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Copper Oxide Supported on Alumina

III. X-Ray K-Absorption Edge Studies of the Cu^{2+} Species

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X-Ray K-absorption edge spectroscopy studies were performed on samples containing cupric ion supported on γ-alumina. It was found that, at lower concentrations of cupric ion, a surface phase is present that resembles the structure of copper aluminate. Parameters that affect the formation of this aluminate phase include the surface area of the alumina and the concentration of cupric ions. The aluminate phase is undetectable by X-ray diffraction. It is proposed that the aluminate surface phase accounts for the sharp rise in magnetic susceptibility that has been previously noted in the susceptibility isotherm of the system copper oxide-on-alumina. When samples containing the aluminate surface phase are reduced and reoxidized in the absence of moisture, the aluminate is converted to cupric oxide. Three distinguishable phases have now been identified in composites containing cupric ions dispersed on alumina: isolated cupric ions, a copper aluminate surface phase, and cupric oxide. The chemical bonds in the first two phases are apparently the same, and different from those in the third one.

INTRODUCTION

In supported metal oxide catalysts, the physical and chemical state of the promoter oxide can affect one or more catalytic properties such as activity, or stability. Variables that may influence the state of the promoter oxide include concentration of the oxide, the chemical or physical state of the support, or the temperature of calcination of the catalytic composite. Information on the composition of the promoter oxide is often useful in correlating structure with catalytic properties. There is usually an inverse relationship between the average degree of dispersion and the concentration of a supported metal oxide. When the concentration is relatively high ($>$ 5–10 wt%, depending on the type and surface area of the support), the metal oxide is present in sufficiently large crystallites that detection and identification of the principle phase present is possible by means of X-ray diffraction analysis. However, at low concentrations, metal oxides dispersed on a high area support such as γ-alumina are not detectable by X-ray diffraction, and other less explicit analytical techniques must be employed for structural analysis.

For example, magnetic susceptibility (*1*) or chemical reduction (*2*) studies have been used to elucidate the nature of highly dispersed supported metal oxides. However, the results of such investigations may indicate valence state of the metal (susceptibility data) or suggest the presence of some interaction between promoter oxide and support oxide (reduction studies), but usually fail to provide a specific identification of the dispersed phase. One technique that has sometimes been successful in identifying the state of highly dispersed metal oxides on supports is that of X-ray K-absorption edge spectroscopy [e.g., Keeling (*3*) in studies of supported cobalt oxide]. This approach was employed in the present investigation of copper oxide deposited on γ-alumina.

Previously, the system copper oxide-on-alumina was studied by Selwood and coworkers (*1*) using magnetic susceptibility measurements; by Pierron *et al.* (*4*) using differential thermal analysis (DTA) and X-ray diffraction analysis (XRD), and by Berger and Roth (*5*) using electron paramagnetic resonance (EPR) studies. Most of the results of the previous work were interpreted in terms of a copper oxide phase and variations in the degree of dispersion of the copper-containing phase. The present investigation, using X-ray K-absorption edge spectroscopy, has generated new information about the chemical nature of the more highly dispersed species. In particular, evidence was obtained that, at lower concentrations or deposited cupric ion, a chemical interaction occurs between the cupric ion and the alumina support.

EXPERIMENTAL METHODS

The X-ray K-absorption edge measurements were performed on a General Electric XRD-5 spectrometer with a chromium CA7-X-ray diffraction tube and a LiF crystal as monochromator. The samples were introduced at the position of the filter in regular diffraction measurements. They were ground to powders of particle size of less than 200 mesh (74 μ). Three slow scans at 0.072°/hr gave reproducibility within ± 0.002° which corresponds to ± 0.45 eV. The absorption edge position was determined by the intersection of tangents to the curve at angles higher than the edge and to the slope of the edge itself. This gave a shift towards higher angles of 0.054° with respect to the half height point for the pure copper powder; however, our interest in relative positions only does not dictate any particular technique for determination of the edge position. For the study of treated samples, flat Pyrex cells of approximately 3×0.7 cm were made from 0.9 cm o.d. tubing. Special care was taken to assure thin uniform parallel walls separated by a constant gap of 0.05 or 0.10 cm. Prior to either reduction by hydrogen or reoxidation by oxygen, each of which was conducted at 400 mm Hg and 500°C for about 15 hr, the samples were evacuated at 500°C down to 10^{-5} mm Hg. The K-absorption edge of these samples was measured at room temperature while keeping them under the hydrogen or oxygen atmospheres, respectively.

Two types of alumina were studied: one was a Harshaw 0104 γ-alumina with surface area of 72 m^2/g, subsequently to be called the low surface area alumina, and the other one Kaiser Chemical XA-331 γ-alumina with surface area of 301 m^2/g, which will be called the high surface area alumina. The impregnation and calcination procedures have been described elsewhere (*4*, *5*). The only changes in this work were that the calcination temperature was varied from 300 to 900°C for some of the samples. Reference materials used were commercial pure copper and copper oxide powders, and a synthesized copper aluminate (*6*). The composition of the aluminate was confirmed by XRD.

The EPR measurements were performed with an X-band Varian 4502 spectrometer. The magnetic susceptibility was measured with a Faraday apparatus, as described in the literature (*1*), equipped with a Varian V-4055 magnet. The thermal gravimetric analysis (TGA) instrument employed was a commercial Thermo-grav by American Instrument Company.

RESULTS AND DISCUSSION

The results listed in Table 1 give the K-absorption edges of the various supported compositions and of the pure reference materials $CuAl_2O_4$, CuO, and Cu. The energy reference in this table is the K-absorption edge of pure copper metal and all the other results represent shifts to higher energy relative to the copper reference. Despite the similarity in valence state, the edge for $CuAl_2O_4$ lies somewhat above that of CuO. A similar result was observed by Keeling (*3*) for CoO and $CoAl_2O_4$.

It may be seen that cupric ion on alumina forms either copper oxide or copper aluminate, or a mixture of the two. In essence, Runs 11 and 14 confirm our previous find-

TABLE 1

X-Ray K-Absorption Edge of Copper on Alumina

Run no.	(Wt %) Copper	Surface area of support (m^2/g)	Calcination temp. (°C)	State	Color	ΔE (eV; ±0.45)
1	3.35	301	500	Ox.	Green	7.94
2	3.35	301	500	Red.	Black	1.72
3	3.35	301	500	Reox.	Gray-black	4.07
4	3.35	301	500	H_2O and reox.	Green	7.94
5	8.80	301	500	Ox.	Green	7.73
6	8.80	301	500	Red.	Black	1.29
7	8.80	301	500	Reox.	Gray-black	4.07
8	10.50	301	300	Ox.	Green	7.94
9	10.50	301	400	Ox.	Green	7.94
10	10.50	301	Not calcined	Ox. nitrate	Light blue	3.00
11	10.30	72	500	Ox.	Black	4.50
12	10.30	72	500	Red.	Black	0.00
13	10.30	72	500	Reox.	Black	3.86
14	10.30	72	900	Ox.	Brown	7.73
15	$CuAl_2O_4$				Brown	7.94
16	CuO				Black	3.86
17	Cu				Brown	0.00

ings with the low surface area alumina using XRD analysis (*4*) and also are consistent with the phase diagram of the CuO: γ-Al_2O_3 system reported by Misra and Chaklader (*7*). However, the results with high surface area alumina are somewhat unexpected as they indicate that for all three concentrations of copper and even at the low calcination temperature of 300°C, we observe the formation predominantly of a surface phase of copper aluminate. By contrast the low surface area sample of Run 11 has its copper-containing phase present mainly as copper oxide. 15 wt% Cu impregnated on the high surface area alumina gave a black composite, presumably containing CuO. We did not run a K-absorption edge spectrum on this sample because of its nonuniform appearance. We infer that at some suitably lower copper concentration ($\ll$10 wt%), one could form predominantly copper aluminate even on the low surface area alumina. Our previous TGA results (*4*) indicated that a temperature of 700°C or higher is necessary to promote the reaction between CuO and γ-alumina to form $CuAl_2O_4$ in a composite known to contain a CuO phase initially. Apparently, the direct formation of a $CuAl_2O_4$ surface phase can occur even at 300°C when there is an appropriate combination of copper concentration and alumina surface area. The copper aluminate phase in the high surface area samples could not be detected by XRD.

The TGA measurements showed that the supported copper nitrate decomposes at about the same temperature (~265°C) as pure bulk copper nitrate. Run 10 indicates that prior to calcination there is little or no aluminate or oxide.

Supplementary EPR measurements showed that the previously reported (*5*) spectrum of cupric ion on the high surface area alumina was obtained also on the low surface area alumina (sample used in Run 11). These spectra were identical to the spectrum measured for a sample consisting of 0.1

mol % of cupric ion in spinel and were very different from those obtained for solid solutions of cupric ions in MgO and CaO (*8*). From these results we infer that those cupric ions supported on alumina that give rise to the observed EPR signals form bonds which have the character of those in an aluminate rather than those in an oxide. This in essence agrees with the interpretation given earlier (*5*) as to the chemical environment of isolated and weakly-interacting cupric ions that generate the EPR signals. However, the present X-ray spectroscopy results indicate that in addition to the magnetically-isolated cupric ions, there can also exist thin domains of copper aluminate (conceived of as a surface phase). This surface phase of aluminate cannot be detected by XRD. Only in the case of Run 14 was a copper aluminate phase detectable by XRD. One may also compare the colors for the samples of Runs 1, 5, 8, and 9 with Run 14. In the latter case, it is presumed that the cupric ions penetrated the γ-alumina lattice to an appreciable extent forming a bulk aluminate phase and causing a sintering of the surface from 78 m^2/g to 32 m^2/g. The formation of an aluminate is plausible since γ-alumina consists of a skeleton having close-packed oxygens with tetrahedral site vacancies that can be occupied by divalent ions to form a spinel structure. The existence of a chemical interaction between CuO and alumina was proposed by Voge and Atkins (*9*), but no spectroscopic data were provided to substantiate the nature of the product.

From studies of the system copper oxide-on-alumina by magnetic susceptibility measurements, Selwood and Dallas (*1*) concluded that such composites do not contain cupric ions at infinite magnetic dilution and that the dependence of susceptibility on concentration arises from a varying paramagnetic neighborhood around each paramagnetic ion. The implication is that this variation in neighborhood consists of a regular change in dispersion of the domains of copper oxide. The EPR results noted here and previously (*5*) indicate that at low concentrations there does, in fact, exist a significant number of cupric ions in a state approximating infinite magnetic dilution. The present X-ray spectroscopy results indicate, moreover, that at low and intermediate concentrations, cupric ions can exist in a crystallographic environment similar to that of copper aluminate rather than copper oxide. Thus, over the concentration range studied, were found three types of species: magnetically dilute cupric ions, a copper aluminate surface phase, and finally at high enough concentrations, crystallites of cupric oxide. In some of the samples, there must undoubtedly be present mixtures of these phases. Two factors that seem to control the proportions of these phases in a composite prepared by impregnation are the concentration of cupric ions and the surface area of the alumina support.

In their magnetic susceptibility studies, Jacobsen and Selwood (*1*) observed a sudden rise in susceptibility value of oxidized samples at around 10–11 wt% copper on a γ-alumina of surface area of 200 m^2/g. This was attributed by these authors to be a continuous diminution of the paramagnetic environment surrounding each paramagnetic supported ion. Presumably, this means a diminution in the size of the oxide domains since there was no suggestion of the formation of a new phase with different chemical bonding. Our present results indicate, however, this rise in susceptibility is due to the formation of a copper aluminate surface phase rather than a dispersed phase of copper oxide. Undoubtedly, this aluminate surface phase will form readily at 500°C only at lower cupric ion concentrations, but it is important to recognize that a new chemical phase exists in terms of interpreting the catalytic properties of such composites. To test this interpretation, we measured the magnetic susceptibility of bulk copper aluminate and obtained a value of $26 \pm 2 \times 10^{-6}$ emu cgs/g of copper which is slightly higher than the limiting value given by Jacobson and Selwood (*1*). An inspection of the data points reported by these authors suggests that extrapolation to a somewhat higher limiting value might have been justified, bringing our value for the bulk aluminate and their limiting value even closer together.

The catalytic oxidation activity data of Mooi and Selwood (*10*) for copper oxide supported on alumina were interpreted entirely in terms of the relative state of dispersion of the catalytic material on the support surface. Our results suggest that this interpretation requires some elaboration to take into account the three distinct phases of cupric ion that are present. In going from intermediate to high cupric ion concentrations, two phenomena occur. There is a change in the nature of the chemical phases present as well as a change in domain size of each phase. Clearly, activity data would be required on the basis of specific surface for each phase to decide whether one phase or another (aluminate or oxide) has a higher intrinsic activity, but no such data are available. It is entirely possible that on a specific surface basis, one might find that the activity of the oxide phase is actually higher than that of the aluminate phase, and that only at concentrations above 10–11 wt% is one dealing strictly with results that are attributable to dispersion effects alone. The decrease in activity that is observed, as the lowest concentrations are approached, is likely due to the transition between surface phase aluminate and magnetically isolated ions. This is consistent with the proposal of Mooi and Selwood (*10*) that a minimum domain size may be required for catalytic activity, although the nature of the phase involved appears to be that of an aluminate.

Reduced samples (Runs 2, 6, and 12) gave results suggesting that the support either prevents complete reduction of cupric ions in the aluminate phase or that one obtains a highly dispersed state (possibly a monolayer) of copper zerovalent atoms bonded to the support which has slightly different energy than copper atoms in three dimensional bulk metallic copper. We prefer the latter choice since the work of Voge and Atkins (*9*) indicates that isolated cupric ions would be the most difficult to reduce, yet the EPR signals attributed to such ions could be eliminated by reductive treatment similar to that used in the present work. Also the results of Voge and Atkins showed that the reduction of cupric ions on alumina could be completed at 200°C.[1]

Reoxidation of several reduced samples was performed without allowing water vapor or moisture to enter the sample cell. In each case (Runs 3, 7, and 13), the reoxidized copper phase consisted mainly of cupric oxide, even though in two of these cases the original copper-containing phase prior to reduction was aluminate. The XRD failed to detect any copper-containing phase in the reoxidized samples of Runs 3 and 7, suggesting that the oxide phase indicated by the K-absorption edge data must be presented in very small crystallites (< 50 Å) below the detection limit of XRD. The present results on reoxidized samples need to be reconciled with the EPR studies (*5*) and magnetic suspectibility studies (*1*) on reoxidized samples.

In the EPR work, substantial (90%) restoration of the original signal occurred upon reoxidation of a reduced sample. However, the EPR signals are attributed to magnetically isolated cupric ions which constituted only a fraction of the total cupric ions present. Hence, even the sample of lowest copper concentration contains both isolated ions and a more continuous aluminate phase. Thus, the EPR and present data on reoxidized samples could be rationalized by assuming that the X-ray spectroscopy results detect only "two-dimensional" aluminate, and the EPR results detect only "isolated" cupric ions, and that the former is transformed to an oxide during reduction and reoxidation, while the latter is not. In the magnetic susceptibility work, restoration of the original signals occurred upon reoxidation of reduced samples. This is difficult to reconcile with our X-ray spectroscopy results and interpretation suggesting a transformation of the aluminate phase to an oxide, with the latter having a lower

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[1] *Footnote added in proof.* The recent publication by L. P. Verma and B. K. Agrawal [*J. Phys.* C1, 1658 (1968)] reports the edges of CuO and Cu_2O as −3.87 and +0.67 eV, respectively. The first one is in perfect agreement with our value, and the latter supports our interpretation of not obtaining predominantly cuprous phase in reduced samples.

magnetic susceptibility. However, one experiment was performed (Run 4) in which a sample was first immersed in water and then reoxidized in the usual way. Instead of cupric oxide, the oxide now obtained was aluminate. Thus, the presence of moisture, or possibly even water vapor, can apparently catalyze the formation of aluminate. Insufficient experimental details are available to compare rigorously the conditions used for reduction and reoxidation in the susceptibility studies and those used in the present work. However, differences in the conditions used might account for the apparent differences in properties of reoxidized samples, especially in view of the observed effect of the presence of moisture.

The results reported herein may be fairly general as applies to the formation of a distinct spinel phase in certain supported metal oxide catalysts. Holm and Clark (*2*) describe the difficulties of reducing nickel oxide-on-alumina and this may be due to formation of an aluminate. Spinel formation is likely not limited to alumina-supported composites, e.g., Ralek *et al.* (*11*) suggest that ZnO and Cr_2O_3 can interact to form a spinel. The present work with X-ray K-absorption edge aluminates can be identified with other metal oxides, e.g., those of Ni, Co, Fe, etc. This will provide further examination of the concept that supported metal oxides can form different chemical compounds, as opposed to the more simplified picture of variations in particle size of a single oxide phase.

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