SOLID STATE, SURFACE AND
CATALYTIC PROPERTIES OF OXIDES

MASTER

Progress Report

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Abstract

We have been conducting fundamental studies on oxide catalysts. In this period, emphasis has been on the investigation of the properties of anion and cation vacancies on an oxide surface, on the characterization of an adsorbed oxygen species on an oxide, and on the determination of surface cation densities in solid oxide solutions.

We have successfully prepared an atomically well ordered surface of ZnO on which a high density of sites resembling those of the anion vacancy is present. Such a surface adsorbs oxygen and methanol more strongly, yet carbon dioxide more weakly than a stoichiometric nonpolar surface.

From the kinetics of adsorption and desorption, we observed evidence of an atomic adsorption of oxygen on iron oxide. The adsorption of this species is activated, and its desorption follows a bimolecular rate law. We are now attempting to obtain the activation energies of adsorption and desorption, and the saturation coverage of the species. Its reaction with hydrocarbons will be studied later.

The surface cation densities of Fe and Cr on a series of solid solutions of Fe_2O_3 - Cr_2O_3 were determined. It was found that Fe was enriched on the surface at low Fe contents, but depleted from the surface at high Fe contents. The surface Cr on air treated samples is Cr(VI). Calculation on the surface cation densities of oxide solid solutions of cubic structure was performed using a pairwise potential, and a statistical model for the surface layer. For dilute bulk solutions, the larger cation is found to be enriched on the surface.

Introduction

The commercial catalysts are mostly either metallic or oxide catalysts. It has generally been known that these two classes of catalysts are specific for different reactions. In particular, hydrogenation and hydrogenolysis reactions are best catalyzed by metals, and oxidation or dehydration reaction by oxides. Isomerization reactions can be catalyzed by both. If it is of interest to attempt to replace one class of catalyst by another, it is important to have understandings on the fundamental interactions during catalysis. The objective of this research is to seek such fundamental understandings for oxide catalysts, with emphasis at present on the materials aspect.

The simplest oxide is made of two components, a metal ion and an oxygen ion. The stoichiometry of the two ions is determined by charge neutrality, and the spatial periodicity is determined by covalent bonding or ionic bonding interactions between atoms or ions. On the surface of such an oxide, the surface morphology and the pretreatment may result in the generation of anion or cation vacancies of different environments. It has long been postulated that such vacancies are of importance in catalytic reactions. In one aspect of this research, ZnO single crystal surfaces of various densities of sites that resemble either anion or cation vacancies are prepared. The chemical properties of these surfaces are being investigated.

The active sites on a binary oxide surface may be formed from the lattice atoms and ions, they may also be formed from adsorbed molecules. In particular, adsorbed oxygen can be of different nature and different effect on catalysis. In the second aspect of this research, the effect of adsorbed oxygen on the oxidation activity of iron oxide is being investigated.

Solid solutions of binary oxides represent the next level of complexity. Analogous to studies of metallic alloys, the first question that one asks

is the relationship between the surface and bulk compositions. We have measured the surface cation ratios of solid solutions of iron oxide and chromium oxide, and have performed calculations to elucidate the relationship between the degree of surface segregation and the various energy contributions in the pairwise potential.

Anion or Cation Vacancies on ZnO Surfaces

Because of the absence of centrosymmetry, the ZnO crystal structure does not possess a mirror plane perpendicular to the c-axis. Making use of this fact, we argued that when a stepped surface is made from a non-polar $(10\bar{1}0)$ plane with steps going towards the positive c-axis, the regions at the step can be thought of as an anion vacancy. On the other hand, a stepped surface also made from $(10\bar{1}0)$ plane but with steps pointing towards the negative c-axis, the region at the step can be thought of as a cation vacancy. The above argument can be more easily seen with a diagram which can be found either in the proposal submitted last year, or in the preprint of an accepted publication on ZnO. The reader is referred to those sources for details. Thus by preparing surfaces of various step densities and orientations, anion or cation vacancy sites (but not both) of various densities can be generated and studied.

We have successfully prepared stepped surfaces in the positive c direction. The adsorption and desorption of small molecules have been studied on these surfaces which have a high densities of sites of the properties of anion vacancies. When compared to the nonpolar (flat) $(10\bar{1}0)$ surface, the stepped surfaces adsorb oxygen and methanol more strongly. The stronger adsorption is being attributed to the anion vacancy sites. On the other hand, the stepped surface adsorbs carbon dioxide less strongly. These observations are consistent with what one would expect from an oxygen vacancy. The de-

composition products of methanol are also different on a stepped and a flat surface. Our preliminary results suggest that carbon monoxide and hydrogen were the main product from the stepped surface, yet carbon dioxide was the main product from a flat surface. More work will be conducted in this area.

Catalytic Properties of Adsorbed Oxygen

Similar to metallic surfaces, oxide surfaces also adsorb oxygen atomically or molecularly. In general, molecular adsorption occurs at lower temperature, and atomic adsorption, which is usually activated, occurs at higher temperature. It has been observed by temperature programmed desorption, oxygen adsorbs on α -iron oxide in several different states. These states differ both in the desorption and in the adsorption temperature. However, assignment to the molecularity of the states has not been conclusively made.

In an attempt to investigate the effect of the various states of adsorbed oxygen on the oxidation reaction on iron oxide, we reinvestigated the adsorption process. By varying the conditions of adsorption and desorption, such as the temperature and time, we followed the kinetics of the process. Thus far, it appears that in the temperature range between 150 to 300°C, there are two kinds of oxygen adsorption. Below about 180-200°C, the first kind dominates. Above 200°C the second kind dominates. The desorption of the second kind appears to follow a second order kinetics which suggests that it is an atomic species. From the data, the apparent activation energy, and the density of this adsorbed oxygen at full coverage can be estimated. These quantities can be extracted from the data obtained thus far, but we are gathering more data to further improve the quality of the numbers. This work would represent the first evidence of atomic adsorption on iron oxide, and the first report on the kinetic parameters involved in the adsorption and desorption of the species.

After this oxygen species has been characterized by our method, its effect on the selective oxidation reaction of butene to butadiene will be studied. The technique to be used will be similar to those used previously, namely the temperature programmed desorption/reaction.

Surface Composition of Oxide Solid Solutions

The surface compositions of metallic alloys are in general different from the bulk compositions. By extrapolation, the surface compositions of solid solutions of oxides may be different from the bulk compositions. A study that is most analogous to that involving metallic alloys will be to determine the surface ratio of cations in a binary solution of oxides to that in the bulk. We chose to measure the Fe/Cr ratio in $\text{Fe}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ solutions of various Fe/Cr ratios. A scanning Auger microprobe was used. It was found that to obtain quantitative density measurement, charging of the samples must be eliminated. We succeeded by trying as much as possible making sample of very small particle sizes, dispersing it well on a conducting support, and using a low electron beam current. Other physical effects that may affect the measurements were minimized using the oxygen peak as an internal standard.

It was found that on air treated samples, the surface density of Fe is higher than the bulk density for $X \leq 0.6$ in $\text{Fe}_x\text{Cr}_{2-x}\text{O}_3$. For $X \geq 0.6$, the surface density of Fe is lower. This observation agrees with the observation made on stainless steel which has high Fe content. Furthermore, by chemical titration it was found that the surface Cr exists as Cr(VI). We postulate that there may be formation of surface compounds of some stoichiometry of Fe(III) with Cr(VI). The relatively strong tendency to form this surface compound results in the change in the surface enrichment of Fe to depletion on changing the bulk composition.

Simultaneously we have been performing a calculation using a monolayer model to determine the possible surface segregation of one of the components in a two component solid solutions. Each component is a cubic oxide. The model used is an improved model over the one we used for the alkali halide mixtures in that a relaxation model, which has been termed successful as the results compare well with experimental data, was used to calculate the bulk substitutional energy changes. A statistical model is used to calculate the surface substitutional energy changes. This statistical model has been used successfully to calculate the heat of solution in bulk compounds. We modified it and apply it to the surface. Because of the uncertainty in the interatomic distances, we only performed the calculation on dilute bulk solid solutions. The results seem to suggest that the bulk strain energy is the dominant factor determining surface segregation. Thus the larger cation is the one preferred to be on the surface.

Publications resulted from this work:

1. "Study of Iron Oxide Surface by Adsorption and Temperature Programmed Desorption," M. C. Kung, W. H. Cheng and H. H. Kung, J. Phys. Chem. 83, 1737 (1979).
2. "Surface Composition of a Solid Solution of Monovalent Ionic Compounds of NaCl Structure," W. H. Cheng and H. H. Kung, Surface Sci., 1979, 88 153.
3. "Selectivity in the Oxidative Dehydrogenation of Butene on Zinc Iron Oxide Catalyst," H. H. Kung, B. Kundalkar, M.C. Kung and W.H. Cheng, J. Phys. Chem 84 (1980) 382.
4. "Methanol Synthesis" H. H. Kung, Catal. Rev., 22 (1980), 235.
5. "Chemical Properties of Anion Vacancies on Zinc Oxide," W. H. Cheng and H. H. Kung, accepted by Surface Sci.
6. "The Surface Cation Densities of Iron Oxide-Chromium Oxide Solid Solutions," M. C. Kung and H. H. Kung, accepted by Surface Science.