Pure & Appl. Chem., Vol. 50, pp. 963-969.
Pergamon Press Ltd. 1978. Printed in Great Britain.
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ACTIVE SITES FOR HYDROCARBON CATALYSIS ON METAL SURFACES

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Abstract -- There is a great deal of experimental evidence associating selective bond breaking ability with low coordination number surface sites on transition metal surfaces. Atomic steps break H-H and C-H bonds efficiently while kinks in the steps are required for additional C-C and C=O bond scissions. The blockage of some of these "active sites" yields the reaction selectivity commonly observed as a result of alloying or upon introduction of certain promoters.

Another important parameter in controlling transition metal catalytic activity is the formal oxidation state of the surface metal atom. Oxidation of the surface atoms by oxygen or halogens or their reduction by electron donors (carbon, alkali metals, etc.) changes markedly the catalytic surface chemistry. H_2-D_2 exchange, hydrocarbon conversion reactions and the hydrogenation of CO are examples to demonstrate the importance of low coordination number sites and surface oxidation state in controlling catalytic activity and selectivity.

INTRODUCTION

In catalyzed reactions of organic molecules that take place over transition metal surfaces producing, selectively, other hydrocarbons at rapid rates is among the most widely utilized chemical processes. The catalytic action of the solid surface involves the 1) adsorption of the reactant molecules at certain sites where 2) bond breaking (C-H, C-C and H-H) occurs followed by suitable 3) rearrangement of the adsorbed reaction intermediate. Finally, the product molecule must 4) desorb from the catalyst surface so that the process could be repeated with other molecules over and over again (Ref. 1).

Over the past several years the molecular details of these catalytic reactions have been investigated using many of the modern surface diagnostic techniques. Electron spectroscopies (Auger and X-ray photoelectron spectroscopy) were used to determine the surface composition and the oxidation state of atoms in the active catalyst surface and low-energy electron diffraction (LEED), to determine the atomic surface structure. New techniques were developed that permit the use of small area (1 cm^2) single crystal surfaces as catalysts with well characterized surface structure and surface composition for these reaction studies (Refs. 2, 3). This way the relationship between the reaction rates and product distribution and the atomic surface structure and composition could be established.

There are several important observations that emerge from these investigations. The active catalyst must have several different sites ("active sites") that are distinguishable by their number of nearest neighbors or by their oxidation state. Atomic steps and kinks (surface irregularities) on various transition metal surfaces are active in breaking C-H, C-C and H-H bonds (Ref. 1). Often, the rearrangement of the hydrocarbon molecules on the active site is an activated process that is influenced by the reaction temperature. The active surface is largely covered with a carbonaceous deposit that, when it is ordered, can influence the selective rearrangement of organic molecules. However, this deposit may also block certain reaction sites leading to poisoning of the catalytic activity. Additives such as oxygen, chlorine or potassium that are often called "promoters" serve to maintain the desired oxidation state of surface atoms or may even participate in forming new reaction intermediates and prevent blockage by the carbonaceous deposit.

EXPERIMENTAL

There are two types of experiments that have been developed for studies of the molecular dynamics of surface reactions. One involves the reactive scattering of a well-defined molecular beam from a well-characterized surface (Ref. 4). Using this technique, the reaction probabilities upon a single collision with the surface can be determined along with the minimum surface residence time necessary to form the product. The scheme of the experiment is shown in Fig. 1. The beam of molecules incident on the surface is chopped at a well-defined

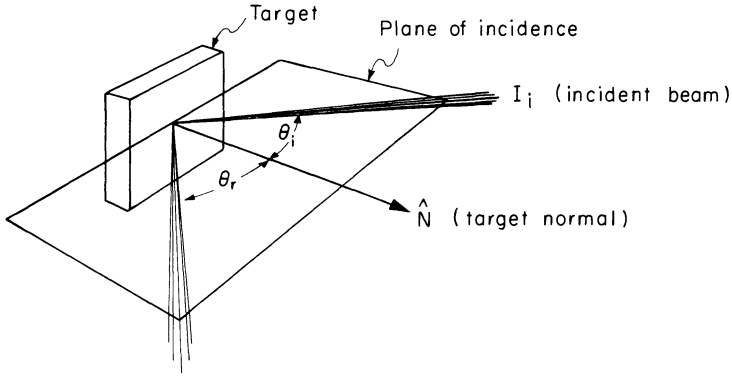

Fig. 1 Schematic representation of the gas-solid scattering experiment.

but variable frequency and the scattered products are detected by a mass spectrometer at various angles. From the time of flight the surface residence time and the velocity of the reaction products is determined. The signal intensity at various angles yields the angular distribution of the reaction probability which, as will be seen later, provides information about the surface structure sensitivity of the reaction.

The other experiment provides the means to study the reactivity of well-characterized surfaces under industrial high pressure conditions (1 to 40 atm) as well as at low pressures (10^{-6} to 10^{-4} torr) in the same reaction chamber (Ref. 5). The apparatus is shown in Fig. 2. The

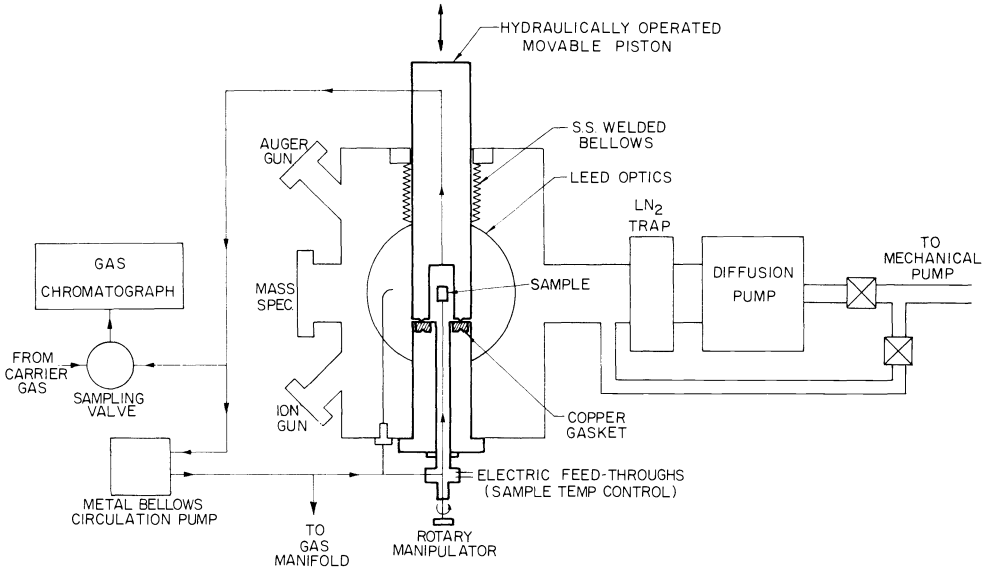

Fig. 2 Surface analysis apparatus for catalytic studies at high pressures (0.1-100 atm) with a small volume isolation cell.

sample is placed at the center of an uhv chamber and it is accessible to the LEED, AES, ion bombardment and mass spectrometer facilities. The shaft of the sample can allow a 180° rotation and heating of the sample at any pressure. The sample may then be enclosed by a small high-pressure cell. This cell is operated by hydraulic pressure from above, and engages a copper sealing gasket below the sample. The internal volume of this chamber is quite small (30 cm^3) and the total volume of the cell and the external gas circulation route is only 100 cm^3. Gases are admitted to the circulation loop and a small metal bellows diaphragm pump is

used to circulate the gases around the loop. The gases can also be directed to pass through a gas sampling valve, which can extract 0.1 ml of gas mixture for gas chromatographic analysis; the reaction rates and product distributions can be determined this way.

The Structure of Surfaces

The chemically active solid surface is structurally heterogeneous and may be viewed as shown by the model in Fig. 3. There are atoms in terraces surrounded by the largest possible numbers of nearest neighbors. There are surface irregularities, steps and kinks, in which atoms have less nearest neighbors. The relative concentration of atoms in the different sites depend

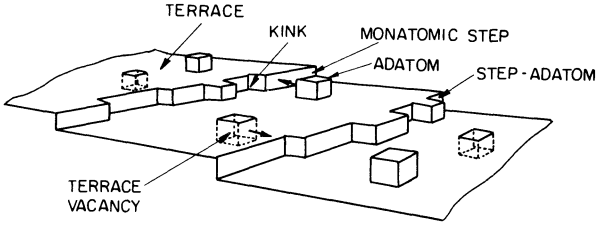

Fig. 3 Model of a heterogeneous solid surface depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.

on the surface preparation (i.e., particle size, mode of catalyst precipitation and reduction). However, once formed, equilibrium is usually established among atoms in the different sites on account of rapid diffusion under most chemical reaction conditions.

It is possible to prepare single crystal surfaces to have predominantly only one type of atom or surface irregularity (Ref. 1). The three types of crystal surfaces that have distinguishable chemical activity are shown in Fig. 4. By cutting the crystal along a Miller Index plane (i.e., (111)), a highly ordered homogeneous surface can be prepared. By cutting along higher Miller Index planes, ordered steps of one type can be produced that are separated by terraces of several atoms wide.(Ref. 6). Similarly, stepped surfaces with high concentration of kinks in the steps can also be prepared.

Many surfaces are stable in the monatomic height step configuration. Others rearrange in the presence of a monolayer of carbon or oxygen to form 2-3 atom height stepped surfaces or surfaces with other atomic structures (Ref. 7). Low-energy electron diffraction is an excellent technique to study these rearrangements as this technique is able to detect the terrace width and the step height as long as atomic order is maintained on the surface.

Calculations indicate that the charge densities of atoms at surface irregularities may be entirely different than for atoms in the terrace sites (Ref. 8). Thus it is not surprising that their chemical activity for adsorption and bond-breaking are also different. Indeed, these surface irregularities can be viewed as the active sites for many catalytic reactions that have been suggested by Taylor as early as 1925.

H_2-D_2 Exchange on Stepped Surfaces by Molecular Beam Scattering

The special activity of atomic steps is clearly revealed by recent studies of H_2-D_2 exchange (that require bond breaking) by molecular beam scattering (Ref. 9). A mixed molecular beam containing both H_2 and D_2 molecules was scattered from a stepped platinum crystal surface from different directions with respect to the step edges and the formation of the HD product molecules was monitored by a quadrupole mass spectrometer. Figure 5 shows the results. When the mixed beam struck the surface in such a way that the atomic step is exposed, the reaction probability is twice as high as when the bottom of the step is shadowed with respect to the direction of the incident molecules (Fig. 5a). That this is a structural effect is also revealed by Fig. 5b. When the molecular beam strikes the surface parallel to the step, the angular dependence of the reaction probability disappears since the step concentration "seen" by the molecular beam is the same at all incident angles. Figure 5c shows the lower reactive scattering rates obtained from the Pt(111) crystal surface. By using a simple geometrical model that divides the surface into step and terrace areas, it turns out that the steps are seven times as active in breaking H-H bonds on platinum surfaces than on the terrace sites and the bottom of the step appears to be the active site for this process (Ref. 10).

Recently the importance of surface irregularities (steps and kinks) for hydrocarbon reactions where C-C, C-H and C=O bond breaking occurs have also been demonstrated (Ref. 11).

obtained when, under otherwise identical conditions, the sulfate, chloride, perchlorate, or nitrate salts of cobalt(II) were aged.

Many more monodispersed sols of different hydrous metal oxides, involving those of chromium (6,7) copper (8), titanium (9), and other metals, have now been prepared following similar procedures.

MECHANISM OF METAL HYDROUS OXIDE FORMATION

The examples in the preceding section clearly show that it is necessary to know the composition of the solution in terms of the nature and of the concentration of all complexes if one is to explain the chemical processes in homogeneous precipitation of metal hydrous oxides. Unfortunately such information is not always available, particularly for solutions at higher temperatures. Thus, one has no choice but to determine the composition of the different solutes under the actual conditions of the solid phase formation.

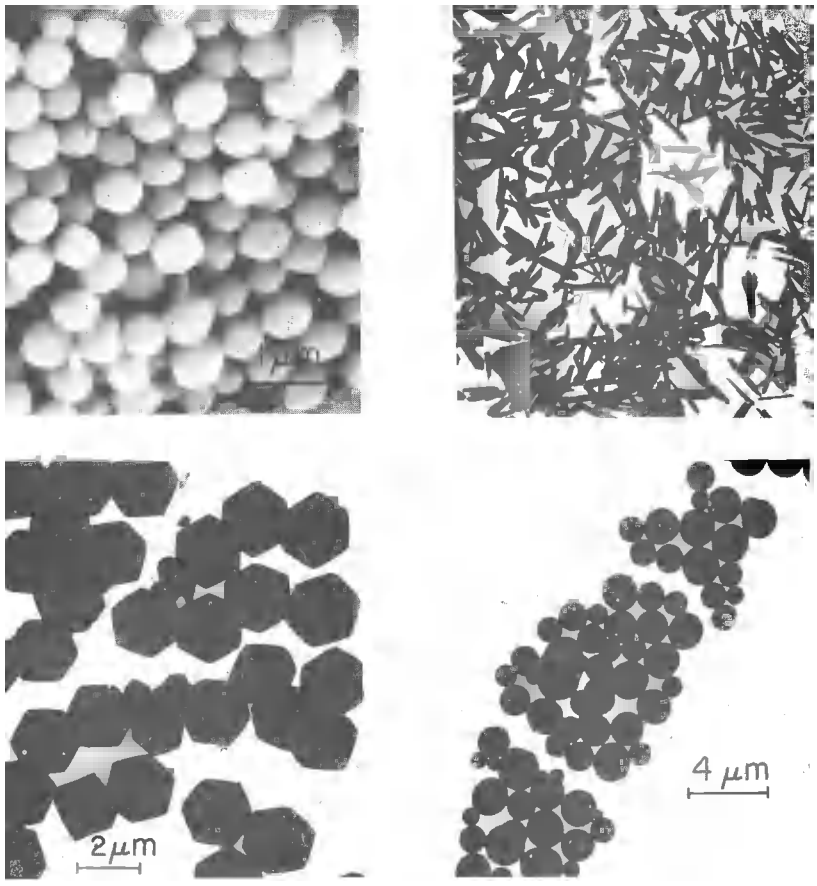

Fig. 1. Scanning and transmission electron micrographs of particles precipitated from various ferric salt solutions. (a) Hematite, α-Fe_2O_3 (solution 0.0315 *M* in $FeCl_3$ and 0.005 *M* in HCl aged for 2 weeks at 100°C). (b) β-FeOOH (solution 0.27 *M* in $FeCl_3$ and 0.01 *M* in HCl aged for 24 hr at 100°C). (c) Ferric basic sulfate $Fe_3(OH)_5(SO_4)_2 \cdot 2H_2O$ (solution 0.18 *M* in $Fe(NO_3)_3$ and 0.32 *M* in Na_2SO_4 aged for 2 hr at 98°C). (d) Ferric phosphate, $FePO_4$ (solution 0.0038 *M* in $FeCl_3$ and 0.24 *M* in H_3PO_4 at pH 1.86 aged for 20 min at 100°C).

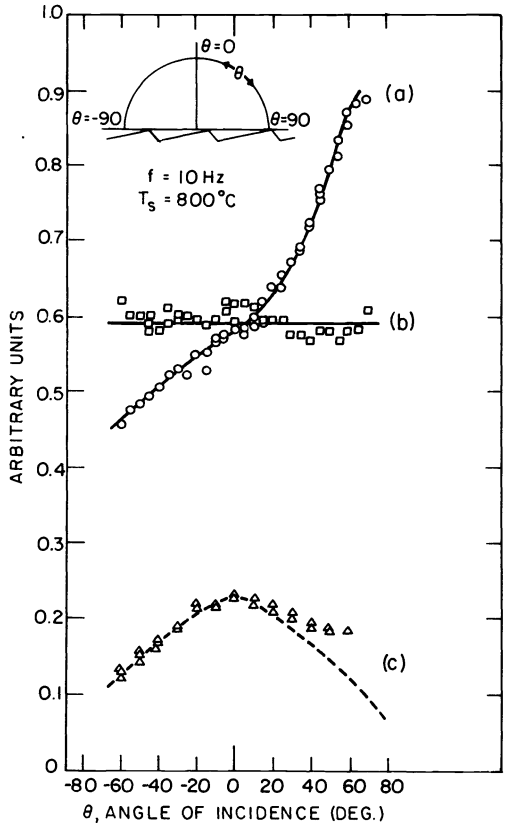

Fig. 5 Dependence of HD production on angle of incidence (θ), measured from the macroscopic surface normal. a) Pt(S)-[6(111)x(111)] surface, with azimuthal angle ϕ = 90°, i.e., the beam is incident perpendicular to the step edges as shown schematically in the insert. b) Pt(S)-[6(111)x(111)] surface with azimuthal angle ϕ = 0°, i.e., the projection of the incident beam on the surface is parallel to the step edges. c) Pt(111) surface.

(stable) surface structures using multiple scattering calculations in which the only adjustable parameters are the locations of the surface atoms. The most probable locations for C_2H_2 in the two states are shown in Fig. 6 In the metastable state the molecule is located almost

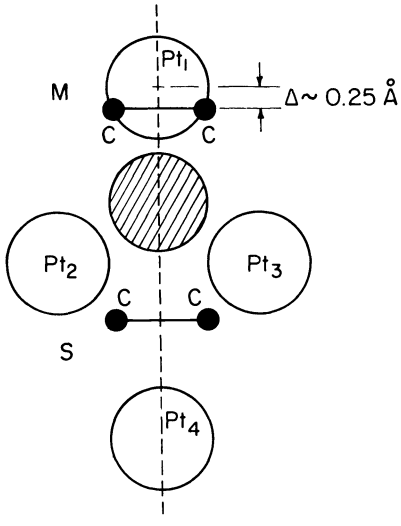

Fig. 6 Schematic of the Pt(111) surface unit cell and the bonding positions of C_2H_2 in the metastable (M) and stable (S) chemisorption states indicated by the LEED analysis (hydrogen atoms are not shown).

on top of the platinum surface atom in a covalent metal-carbon distance of 2.5 Å. The best fit is obtained if the molecule is shifted by a small amount (0.25 Å) in a direction where there is a platinum atom in the second layer under the triangular site (Ref. 13). Upon heating by only 75°C, the molecule shifts into a triangular site, bonding more strongly now to three platinum atoms that are at distances of (2.2 and 2.6 Å). The Pt-C distance perpendicular to the surface is also very much shortened (1.9 Å). The strong Pt-C bond is almost certainly caused by an elongation of the carbon-carbon bond which then becomes much weaker.

These results indicate that the molecule seeks new locations of stronger chemical bonding on the surface that become accessible upon surmounting a small potential energy barrier. This can occur by a small increase of the surface temperature. Once in a stronger binding site bond scission, hydrogen shift and other chemical rearrangements can all take place. It appears that even the (111) crystal face is inhomogeneous and provides different binding sites for the organic molecules.

The Roles of Carbonaceous Deposits and Promoters

During hydrocarbon reactions, the surface of the metal catalyst is covered with a carbonaceous deposit in amounts of half to one monolayer as indicated by Auger electron spectroscopy (Ref. 11). Thus the surface reaction takes place in the presence of, or with the participation of, such a deposit. Recent studies in our laboratory indicate that this carbon containing layer may actively participate in the surface reaction. We find evidence for the dissociation of carbon monoxide on iridium and rhodium (Ref. 15) crystal surfaces that are covered with a partial carbonaceous monolayer while there is only molecular adsorption of CO on the clean metal surface. This "active" carbon does not appear to hinder the chemical activity of the transition metal that manifests itself through controlling of both the rate and product distribution in hydrocarbon reactions. Graphitic carbon layers that can also be formed and identified by LEED do poison the activity of the metal surface. Further investigations my reveal that carbon in the active state may behave as an unsaturated carbene or carbyne species and exhibit the rich and complex chemistry expected from such chemical systems.

That portion of the carbon covered surface that is not chemically active may play an important role in accelerating the desorption of the reaction product. Since desorption is always endothermic, sites where the molecule can migrate and is weakly bound are the likely desorption sites and therefore important in keeping the rest of the surface available to the newly arriving reactants. Product inhibition due to blockage of the surface by the reaction product is an important concern in many hydrocarbon reactions which produce higher molecular weight products.

We have found evidence that the presence of oxygen and potassium that are frequently present during catalytic reactions are required to obtain certain reaction products whose formation was associated usually only with the transition metal catalyst. For the dehydrocyclization of n-heptane to yield benzene and toluene we find that the presence of oxygen at the platinum surface is necessary (Ref. 16). The stepped platinum crystal has to be heated in oxygen to increase the oxygen solubility in the near surface region. When the hydrocarbon is adsorbed on this oxygen pretreated surface an ordered surface structure forms (that contains carbon, oxygen and platinum as detected by Auger electron spectroscopy) which is active for dehydrocyclization. In the absence of oxygen pretreatment, the platinum surface does not catalyze this complex reaction although dehydrogenation or hydrogenolysis do take place. It appears that the oxide support provides the necessary oxygen activity for the metal surface during this reaction in supported metal catalysts.

During the hydrogenation of CO on iron, potassium is used as a "promoter." We find that in the absence of potassium, the iron surface is covered with an "active" carbon monolayer that is not stable but on top of it there is a build-up of a multilayer of carbon that poisons the catalyst. In the presence of potassium the catalyst surface with its active carbon layer is stabilized and the product distribution altered as well indicating the participation of potassium in the reaction (Ref. 17). Whether the additive (oxygen or potassium) maintains the proper oxidation state of the surface atom or participates in forming different reaction intermediates, their role is so important in determining the chemical activity that it is worth exploring in all its molecular detail. It is more appropriate then to consider the catalytic activity of transition metals as due to the metal-support-additive-carbon-hydrogen system as the support, the promoters and the reactants that control the bonding and concentration of carbon and hydrogen all influence the molecular dynamics (rates and product distributions) of the catalytic reactions.

Acknowledgment -- This work was performed under the auspices of the U. S. Energy Research and Development Administration.

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