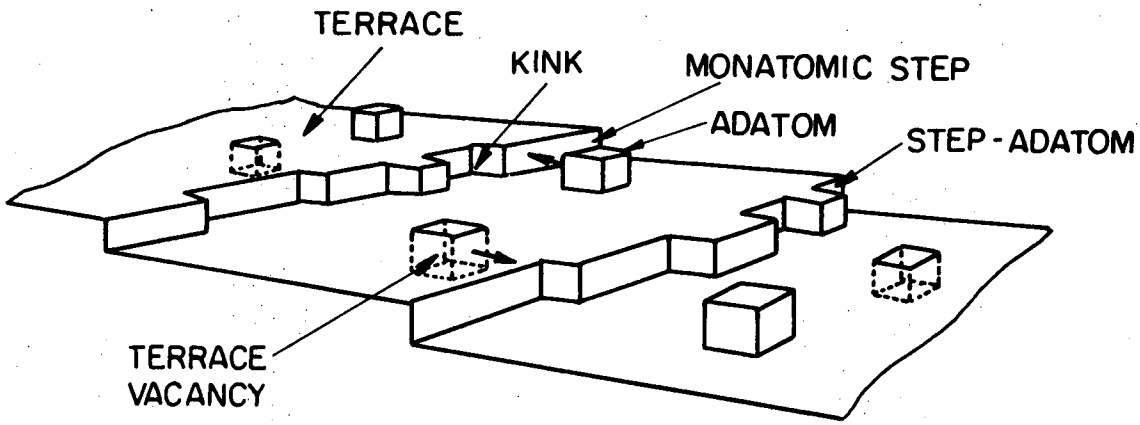

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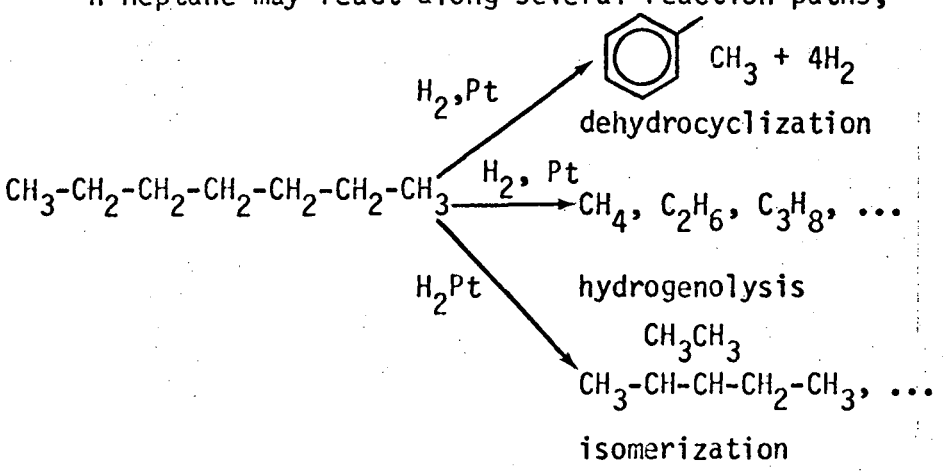
Fig. 1

were possible, microstructures on the surface have been identified where C-C bond breaking also occurs in addition to C-H and H-H bond breaking processes. It appears that surface irregularities or various surface sites with different and distinct chemical activities. Curiously, gold, a neighbor of platinum, did not show such a structure sensitive reactivity as Pt does.[6] It appears that transition metals with unfilled d-orbitals (and high electron density of states) are the group that exhibit multifunctional reactivity behavior that is controlled by the detailed atomic structure of the heterogeneous surface. By preparing transition metal surfaces with controlled concentrations and configurations of atomic steps and ledges, the reaction rate as well as the reaction specificity may also be controlled.

n-Heptane may react along several reaction paths,



Studies of this reaction on platinum crystal surfaces of various atomic surface structure have been performed. The rates of the hydrogenolysis and isomerization reactions have not varied markedly (less than a factor of 10) from crystal face to crystal face, but the product

distributions were a strong function of the atomic structure. The rate of formation of toluene on the other hand, may vary by a factor of 100 from crystal face to crystal face. It was found that shortly after the beginning of the reaction the surface became covered with an overlayer of carbonaceous deposit that was either disordered or ordered depending on the conditions of the experiment and on the platinum surface structure. The high initial rates were reduced somewhat as the carbonaceous residue formed, but the surface was not poisoned by the formation of this deposit. Whether the reaction was carried out at low or at high pressure, the catalyst surface was always largely covered by the carbonaceous overlayer. The model of the platinum surface that yields steady state rates and product distribution during the catalysis of hydrocarbon reactions is shown below.

Islands of platinum atoms perform the various C-C, C-H, and H-H bond breaking functions and perhaps some of the molecular rearrangements. Then the specie break away from the metal atoms, diffuse onto the terrace where further rearrangement may occur followed by desorption of the product molecules.

Other important catalytic reactions such as the nitrogen fixation that require N≡N bond breaking or the reaction of CO with H_2 that necessitate C=O and H-H bond breaking are being studied. Similar studies on other metal surfaces will certainly lead to a molecular level understanding of the elementary steps of heterogeneous

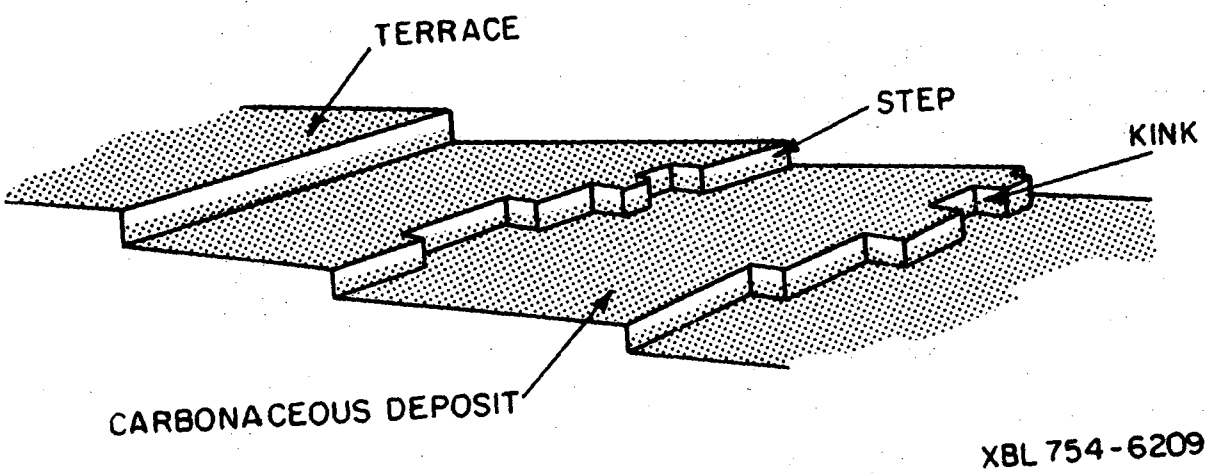


Fig. 2

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catalysis -- adsorption, surface diffusion, bond breaking, rearrangement and desorption. The understanding of catalytic surface reactions on the atomic scale is the foundation of catalysis science that attempts to develop more selective, more poison resistant, and more efficient catalysts.

Alloy Catalysts. Commercial application of several alloy catalysts has clearly emphasized the unique character of these systems such as specificity to obtain desired product distributions and greater resistance to poisoning. The application of Ir-Au and Pt-Re alloy catalysts are just two examples of systems that are being used in large-scale industrial application. John Sinfelt has shown[7] that systematic variation of alloy composition can change the product distributions in a controlled way which is one of the desired goals in catalyst applications. It is hoped that the adsorption and bond breaking characteristics may be "titrated" by suitable changes in alloy composition.

The addition of a second component may have several effects on the heterogeneous surface. The new metal constituent may block certain surface sites by preferential adsorption. By "poisoning" the catalytic activity of certain sites, the product distribution may be markedly altered.

The second metal component may not distribute equally between the surface and the bulk. Indeed, surface thermodynamic models show that the metal component

with the lower surface tension (that is proportional to the heat of sublimation) accumulate at the surface.[8] Thus, the surface and bulk compositions may be related, but certainly not equal. Such a surface segregation makes systematic variation of the composition and its correlation to the reactivity more difficult.

It has been found that small particles may have surface compositions very different from large particles. Several alloys showed excellent miscibility in small particle form while immiscible according to their bulk phase diagram. Thus, the presence of surface phases whose existence cannot be predicted from bulk alloy properties should be explored.

Finally, the presence of an adsorbate may change the surface composition of a multicomponent system with respect to the composition of the clean alloy surface. If the adsorbate forms a stronger bond with one of the alloy constitutents, this metal would accumulate at the surface in the presence of the adsorbate. Thus, the same alloy may change surface composition as a result of changes in reaction conditions.

These are some of the difficulties that are encountered in studies of catalysis by surfaces of alloys and other multicomponent systems. Nonetheless, this is a very important area of investigation if our aim is to control the product distribution (specificity) and rates of surface reactions. It appears that this aim is best to be reached by controlling the a) atomic structure and

b) the surface composition of catalyst surfaces.

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