XPS Study of Silica-Supported Copper Catalyst Derived from Binuclear Copper(II) Acetate Monohydrate or Mononuclear Tetraammine Copper(II) Complex

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Synopsis. The surface copper(II) species on a CuO/SiO_2 catalyst derived from binuclear copper(II) acetate monohydrate has been studied using XPS in comparison with that from the mononuclear tetraammine copper(II) complex. From the binding energy of Cu $2p_{3/2}$ peak and the peak ratio of Cu $2p_{3/2}$ and Si 2p together with the results by EXAFS, it was deduced that the highly dispersed one or two dimensional copper oxide cluster, which is interacted more weakly with SiO_2, is developed on the copper(II) acetate monohydrate derived catalyst.

An active site on heterogeneous catalysts has become of interest in the recent year. We have examined to prepare a supported binuclear copper oxide catalyst from typical binuclear copper(II) acetate monohydrate $[Cu_2(CH_3COO)_4 \cdot 2H_2O]$, and have compared it with a conventional catalyst from a mononuclear tetraammine copper(II) complex.1—6) The recent EXAFS study, however, suggested that the one or two dimensional copper oxide cluster was developed on SiO_2 instead of the binuclear copper oxide.6) Also, the copper(II) species derived from copper(II) acetate monohydrate has been found to show following properties: 1) It reacts easily with acetic acid to give the binuclear structure of copper(II) ions, which was identified by ESR1,2) or IR,2) 2) it shows a tremendous high catalytic activity for CO oxidation with N_2O, CO isotope equilibriation reaction,1,2) or oxygen isotope-exchange reaction between CO and CO_2,5) 3) it is reduced easily to metallic copper with CO under mild conditions.3,6)

To obtain a further detailed information about it, we have applied a X-ray photoelectron spectroscopy (XPS) technique to above two kinds of silica-supported copper catalyst, finding that the acetate derived catalyst retains a highly dispersed copper oxide cluster.

Experimental

Two kinds of silica-supported copper catalyst were prepared from copper(II) acetate monohydrate (denoted Ac-Cu/SiO_2) and a copper(II) tetraammine complex (denoted Am-Cu/SiO_2), as described in earlier papers.1,2) Each sample was found to contain copper of 3.7 or 3.4 wt%, respectively. A Vacuum Generators ESCA 3 system was used with Mg*Kα* radiation (1253.6 eV) for XPS measurements. The samples pressed into disk were pretreated by the way similar to that in the previous paper1,2) with an IR lamp in the preparation chamber of ESCA instrument. CuO was also used for reference measurements. The binding energies (BEs) were referenced to the Si 2p peak at 103.4 eV, or the C 1s peak at 285.0 eV. The binding energies reported here are in accuracy with ±0.2 eV.

Results and Discussion

Figure 1a shows the XPS spectrum in the Cu $2p_{3/2}$ region, which was obtained on the Ac—Cu/SiO_2 catalyst activated under vacuum from room temperature to 300 °C and calcined with 100 Torr (1Torr=133.322Pa) of oxygen at 300 °C; the binding energy of Cu $2p_{3/2}$ is evaluated at 933.8 eV. The identical value was obtained on the reference sample of CuO. The satelite peak usually observed for typical Cu(II) compounds was unable to detect clearly on this sample. It might be due to the low loading of copper on it. We have used the Ac-Cu/SiO_2 catalysts containing rather a small amount of copper, because the specific features described previously were found to be lost by increaseing it above ca.7 wt%. An effort to detect the satelite peak due to the Cu(II) species was made at liquid nitrogen temperature, but only the spectrum similar to that of Fig. 1a was observed on it. This result indicates that the Cu(II) species was not reduced during the XPS measurement, as pointed out by Kevan et al.7)

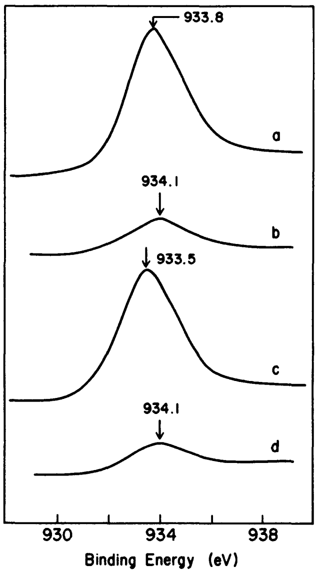

Fig. 1. Cu $2p_{3/2}$ XPS spectra of calcined Ac-Cu/SiO_2 (a), calcined Am-Cu/SiO_2 (b), reduced Ac-Cu/SiO_2 (c) or reduced Am-Cu/SiO_2 (d). All spectra were measured at room temperature.

Figure 1b shows the spectrum observed on the Am-Cu/SiO_2 catalyst, which was activated under vacuum at 300 °C for 1 h and followed by calcining with 100 Torr of oxygen at 300 °C for 1 h. This was also unable to identify the satelite peak in the Cu $2p_{3/2}$ region. The BE is evaluated at 934.1 eV. This value is higher than that of the Ac-Cu/SiO_2 catalyst or CuO.

In general, it is known that the BEs for metal oxides on supported catalysts tend to be higher than those of metal oxide themselves.8,9) The authors have ascribed it to a coordination effects of supports or

Table 1. Surface Composition of Cu and Si on Ac-Cu/SiO_2 or Am-Cu/SiO_2

Treatment	$Cu(2p_{3/2})/Si(2p)$[a]	
	Ac-Cu/SiO_2	Am-Cu/SiO_2
Calcined	1.36	0.23
CO reduction	0.95	0.20

a) Estimated uncertainty is within ±5%.

the formation of the new compounds like MAl_2O_4, $MSiO_3$ etc. (M: metal cations). In this point of view, the copper(II) ions on the Ac-Cu/SiO_2 catalyst interacts more weakly with SiO_2 than those on the Am-Cu/SiO_2 catalyst.

The surface composition of Cu and Si can be evaluated from the peak intensities of their spectra. The ratios of Cu and Si are summarized in Table 1. Although both catalysts contain almost the same amount of copper as described previously, the Ac-Cu/SiO_2 catalyst has ca. 6 times higher concentration of the surface copper species than the Am-Cu/SiO_2 catalyst on their calcined states. These results are in agreement with those by EXAFS study⁶⁾; it was found that one or two dimensional copper oxide cluster was loaded on the Ac-Cu/SiO_2 catalyst, while three dimensional one on the Am-Cu/SiO_2 catalyst.

When the calcined Ac-Cu/SiO_2 catalyst was reduced with 100 Torr of CO at 300 °C for 1 h, followed by outgassing it at 300 °C for 1 h, the spectrum was changed as shown in Fig.1c, giving the peak at 933.5 eV for Cu $2p_{3/2}$. It is somewhat higher than Cu_2O or metallic copper in literature.¹⁰⁾ The EXAFS study, however, showed that metallic copper was developed on the reduced Ac-Cu/SiO_2 catalyst.⁶⁾ The BE shift by the CO reduction therefore should be reflected by the presence of metallic copper.

On reducing the calcined Am-Cu/SiO_2 catalyst with 100 Torr of CO at 300 °C, a little change was observed in the spectrum (Fig.1d). However, it seems to be broadened, suggesting that a small part of the copper(II) species was reduced by CO at 300 °C. The Cu(I) species was detected by EXAFS experiment on it. The surface compositions of Cu and Si on the reduced samples are listed in Table 1.

In conclusion, the Ac-Cu/SiO_2 catalyst retains the highly dispersed low dimensional copper oxide cluster on silica, which is interacted weakly with the silica support. We believe that these features must give several particular catalytic properties different from the Am-Cu/SiO_2 catalyst.

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