Article

The Preparation of Mixed Valent Oxide Thin Films by Alloy Oxidation: Planar Model Hopcalite Catalysts

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Recent results on the preparation of planar model mixed oxide catalysts by alloy oxidation are presented. The oxidation processes were monitored by X-ray photoelectron spectroscopy (XPS) and the structure and chemistry of the overlayers were determined by the spectra. The controlling factors are delineated and illustrated using copper-manganese alloys to prepare Hopcalite overlayers that appear to be very similar to the actual catalyst.

Introduction

The preparation of planar model catalysts is a fascinating process in the quest for fundamental information on the structure-performance relationships in heterogeneous catalysis. The "planar" means a thin flat oxide layer or free-standing oxide of uniform thickness less than 1 μm. This is an excellent approach to investigate those surface phenomena that directly or indirectly affect the catalyst. Increased complexity of heterogeneous catalysts such as multicomponent mixed oxide and multimetallic catalysts is a current trend. The challenge to make planar models of these catalysts is testing the state of our knowledge about the surface chemistry of the complex systems. Advantages of using the planar model catalysts are severalfold: planar morphologies are ideal for modern plane focusing surface techniques, planar samples allow low incident and low take-off angle measurements, in situ preparation is possible in ultraclean UHV systems, and chemical and physical structures can be better controlled. Because of their numerous advantages, planar models of heterogeneous catalysts are being vigorously studied.[1]

There are three major types of heterogeneous catalysts: amorphous solids, polycrystalline solids, and supported catalysts. These are illustrated in Figure 1 along with the analogous planar models which are obtainable by alloy oxidation. It is to be noted that all the types of surface structures found on heterogeneous catalysts are prepared on oxidized metals and alloys.[2] Even amorphous oxide structures are found on metal surfaces. The requirement for amorphous overlayer growth is that the reaction rate of the process creating the overlayer must be fast with respect to long range order development. Polycrystalline overlayers form on polycrystalline substrates if the rate of long range order development is comparable to the rate of overlayer growth. Single crytalline overlayers can also be grown over single crystalline substrates. Finally, the overlayers can be used as support materials. The supported phase can be either added from an external source or developed from the support material itself as it has been illustrated for the Ni supported on titania system.[3] All those required are available for producting models of the major heterogeneous catalyst types. It is left to the researcher to design the model system and produce it based on established fundamental understanding.

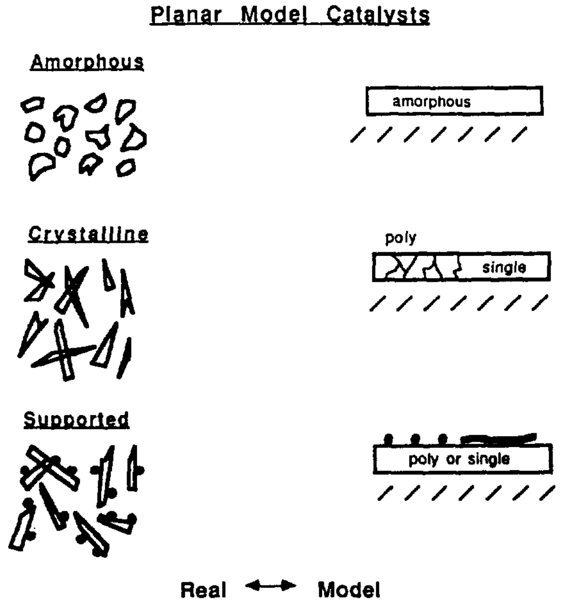

Figure 1. Illustration of the three major types of real heterogeneous catalysts and their planar model counterparts prepared by alloy oxidation. The crystalline and supported catalysts can be modelled on polycrystalline or single crystal surfaces.

Mixed valent oxide catalysts are well known for complete and selective oxidation of carbon containing compounds.[3,4] Hopcalite, $CuMn_2O_4$, is a well known oxidation catalyst which is used for the removal of air pollutants like carbon monoxide and nitrous oxide from exhaust gas.[5-9] It is also important in respiratory protection in military, mining and space applications.[10] Planar models are needed because of the complex nature of these catalysts, requiring to examine highly pure systems with optimally performing surface techniques.

In this paper we report the preparation of a planar model of Hopcalite by the alloy oxidation

Experimental

Materials. The alloys were produced by an arc melting device from Cu shot (99.9999%, Johnson Matthey) and Mn flake (99.995%, Johnson Matthey). The arc melting device with a water-cooled copper crucible was operated under 10 Torr of argon pressure. The bulk compositions of the alloys were determined on a Jeol 35 CF SEM using Tracor Northern System energy dispersive spectroscopy (EDS) with copper and manganese standards. The alloys were found to be homogeneous after several remelting and turning cycles. The alloy samples examined were Cu-Mn (10%), Cu-Mn (33 %), Cu-Mn (50%), and Cu-Mn (67%). Commercial Hopcalite catalyst (99.7%, Auergesellschaft) was used in order to compare surface oxides prepared to a working catalyst.

Specimen Preparation and Treatment. Specimens of the alloys were prepared by abrading with sandpaper (600 grit alumina) and polished successively with 30, 15, 6, and 1 μm diamond paste. specimens were positioned on a glass plate in a center of a cylindrical quartz tube within a furnace. They were treated at 25, 100, 200, 300, 400, 500℃ for 1 h in 1 atm of oxygen flowing through the quatz tube with the rate of 30 m*l*/min. Research-grade oxygen (Ashland Chemical) and sputter-grade argon (99.9999%, Scott Environment Technology) were used and manipulated in a separate preparation chamber attached to X-ray photoelectron spectrometer (XPS).

Surface Characterization. XPS spectra were taken with a Kratos-XSAM 800 spectrometer equipped with a DS 300 data processing system. MgKα radiation was used as the primary X-ray excitation source. The spectrometer was operated in the fixed analyzer transmission (FAT) mode with the pass energy of 38 eV. The spectral areas determined by computer integration were corrected for instrumental parameters, photoionization cross-sections, and difference in electron mean-free-path. Binding energy shifts of photoelectrons, kinetic energy shifts of Auger elecrons, and changes in peak shapes were carefully followed to obtain detailed information on oxygen interactions with the surfaces during diverse oxidation treatments.

Catalytic Activity Tests. Catalytic activities for CO oxidation were measured on 100 mg of ground Cu-Mn (33%) alloy (surface area of 0.01 m^2/g) and commercial Hopcalite (surface area of 100 m^2/g). Their catalytic activities were tested using a continous flow reactor, monitored by gas chromatography. After activation, 12 : 1 O_2-to-CO mixture was reacted over both catalyst systems.

Results and Discussion

The preparation of a planar model Hopcalite catalyst by alloy oxidation requires that conditions be chosen that give a reasonably known oxidation rate of each component. In this particular case it requires reasonably high pressures and temperatures to allow Cu oxidation to be comparable to manganese oxidation with its high negative free energy of oxide formation. Based on these considerations the Cu-Mn alloy was oxidized at atmospheric pressure in oxygen and temperatures in excess of 400℃.

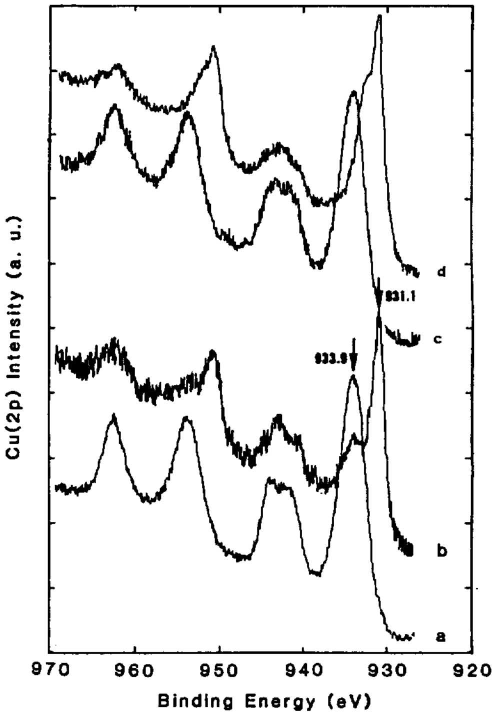

Figure 2. Representative spectra of the Cu(2p) region of: (a) an oxide layer of Cu-Mn (33%) alloy oxidized under 1 atm oxygen for 1 h at 300℃, (b) the same as in (a) at 400℃, (c) a commercial Hopcalite activated in 1 atm oxygen for 2 h at 220℃, (d) a commercial Hopcalite deactivated in 1 atm nitrogen for 10 h at 550℃.

Representative spectra of the Cu(2p) region of planar model catalyst and commercial Hopcalite are shown in Figure 2. The XPS spectra of Hopcalite are shown in both the amorphous and crystalline states (Figure 2c and 2d). These spectra when compared to the XPS spectra of the surface oxide (Figure 2a and 2b) clearly show that a planar Hopcalite catalyst was prepared by alloy oxidation, as will be discussed latter.

The turnover number also must be established to investigate the quality of catalytic sites on the amophous and crystalline systems. First the preliminary activity tests were run to demonstrate the catalytic nature of the planar model catalyst. More detailed studies are now under way to answer catalytic questions relevant to Hopcalite chemistry.

CO conversion is plotted against reaction time for model and commercial catalysts in Figure 3. Note that Figure 3a scale is expanded by 10 times. The commercial catalyst was reacted at room temperature by the model catalyst at 160 and 260℃ due to extremely low surface area (0.001 m^2 *vs.* 10 m^2). On the basis of the rough assumption that the activity doubles with every 10℃ rise in reaction temperature and taking surface areas of the catalysts into account, the activity of the model catalyst is approximately the same as the commercial catalyst. The model catalyst run at 160℃ was dead after 55 min, but the commercial catalyst run at room temperature was dead after 150 min (Figure 3a and 3c). In these cases CO conversion declined after 25 min. Interestingly even the model catalyst was not deactivated at 260℃ (Figure

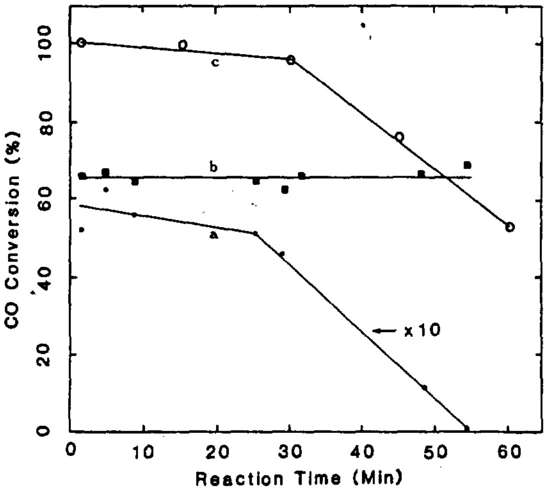

Figure 3. Plot of CO conversion against reaction time for: (a) a model catalyst prepared by Cu-Mn (33%) alloy oxidation run at 160℃, (b) the same as in (a) at 260℃, (c) a commercial catalyst run at room temperature.

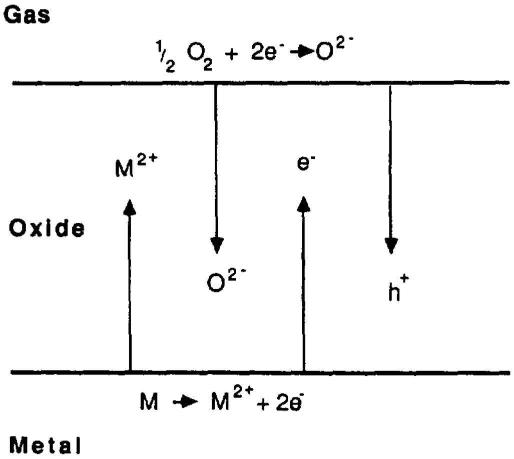

Figure 4. Illustration of transport of ions and electrons in gradients of oxygen activity and electric potential across a growing oxide thin film. A positively charged lattice vacancy is represented by h^+.

3b).

What controls alloy oxidation? The growth of model catalyst surfaces on an alloy substrate would be a straightforward process if the fundamentals of alloy oxidation were well understood. This is unfortunately not the case. Much research remains to be done on the adsorption of oxygen, its dissociation and ionization, place exchange, nucleation, lateral growth, and thickening. Reesearch directed toward the production of model catalysts on alloy surfaces must consider the above processes in order to design the model system by controlled oxidation. Since the alloy oxidation seems to lead to catalyst models, it is appropriate to ask what parameters must be considered in the preparation of the catalyst models.

Thermodynamics provides the conditions of temperature, pressure, and chemical composition under which an oxide can form on a metal. The chemical reaction involved in the oxidation of a metal is

$$xM + 1/2y\, O_2 \rightleftarrows M_xO_y \tag{1}$$

where the driving force for the reaction is the Gibbs free energy change $-\Delta G_f$ associated with the formation of the oxide. The formation of the oxide consequently depends on the oxygen pressure being greater than the dissociation pressure of the oxide in equilibrium with the metal. Here the dissociation pressure p is given by

$$p = \exp(\Delta G_f/RT) \tag{2}$$

where R and T are the gas constant and the absolute temperature, respectively. In case of the alloy oxidation where mixed oxides are not formed, the oxides appeared at a given set of conditions are predictable from the above. This must be utilized in the design of model oxide surfaces.

Since transport of reactive species through the oxide is necessary for film development, kinetic factors become very important for determining the oxide structure. The theory of oxide growth is best considered for two regimes-thin films and thick films. The theories of Cabrera and Mott (and their extensions) and of Wagner (and their extensions) are good limiting cases for the two regimes, respectively.[11,12] Since the work described here involves thin films the first models will be emphasized. Transport of ions and electrons in gradients of oxygen activity and electric potential across a growing oxide thin film is illustrated in Figure 4. According to the Cabrera and Mott theory, the oxidation is driven by the field created by electron transfer across the film where slow ion transport under the field causes the film to thicken. Grimley's extension[13] of the Cabrera and Mott theory is quite useful for examining the effects of various parameters on the voltage across the film. Here the assumption is made that the adsorbed layer of charged oxygen species is in equilibrium with the gas:

$$1/2\, O_2(\text{gas}) + 2e^-(\text{metal}) \rightleftarrows O^{2-} \tag{3}$$

With the assumption the approximate relationship between the potential across the growing oxide, V, and the Gibbs free energy change of oxide formation at the surface, ΔG_f, the temperature, T, the oxygen activity, $a(O_2)$, and the film thickness, x, is

$$V = \frac{-\Delta G_f}{2e} + \frac{kT}{2e} \ln \frac{4e^2 N_s a(O_2)^{1/2} x}{kT\varepsilon\varepsilon_o} \tag{4}$$

where e is the electric charge; k, the Boltzmann constant; N_s, the concentration of the surface oxygen; ε, the electron permittivity; ε_o, the electron permittivity in a vacuum. The design of planar model catalysts requires an operational understanding of the manipulation of parameters that control chemical and physical structures. Eq. (4) shows the temperature and pressure dependences of the potential.

Finally since an alloy is being considered, composition is also a viable parameter both in the thermodynamic and the kinetic processes involved in oxide growth. It is apparent that the oxidation rate depends on the copper surface concentration, decreasing with increasing copper contents. The reaction properties, even of Cu-Mn surfaces with high copper composition show more similarities of manganese than to copper. Manganese surface enrichment during the oxidation was observed, depending on the oxidation temperature and bulk compositon.

Preparation of Planar Model Catalysts. We can find out optimum experimental conditions based on the above discussion. The mixed valent oxide was obtained only after understanding the effects of the oxidation temperature, oxygen activity, oxidation time, and Cu-Mn alloy bulk composition on the structure and chemistry of the oxide overlayer. Details of the oxidation behavior of these Cu-Mn alloys can be found in the literature.[14] The mixed valent oxide could be prepared only under a very specific set of conditions. For the Cu-Mn (33%) and Cu-Mn (50%) alloys, chemically mixed oxide layers were identified after oxidation at 400 and 500℃ under atmospheric oxygen pressure. For other conditions only separated, layered mixtures of oxides, or almost solely manganese oxides or copper oxides were obtained. Ultrapure $CuMn_2O_4$ thin films were identified on the oxidized Cu-Mn alloy surfaces by comparison of XPS spectra with those of a comercial catalyst and the presence of a low-binding energy Cu(2p) line (931.1 eV) in the crystalline $CuMn_2O_4$ state. This unusual negative binding energy shift (-1.7 eV) with respect to metallic copper (932.8 eV) should be attributed to a specific Madelung potential in the spinel structure of $CuMn_2O_4$. The binding energies and peak shape in the Cu(2p) region of Cu-Mn (33%) alloy oxidized at 400℃ (Figure 3b) resemble those of the crystalized commercial Hopcalite (Figure 3d). Moreover, the planar model catalysts prepared in this study is very similar to bulk $CuMn_2O_4$ prepared by Broemme and Brabers.[15]

Catalytic Questions. Hopcalite is highly active for CO oxidation in an amorphous state even at room temperature but it loses activity above about 500℃ where crystallization to $CuMn_2O_4$ spinels occurs.[16,17] Thus the deactivation might be due to the phase transition. However, this is controversial point since crystalline $CuMn_2O_4$ has also been reported by Schwab and Kanungo.[18] The charge exchange reaction has subsequently been discussed several times as the basis for the activity of Hopcalite.[17-21] Recently Cocke *et al.*[22,23] reported direct experimental evidence for the redox couple by XPS. However they observed irreversible potassium segregation induced by the phase change, incurring catalyst deactivation. Accordingly, the segregation of potassium prevented the correlation of the charge exchange with the catalytic activity. This will require states of highly pure systems free from contaminants, dopants and promoters.[24] A planar model catalyst would be ideal for this study. Our results offer a possible explanation of the observations. These exhibit neither impurities and dopants on the model catalyst surface nor deactivation induced by the phase change. Therfore potassium segregation is mainly responsible for the deactivation of the Hopcalite catalyst. The charge transfer resonance of Hopcalite is now open for further investigation, utilizing the planar model catalyst.

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