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XANES/EXAFS STUDY OF THE COPPER ACTIVE SITE IN METHANOL SYNTHESIS CATALYSTL.S. KAU, E.I. SOLOMON⁽¹⁾ and K.O. HODGSON⁽¹⁾*Department of Chemistry, Stanford University, Stanford, CA 94305, U.S.A.*Summary

We have used X-ray absorption spectroscopy to determine the electronic and geometric structure of the copper active site in methanol synthesis catalysts. Compared to the edge and FT of the EXAFS data of CuO, the data suggest that most of the Cu(II) in the calcined form does not have the same ligation as in the CuO lattice and more importantly that some of the Cu is dissolved in the ZnO lattice. For the reduced sample, the edge shifts to lower energy after reduction, indicating the presence of either Cu(I) or Cu(0). The EXAFS data analyses of reduced catalysts show the presence of copper clusters. Reaction with H₂S is shown to decompose the Cu clusters in the reduced catalyst and the level of Cu cluster decomposition increases with further reaction at higher temperature and longer time period.

Introduction

A number of important industrial processes involve metal oxide-based heterogeneous catalysts. For example, hydrogenation of CO on Cu/ZnO goes quite selectively to methanol ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$). The Cu/ZnO system is a low temperature, low pressure catalyst in which the Cu is thought to act as an intracrystalline promoter which significantly lowers the activation barrier for the reaction. Recent studies have led to the proposal of Cu(I) active sites on the ZnO surface [1].

The X-ray absorption spectroscopy technique has been used by three other research groups to investigate the copper active site in the Cu/ZnO catalyst. With the 30% (wt.) Cu ternary catalyst Cu-ZnO/Al₂O₃, Vlaic et. al. [2] concluded that there are highly dispersed copper clusters and ZnO after reduction. Clausen et. al. [3] collected the EXAFS data of 5% (wt.) binary and ternary calcined samples at liquid nitrogen temperature and concluded that there is no evidence of copper doped in the ZnO lattice. Udagawa et. al. [4] collected the XAS data of 30% binary sample at different temperatures (from room temperature to 673K) and concluded that the local structure around the copper atoms in the reduced catalysts changes reversibly with heating/cooling cycles in H₂ stream.

As part of our study of the coordination chemistry of metal oxide catalysts [5], we have also been using X-ray Absorption Spectroscopy to determine the electronic and geometric structure of the copper active site in methanol synthesis catalysts [6]. In particular, we have been studying, as a function of Cu weight percent, the calcined catalyst and the effect of

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different reducing conditions. We have also begun to look at the interaction of the catalyst with poisons.

Experimental

The 0.5%, 1%, 5% and 10% (wt. Cu) calcined binary Cu/ZnO catalysts samples were prepared and characterized using published procedures [3] by Haldor Topsoe A/S, Denmark. The reduction of the CuO/ZnO catalysts was conducted at 493K under a steady flow of reducing gas with CO₂/CO component. Another 10% calcined sample was reduced at 493K under a steady flow of only reducing gas to study the effect of the CO₂/CO component in reduction. A 1% reduced sample was treated at room temperature for 15 minutes (CAS1 sample) and at 473K for 2 hours (CAS2 sample) under a steady flow of H₂S/N₂ gas to obtain the poisoned catalysts. All X-ray absorption data were collected at Stanford Synchrotron Radiation Laboratory on beam line VII-3, dedicated beam at 3.0 GeV, 50mA with Si[220] monochromator. Analysis of the data was performed using previously reported methods [7].

Results and Discussions

X-ray absorption edge spectra at the Cu K edge for four calcined Cu/ZnO samples (10, 5, 1 and 0.5%) have been collected. These samples were run under atmospheric conditions. The energy of the absorption edges, and the presence of the 1s→3d transition (weak feature at 8978 eV) both indicate that these samples contain predominantly Cu(II). Although the edge structure is similar for the different concentrations, it is more resolved for the samples with a lower copper concentration. When compared to the CuO edge spectrum (figure 1A), it appears that the edge of the catalyst does not have the 8986 eV shoulder as in that of CuO but there is a trend in the edge for the higher percentage to approach the edge spectrum of CuO. Thus, the absence of this 8986 eV feature in the edge of the catalyst indicates that the site symmetry of the Cu in the catalyst is not the same as in CuO.

We have also collected EXAFS data for the 1, 5 and 10% calcined samples at room temperature. The Fourier transforms (FTs) of the EXAFS data for the calcined catalysts are shown in figure 1B. We find that the FTs of the EXAFS of the calcined samples compared to that of CuO are quite different, in particular in the absence of strong outer shells seen in the CuO FT. There are two possibilities for explaining this observation. One, there may be inhomogeneity in the copper site environment such that no outer shells could be observed. Alternatively, the long range environment (to ~6 Å) of Cu in the calcined samples differs from that of CuO. Further, the second backscattering peak at ~2.8 Å (which is above the noise level of the data) in the FT spectrum is shifted to shorter distance as the Cu concentration of catalyst increases. It is relevant to observe that there is a strong Zn-Zn backscattering feature

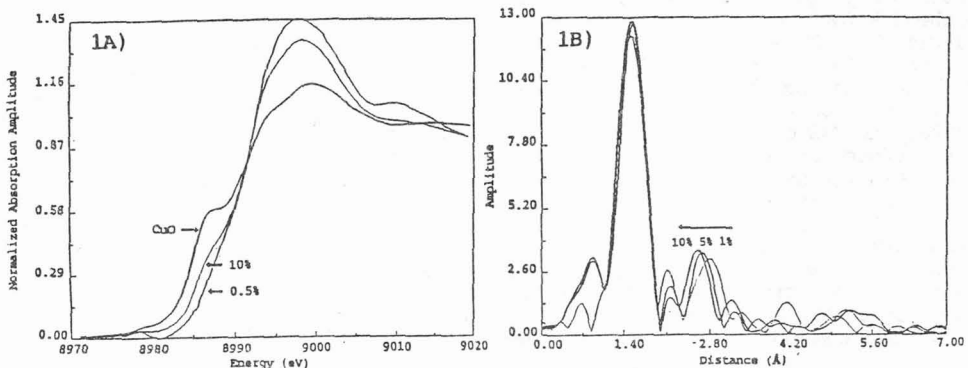


Fig. 1A) Cu K-edge absorption spectra of calcined 0.5% and 10% Cu/ZnO compared with that of CuO. 1B) FTs of the Cu EXAFS for calcined 1%, 5% and 10% Cu/ZnO.

in the spectrum of ZnO at about the same distance. If Cu was doped into the ZnO lattice, it should have the same structural environment as Zn does in ZnO. Thus, this 2.8 Å feature could be evidence of Cu doped into the ZnO lattice. We are using curve fitting analysis to further quantify the nature of the 2.8 Å feature and these results will be reported in detail in a future publication [6].

Edge and EXAFS data for the reduced samples have been collected. The absorption edge shifts to lower energy after reduction (figure 2A), indicating the presence of either Cu(I) or Cu(0). The edge spectra of these reduced catalysts appears to be composed of Cu(0) clusters and Cu(I) sites. The intensity of the feature at 8984 eV [8] indicates that the coordination number of the Cu(I) sites is larger than 2. The FTs of Cu EXAFS for 1, 5 and 10% reduced samples are shown in figure 2B. In general, the FTs of the EXAFS spectra show 3 regions of features 1) a Cu-O feature at 1.92-1.97Å, 2) a Cu-Cu first shell feature at ~2.54 Å and 3) three outer Cu...Cu shells features at same distance as those in Cu foil. The ratios of the amplitude of those three outer Cu...Cu shells in the catalysts to that in the Cu foil are found to be constant (0.12, 0.18 and 0.28 for 1%, 5% and 10% respectively). Based on the statistical calculation done by Gregor and Lytle [9], the constant ratio of outer shells in the catalyst to that in the Cu foil indicates the presence of large Cu clusters in the reduced catalyst which have similar EXAFS amplitude to the Cu foil. The EXAFS of the large Cu clusters can be subtracted out giving difference EXAFS spectra. Preliminary curve fitting analysis of this data suggests that there are in addition small Cu clusters present. Further, we note that the Cu-O distance in the reduced catalyst is between that of Cu-O in Cu₂O (1.85 Å) and Zn-O in ZnO (1.97 and 1.99 Å) and that there is a trend of the Cu-O distance to shorter distance as the Cu concentration increased.

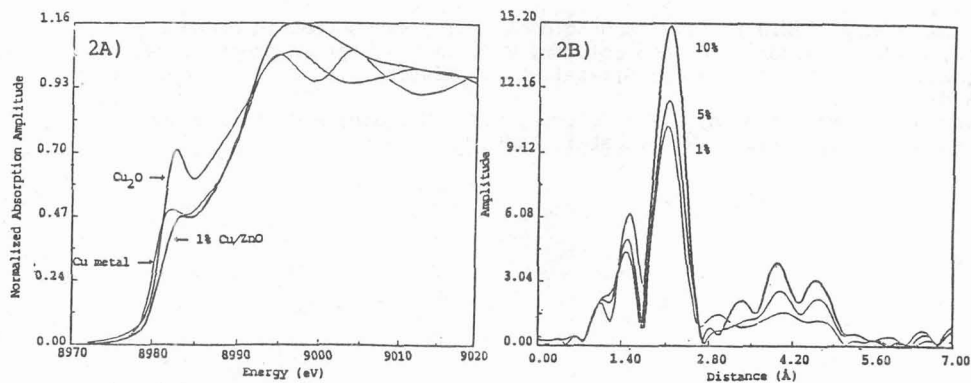


Fig. 2A) Cu K-edge spectra of Cu metal, Cu₂O and 1% reduced Cu/ZnO.
2B) FTs of Cu EXAFS for 1%, 5% and 10% reduced Cu/ZnO.

We have also collected EXAFS data on the catalyst with different chemical perturbations (reduction without CO₂/CO in the reducing gas and, in particular, reaction of the reduced catalyst with the catalyst poison, H₂S). The FTs of the EXAFS of the 10% sample reduced with and without CO₂/CO show that more of the large Cu cluster phase and less Cu-O phase is formed for reduction without the CO₂/CO in the reducing gas. This result is interesting in light of the fact that presence of a small amount of CO₂ in the feed gas is required to prevent catalyst deactivation. The effect of reaction of the reduced catalyst with H₂S perturbation is shown by the FTs of the EXAFS of poisoned samples in figure 3. It is clear that reaction with H₂S decomposes the Cu clusters in the reduced catalyst and that the level of Cu cluster decomposition increases with further reaction at higher temperature and longer time period. It is interesting to note that the Cu-O phase is quite stable and is not affected by H₂S reaction. Again, curve-fitting will be used to further quantify these observations [6].

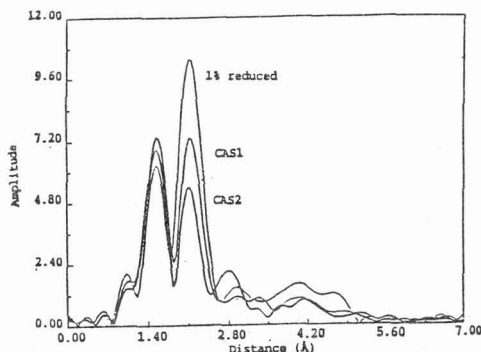


Fig. 3) FTs of Cu EXAFS for 1% reduced catalyst, treated with H_2S for 15 mins at 300K (CAS1) and treated with H_2S for 2 hrs at 473K (CAS2).

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