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Building and characterization of catalysts on single crystal surfaces

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The components of complex catalyst systems include transition metals, oxides, alkali metal or halogen additives and strongly chemisorbed sulfur or carbonaceous species. Modern surface science techniques identified the chemical and structural roles of these ingredients when used in combination with catalytic reaction rate studies. Using metal single crystal substrates, catalyst components have been deposited from the vapor phase and the complex catalyst system could be built this way. The Pt–Re–S, Rh–TiO_2, and Mo–Co–S systems are reviewed and the requirements for the proper surface structure and composition to obtain high reaction rates and selectivities are discussed.

Keywords: Single crystal catalysts; building of catalysts

1. Introduction

There are considerable advantages in using the external surface of a solid for studies of surface reactions as compared to the internal surfaces of microporous solids utilized as catalysts in the technology. Many surface characterization techniques using electrons or ions (low energy electron diffraction (LEED), Auger electron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), scanning tunneling microscopy (STM), ion scattering spectroscopy (ISS), and secondary ion mass spectroscopy (SIMS)) can only be employed for external surface atoms to yield atomic level information on structure, bonding, and composition. The disadvantage of using a small area (≈ 1 cm^2) surface is the much lower detection sensitivity to monitor catalyzed surface reactions as compared to large surface area (≈ 400 m^2/g) microporous systems. In order to achieve a molecular level understanding of surface chemical processes, however, we need to apply all the surface characterization techniques that are available. For this reason we utilize small area (≈ 1 cm^2), mostly single crystal surfaces or polycrystalline foils and thin films as model catalysts. We also developed a catalytic reactor [1] that permits us to carry out reaction rate studies on these model catalysts at atmospheric or higher pressures and at elevated temperatures ($\leqslant 1000$ K) and also permits surface characterization before and after reactions by direct transfer of the samples into an ultra high vacuum cell that is equipped with all the available surface preparation and surface analytical techniques. By keeping the catalytic reactor volume small (≈ 200 cm^3) the detection sensitivity to monitor reaction rates and product distributions is high enough to detect products above turnover rates of 10^{-4} molecules/surface site/s.

However, catalysts that are used in the chemical technology are complex systems containing several additives. To explore the roles of these "promoters" they have to be deposited on the model catalyst surfaces with controlled concentrations and in proper locations. For example the iron (111) crystal face, a good catalyst for ammonia synthesis, is promoted by 10% of a monolayer of potassium that greatly increases its reaction rate by modifying the surface bonding of NH_3 and N_2 (bonding modifier) to the metal surface [2]. The presence of alumina in small concentrations helps to restructure the various crystal faces of iron to produce the (111) crystal face (structure modifier) which is much more active for the dissociative chemisorption of N_2 than other crystal faces [3]. This is a very important effect since ammonia synthesis is a strongly "structure sensitive" reaction.

In our studies these additives or promoters are deposited from the vapor phase onto the model catalyst surface by direct evaporation or by using a plasma gun [4].

Over the past several years we have studied the following catalyst systems:

(1) Hydrocarbon conversion over platinum catalyst systems [5] (*n*-heptane, *n*-hexane, methyl-cyclopentane, cyclohexane, ethylene, benzene):

Substrate	*Promoters*
platinum crystal faces	rhenium rhenium, sulfur potassium gold copper
platinum foil	alumina alumina, chlorine
rhenium crystal face	platinum platinum, sulfur
alumina film deposited on gold foil	platinum platinum, chlorine

(2) Ammonia synthesis over iron catalyst systems [6]:

Substrate	*Promoters*
iron crystal faces	alumina
	potassium
	alumina, potassium

(3) Hydrodesulfurization of thiophene over molybdenum catalyst systems [7]:

Substrate	*Promoters*
molybdenum crystal faces	sulfur
	cobalt
	cobalt, sulfur
	carbon
	cobalt, carbon

(4) CO, CO_2, acetone hydrogenation over rhodium catalyst systems [8]:

Substrate	*Promoters*
rhodium foil	titanium oxide
	vanadium oxide

In addition, surface science studies have been completed on the Cu(110)/ZnO [9], Pt(111)/ZrO_2 [10], Pt(111)/FeO [11] systems to lay the foundation for their future use in catalysis. Several reactions are also under study using small area single component model catalysts ($NH_3 + NO$, hydrogenation of propylnitrile, $CO + H_2$, $CO + O_2$, $H_2 + O_2$) in preparation for their investigations on more complex catalyst systems.

2. Experimental techniques to produce multicomponent systems of model catalysts

For studies of surface structure sensitive catalytic reactions (hydrogenolysis or ammonia synthesis for example), single crystal surfaces are utilized as substrates. These are cut and prepared to expose low Miller index close packed surfaces (face centered cubic (111) or (100) for example) or to expose high Miller index more open surface (Fe(210) or Rh(311)) or surfaces with periodic steps and kinks separated by terraces of close packed atoms. We then deposit "promoters" on these surfaces from the vapor phase in controlled concentrations by direct thermal evaporation or by using a plasma gun (metals on metals) [4].

The concentration and the growth mode of the deposit is usually monitored by Auger electron spectroscopy (AES) and by selective chemisorption (CO for example) that titrates the remaining substrate sites. Often oxidation in an oxygen ambient follows the vapor deposition accompanied by heat treatment to permit ordering of the deposited film, if desired (FeO or TiO_x on Pt or Rh for example). Chemical vapor deposition is used in some cases (Cl deposition on Pt by the decomposition of $CHCl_3$ for example). Deposition by argon ion sputtering has been found successful for the preparation of complex oxide thin films (Y-zeolite on gold) [12].

For studies of surface structure insensitive catalytic reactions (hydrogenation for example) a small area polycrystalline foil may be used as a substrate since the presence of several different crystal faces does not influence the reaction rates.

Usually, X-ray photoelectron spectroscopy (XPS) is employed to determine the oxidation state of the deposit. Ion scattering spectroscopy (ISS) determines the composition of the topmost layer only thereby revealing surface segregation effects in a multicomponent deposit (sodium segregation on top of iron oxide deposits, for example) [13]. Recently, scanning tunneling microscopy (STM) has proved to be a valuable tool to monitor the surface structure and spatial distribution of deposits on the atomic scale (sulfur on rhenium [14] or titanium oxide on rhodium, for example).

The substrate, covered with the multicomponent deposit so characterized by the combination of surface science techniques is then exposed to the reaction mixture at high pressures and at the desired temperatures and the catalytic reaction rates and product distributions are monitored as a function of time using a gas chromatograph or mass spectrometer. After the run, the sample is characterized again in uhv that is produced by the evacuation and opening of the reaction chamber.

3. Case histories of studies of model multicomponent catalyst systems

3.1. THE PLATINUM–RHENIUM–SULFUR MODEL CATALYSTS

New generations of platinum catalysts that are utilized to produce aromatic molecules (dehydrocyclization) and branched isomers (isomerization) from straight chain saturated hydrocarbons (*n*-hexane, *n*-heptane) are improved by the addition of both rhenium and sulfur. These "promoters" improve both the

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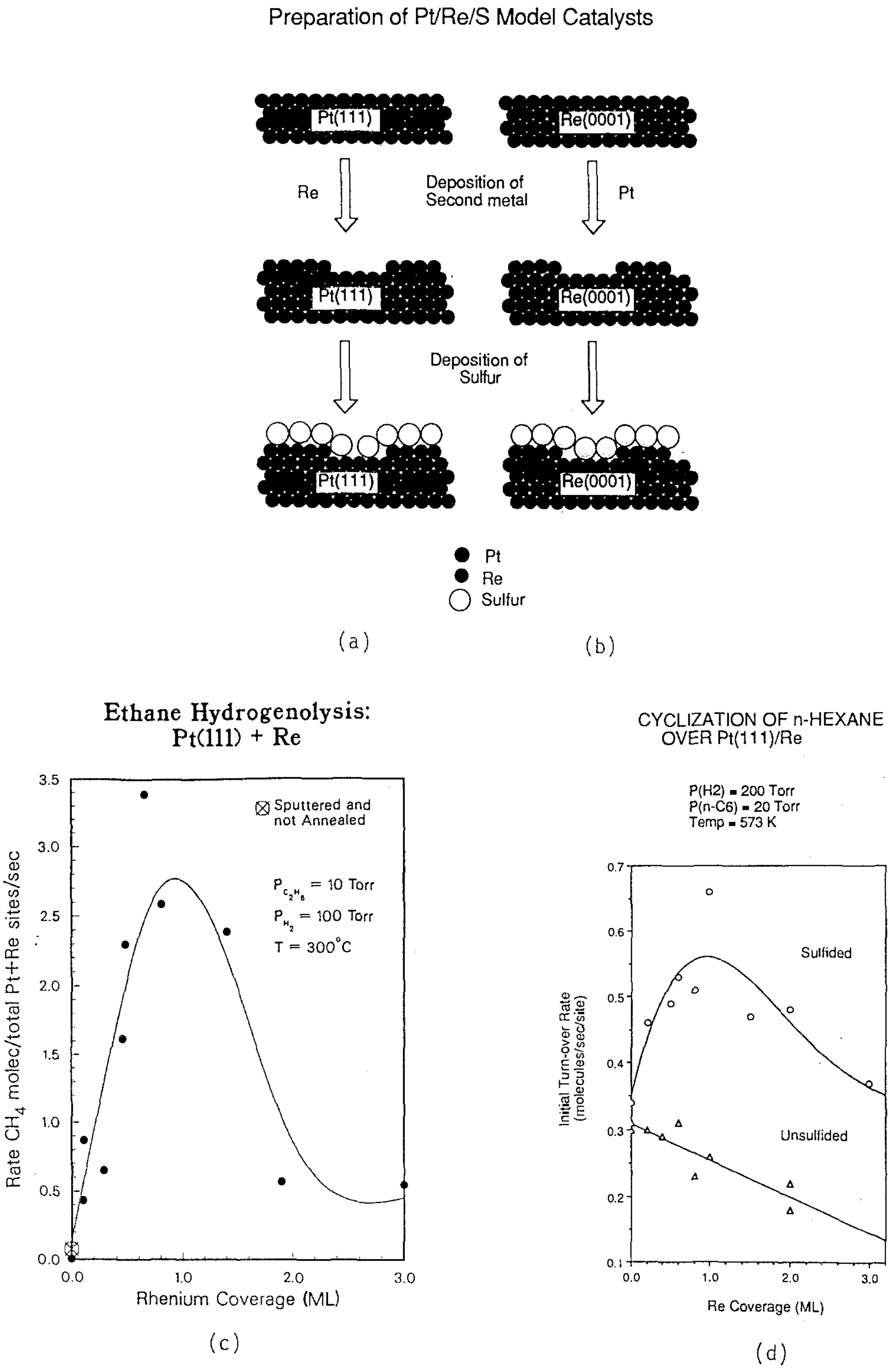
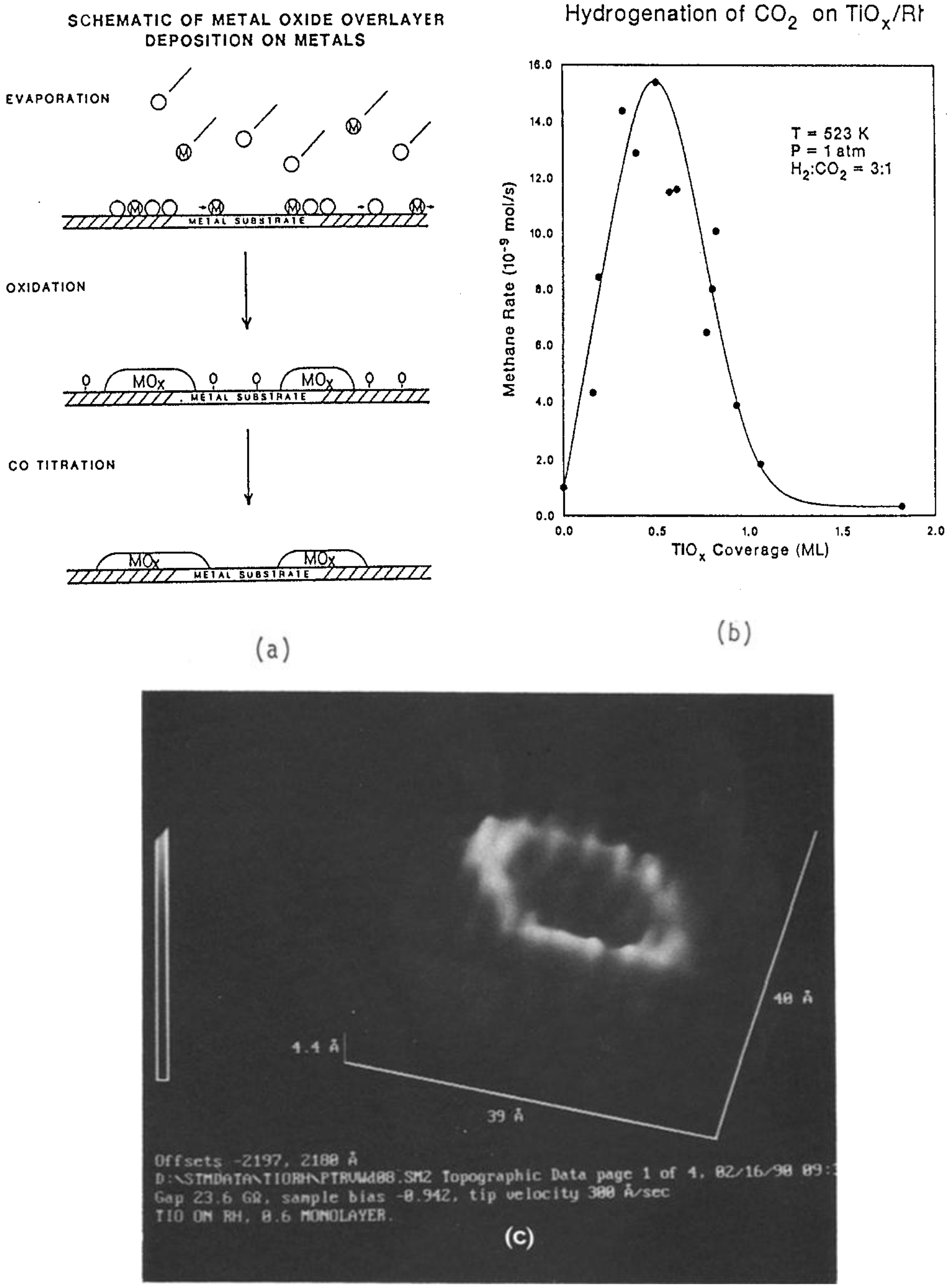
Fig. 1. Schematic diagrams showing (a) the sequential deposition of rhenium and sulfur onto the platinum (111) surface; (b) the deposition of platinum and sulfur onto the rhenium (0001) crystal face; (c) the hydrogenolysis of ethane as a function of rhenium coverage over Pt(111); (d) the cyclization rate of *n*-hexane as a function of rhenium coverage over the sulfided and unsulfided surfaces.


Preparation of Pt/Re/S Model Catalysts
Pt(111)
Re(0001)
Re
Deposition of Second metal
Pt
Pt(111)
Re(0001)
Deposition of Sulfur
Pt(111)
Re(0001)
● Pt
● Re
○ Sulfur
(a)
(b)
Ethane Hydrogenolysis: Pt(111) + Re
⊠ Sputtered and not Annealed
$P_{C_2H_6}$ = 10 Torr
P_{H_2} = 100 Torr
T = 300°C
Rate CH_4 molec/total Pt+Re sites/sec
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
1.0
2.0
3.0
Rhenium Coverage (ML)
(c)
CYCLIZATION OF n-HEXANE OVER Pt(111)/Re
P(H2) = 200 Torr
P(n-C6) = 20 Torr
Temp = 573 K
Sulfided
Unsulfided
Initial Turn-over Rate (molecules/sec/site)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.0
1.0
2.0
3.0
Re Coverage (ML)
(d)



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Offsets -2197, 2188 Å
D:\STMDATA\TIORH\PTRUWd88.SM2 Topographic Data page 1 of 4. 02/16/90 09:
Gap 23.6 GΩ, sample bias -0.942, tip velocity 300 Å/sec
TIO ON RH, 0.6 MONOLAYER.
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Fig. 2. (a) Schematic diagram showing the deposition of titanium oxide islands on rhodium; (b) the rate of CO_2 hydrogenation plotted as a function of the oxide coverage (note the large enhancement at 0.5 monolayer coverage); (c) STM image of a titanium oxide island that indicates large charge density at the island periphery; (d) schematic diagram to show reduced Ti^{3+} ions at the oxide periphery and different bonding of CO at these sites of high catalytic activity.

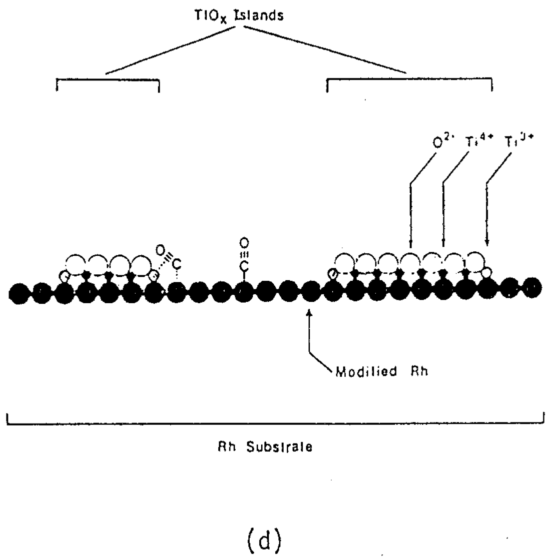

SCHEMATIC MODEL FOR TITANIA OVERLAYERS ON RHODIUM

Fig. 2. (continued).

reaction rate and the selectivity and permit the use of the catalyst at higher temperatures without experiencing deactivation commonly observed for platinum without these additives. We prepared a series of platinum single crystal catalysts by depositing rhenium from the vapor phase using a plasma gun and studied their reactivity as a function of rhenium surface coverage [15]. We also prepared a series of catalysts by vapor depositing platinum on rhenium single crystal surfaces [15]. Sulfur was then added by using H_2S gas that decomposes on the metal surfaces. The scheme of the catalyst preparation and representative results of reaction rate studies as a function of these pretreatment procedures are shown in figs. 1a and 1b. The activity of the catalyst for the hydrogenolysis of ethane to methane was greatly improved either by adding a monolayer of rhenium to platinum (fig. 1c) or by depositing a monolayer of platinum onto rhenium [16]. The results obtained are the same in both cases; the one monolayer covered bimetallic system is much more active than either one of the metals alone.

The addition of sulfur inhibits the hydrogenolysis activity of the bimetallic system and thus, other, more desirable reactions become dominant [17]. This is shown for the cyclization of *n*-hexane (fig. 1d). The rate of this reaction is greatly enhanced in the presence of one monolayer of sulfur.

3.2. THE RHODIUM–TITANIUM OXIDE MODEL CATALYSTS

The hydrogenation of molecules with C–O bonds over transition metal catalysts, like rhodium, is greatly enhanced by the presence of titanium oxide

[18] (or several other oxides like VO_x, LaO_x, ZnO_x on the surface. Fig. 2a shows schematically how the titanium oxide islands are deposited on rhodium by condensation and subsequent oxidation of the titanium metal. When the reaction rate, CO_2 hydrogenation in this case, is monitored as a function of the oxide coverage [19], a large increase in the rate occurs which exhibits a maximum at one-half monolayer oxide coverage (fig. 2b). This coverage produces the largest oxide island–metal interface area. Scanning tunneling microscope studies reveal a large charge density at the oxide island periphery which is associated with Ti^{3+} ions in the oxide indicating partial reduction at the edge sites ($Ti^{4+} + e^- \rightarrow Ti^{3+}$) (fig. 2c). These reduced oxide–rhodium periphery sites provide enhanced dissociation probability for the CO bonds as indicated schematically in fig. 2d perhaps by facilitating the periodic restructuring of the

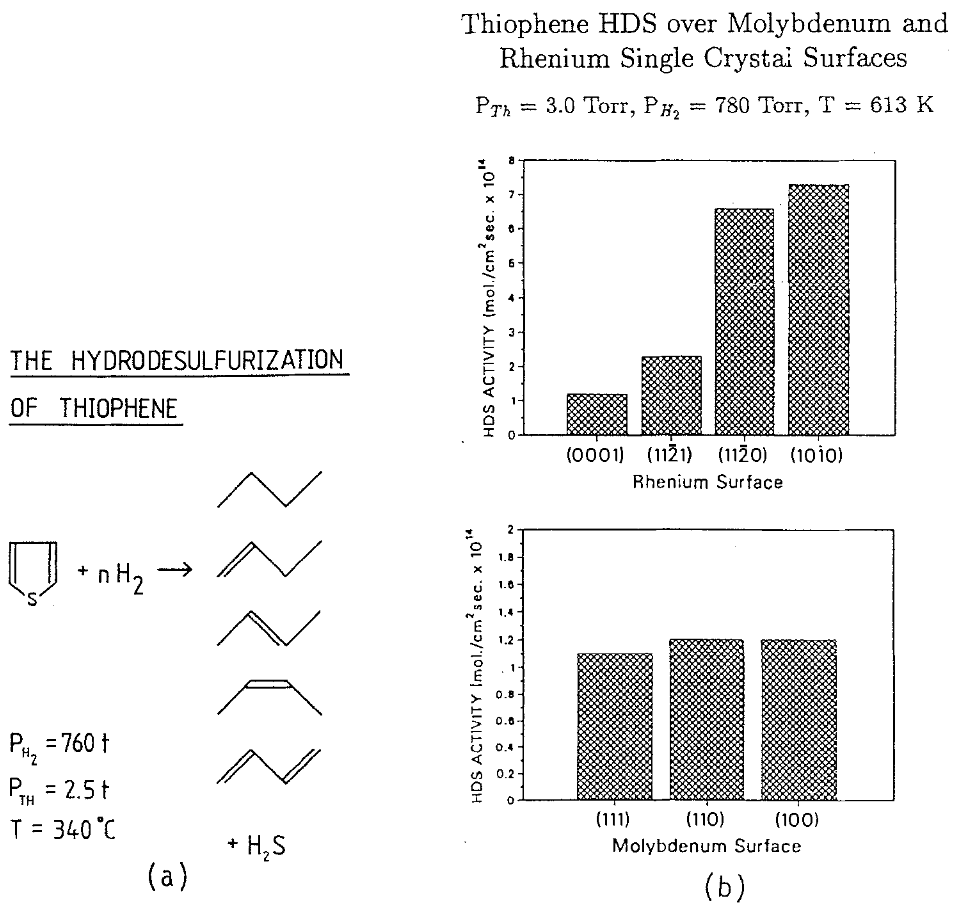
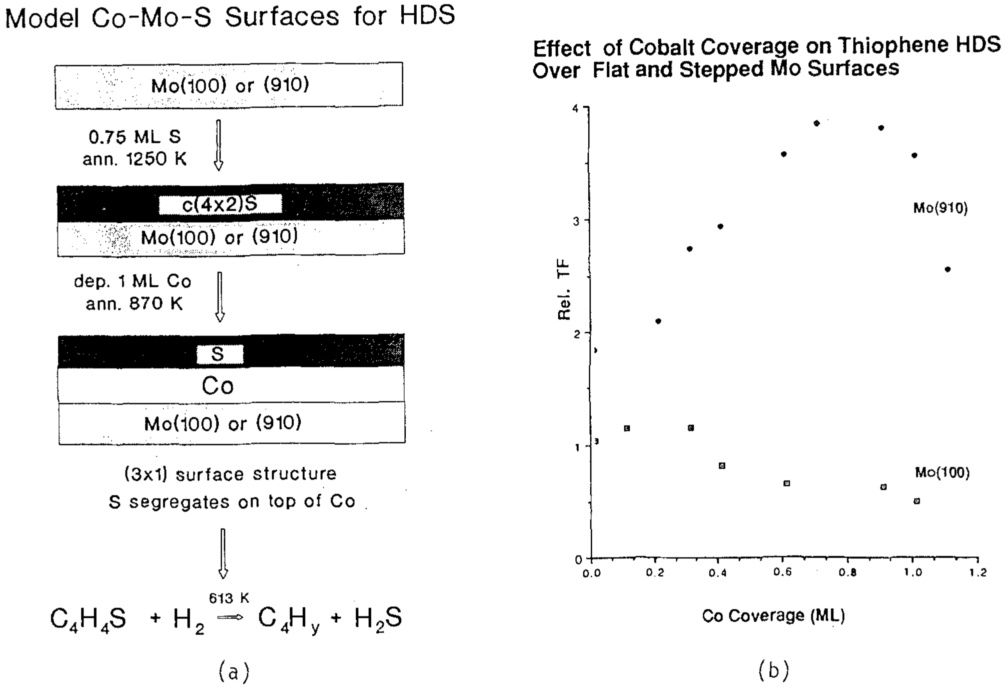


Fig. 3. The rates of hydrodesulfurization of thiophene on several different single crystal surfaces of (a) molybdenum; (b) rhenium. The reaction is surface structure insensitive over Mo while it is structure sensitive over Re.



(a) (b)

Fig. 4. (a) Schematic diagram displaying the sequential deposition of cobalt and sulfur on the flat (100) and stepped (910) molybdenum crystal faces; (b) the reaction rate increases or decreases as a function of Co coverage over the Mo(910) and Mo(100) surfaces, respectively.

metal at the oxide interface. We hope to be able to image the oxide–metal interface sites *during* the catalytic reaction in the near future.

3.3. THE MOLYBDENUM-COBALT-SULFUR MODEL CATALYSTS

The sulfides of molybdenum are used to remove sulfur from organic sulfur compounds by the hydrodesulfurization reaction (HDS). Model studies of thiophene HDS were carried out on molybdenum and rhenium single crystal surfaces [7] and the results are shown in fig. 3. The reaction rate is insensitive to variations of surface structure on molybdenum while it is surface structure sensitive on rhenium [7].

Cobalt is used as a promoter on molybdenum catalysts and therefore we explored the effects of adding cobalt as well as sulfur on the reactivity of molybdenum. Sulfur is always present on the metal surface (along with carbon) during the reaction. When cobalt and sulfur were deposited, sulfur was found to migrate to the top of the cobalt regardless of the sequence of deposition [20]. When Co and S were condensed on a Mo(100) surface, the rate of thiophene HDS actually decreased as shown in fig. 4b. However, when a (910) stepped surface of molybdenum was used in the reaction studies, the reaction rate increased when Co and S were added (fig. 4b). Sulfur had the effect of doubling the height of the step [20] from one to two atoms in height on the average and cobalt deposited primarily along the step edges. Thus, in the presence of the cobalt promoter, the HDS reaction becomes structure sensitive over molybdenum.

4. The roles of various ingredients of complex catalyst systems. Structure modifiers and bonding modifiers

By investigating the roles of each component of a complex catalyst system, many of the molecular ingredients of heterogeneous catalysis could be identified. The *structure of the surface* often determines the rate of the reaction (structure sensitive reactions). Stepped surfaces of platinum were more active for H_2/D_2 exchange and for most hydrocarbon conversion reactions than flat low Miller index close packed surfaces [21]. The more open (111) and (211) crystal faces of Fe are orders of magnitude more active for NH_3 synthesis than the close packed Fe(110) crystal face which showed no detectable reaction rate [22].

The proper surface structure of a metal catalyst can also control the selectivity of the reaction path. Kink sites on platinum readily break C–C bonds while step sites are only active for C–H and H–H bond scission [23].

The catalytically active surface is covered with a *strongly adsorbed chemisorbed overlayer*. During hydrocarbon conversion reactions, the platinum or other transition metal surfaces are covered with a carbonaceous overlayer of average composition of CH [24]. During ammonia synthesis, the iron crystal faces are covered by chemisorbed N. The Mo surface is covered with a mixture of S and C during hydrodesulfurization [7]. Nevertheless, the reactions proceed at a steady state rate in the presence of these overlayers. ^{14}C and ^{35}S labeling studies indicate that these overlayers are stagnant; they exchange with the gas phase reactants at rates that are orders of magnitude slower than the turnover rates of the catalytic reactions. Thus, they do not seem to impede the reaction turnover while they do not participate as reaction intermediates.

Many oxide–metal interfaces exhibit uniquely high reactivity. Depending on the oxide support, the high surface area transition metal catalyst can exhibit orders of magnitude variations of the reaction rates for the same reaction [25]. Recent studies indicate that TiO_2 is capable of increasing the activity of many transition metals for this reaction. There are several oxide–metal interfaces that exhibit similar large increases of activity as compared to the metal alone.

Many bimetallic catalyst systems exhibit uniquely high reactivity. When gold was added to a Pd catalyst used for the H_2/O_2 reaction to produce water, the reaction rate increased 50-fold at a certain gold concentration [26]. Gold itself is a poor catalyst for this reaction. Enhancement of hydrocarbon conversion rates of platinum by the addition of gold were also reported from our laboratory using model single crystal systems [27]. There are many bimetallic catalyst systems Pt/Re, Os/Cu, that show much enhanced reactivity by the addition of a second inactive metal as compared to the turnover rate of the active metal component.

Coadsorbed promoters that are bonding modifiers and structure modifiers. Increasing the coverage of a given chemisorbed atom or molecule usually leads to a decrease in its heat of adsorption [28]. This is due to repulsive interactions among the adsorbates. When two different species are coadsorbed, one an electron donor and the other an electron acceptor to the transition metal substrate, the molecules order to form structures in which the molecules alternate [29]. Such a packing indicates an attractive interaction between the coadsorbates. Donor acceptor interaction appears attractive on transition metal surfaces, while the coadsorption of two donors or two acceptors leads to surface phase separation and island formation indicating repulsive interactions.

Alkali metal atoms are electron donors to transition metal surfaces. When coadsorbed with reactants that are electron acceptors, they interact to increase the heat of adsorption of the reactant. This is the case when K is used as a promoter in CO hydrogenation. K increases the heat of adsorption of CO thereby increasing its dissociation probability [30]. CO dissociation is one of the elementary steps for this catalytic reaction.

When K is used as a promoter during NH_3 synthesis, it reduces the heat of adsorption of ammonia, another electron donor on the Fe surface. Thus, this donor–donor repulsive interaction reduces the NH_3 reaction product surface concentration thereby reducing product poisoning in this catalytic reaction [6].

Chlorine is an electron acceptor and its promoter action may be associated with this property.

In all these descriptions of coadsorption, we neglect the possibility of the restructuring effects due to alkali metals or other bonding modifiers. There is evidence that such restructuring does occur on Fe_2O_3 in the presence of sodium and possibly for other catalyst surfaces as well [31]. Of course, Al_2O_3 on Fe exerts its promoter influence solely by restructuring the transition metal. Structure modifier and bonding modifier promoters may not be readily separated into two distinct classes in most circumstances. There are adsorbate promoters that block sites, thereby deactivating it for a given undesirable or desirable reaction. In the first case, such a blocking adsorbate is a promoter; in the second it is a poison. Sulfur is often used as an inhibitor of hydrogenolysis but it can also readily poison transition metal surfaces both by blocking active sites and by restructuring the surface.

5. Future directions of research using model catalyst systems

One of the important new directions of model catalyst studies is to probe surface reactions that are carried out in the liquid phase. For this purpose we built a reaction cell that is connected to an uhv surface characterization chamber but can also be filled with a liquid when it is isolated from uhv. We are studying the hydrogenation of nitriles to amines and of olefins on nickel and rhodium surfaces using the configuration that is shown in fig. 5. It is hoped that one can explore liquid phase low temperature catalytic reactions this way and can move in directions to probe bio-catalytic reactions to form optically active, stereospecific products. We aim to develop correlations between liquid phase heterogeneous catalysis and bio-catalysis.

In order to take advantage of the capabilities of the scanning tunneling microscope (STM) for catalytic reaction studies, we developed an atmospheric pressure and high temperature ($\leqslant 500$ K) operating STM that can monitor the catalyst surface structure [32] with atomic spatial resolution (fig. 6). We aim to monitor changes of surface structure during the surface reactions and image molecules chemisorbed on the active surface under the reaction conditions, in situ. Surface structure analysis and detection of adsorbed molecular structure during catalytic reactions have not been possible until now. We hope that STM will provide this opportunity. We are also exploring a new method for studies of the surface science of solid acid catalysts. Many of these are high surface area microporous zeolites. There is evidence that ion sputtering deposition can produce thin films of chemically active alumina silicates. By producing films of $\leqslant 200$ Å thickness, many surface characterization techniques could provide us with the structure–catalytic function relationships that eluded us in the field of acid catalysis until now [12].

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