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THE CATALYTIC ACTIVITY OF A NOVEL SILICA-SUPPORTED COPPER CATALYST FOR THE CO OXIDATION WITH N_2O

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A novel silica-supported copper catalyst, prepared from cupric acetate monohydrate having a dimeric structure of cupric ions, showed a very high activity for the CO oxidation with N_2O at 150°C as compared with a conventional silica-supported copper catalyst. It was suggested on the basis of the ESR spectroscopic characterization that such an extraordinary catalytic activity resulted from the structure of the Cu^{2+} ions derived from cupric acetate monohydrate on silica.

Copper is one of the typical components of catalysts for the oxidation of CO or hydrocarbons, and there have been many reports on the characterization of it on various supports by spectroscopic techniques.[1-3] This report is concerned with a novel silica-supported copper catalyst prepared from cupric acetate monohydrate, which is known to have the dimeric structure of cupric ions with Cu-Cu bond of 2.61 Å long.[4] The catalytic activity for the CO oxidation with N_2O and the states of the copper ions were studied by kinetical or ESR spectroscopic techniques.

The catalyst (termed A) was prepared by impregnation of silica-gel (kiesel gel 60, Merk) with the aqueous solution of cupric acetate monohydrate, and then dried at 100°C overnight. 3.7 wt% of copper was detected in it by chemical analysis. A conventional silica-supported copper catalyst (termed B) was also used in this study, which was prepared by exchanging the proton in hydroxyl of silica-gel with the cupric ammine complex in excess ammonia solution, washed with distilled water, and dried at 100°C overnight. 3.4 wt% of copper was detected in it.

These samples were heated stepwise to 300°C in vacuo each for 1 h, and followed by calcination in 100 torr of O_2 at 300°C for 1 h and outgassing at 300°C for 1 h.

The CO oxidation with N_2O was carried out in a conventional circulation system.

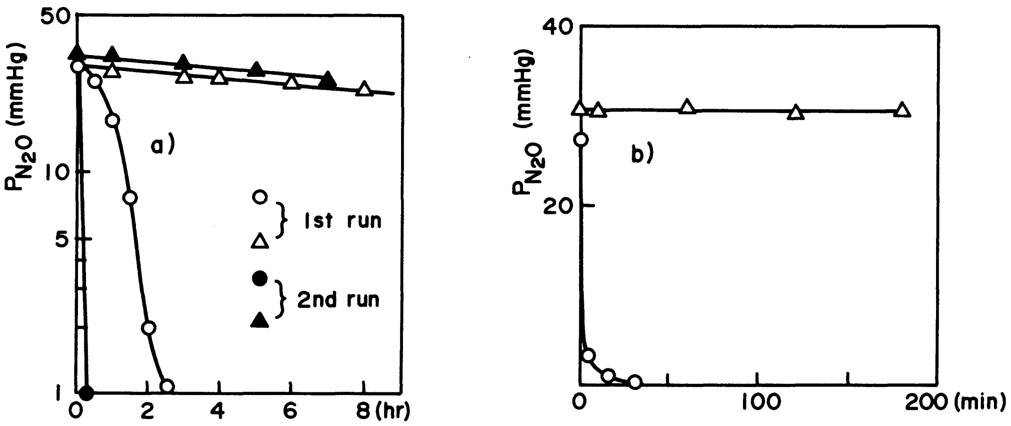

Figure 1

The time courses of CO oxidation with N_2O on silica-supported copper catalysts; a) calcined with O_2 at 300°C; reaction temp. 150°C, b) reduced with CO at 300°C, reaction temp. 18°C.

○, ● catalyst A, △, ▲ catalyst B.

Figure 1a shows the time course of the partial pressure of N_2O in the reaction of CO with N_2O at 150°C, each at 30 torr. The pressure decrease of N_2O was balanced with the formation of CO_2 within its experimental error, indicating that the reaction proceeds stoichiometrically on both catalysts. The catalyst A is much more active for this reaction than the catalyst B, and the reaction rate over the former catalyst is accelerated in the course of the reaction, even though the reaction over the latter catalyst obeys the first-order kinetics with respect to the N_2O pressure. In the second run over the catalyst A, N_2O was consumed within several minutes. The catalyst A reduced with 100 torr of CO at 300°C for 1 h showed a tremendous high activity even at room temperature, as seen in Figure 1b. Consequently, the high activity observed on the calcined catalyst A can be attributed to the reduced copper ions, which was formed in the course of the reaction. The catalyst B reduced with CO at 300°C, on the contrary, was not active at all for this reaction at room temperature as shown in Figure 1b, even though it was estimated to be reduced nearly to the level of the catalyst A from the amount of CO consumed by the reduction.

In order to estimate the valence state of the reduced copper ions on the catalyst A, the chemical titration with N_2O was applied to the reduced catalyst A according to Scholten et al.[5)] The sample was exposed to 40 torr of N_2O at 100°C for 1 h. The evolution of N_2, which has been attributed to the presence of free copper, was not detected by mass spectroscopy within its experimental error, indicating that the Cu^{2+} ions on the catalyst A were reduced to the Cu^{+} ions but not to free copper by the reduction above mentioned.

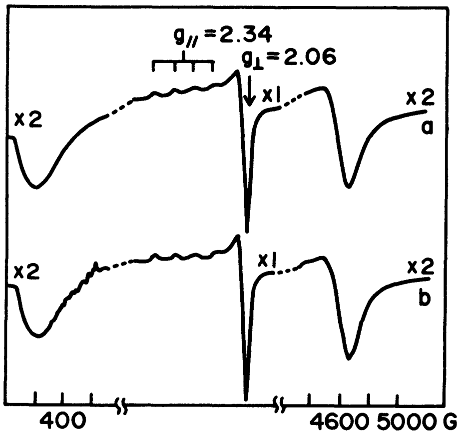

Figure 2
ESR spectra of catalyst A exposed to acetic acid
a) fresh sample, b) calcined sample

The states of cupric ions on these two samples were examined by ESR spectroscopy. Two kinds of ESR signals were obtained on the fresh sample of A, as shown in Figure 2a;6) two broad signals (termed signal A) at low and high magnetic field (400 and 4600G) are characteristic of the dimeric structure of cupric ions in cupric acetate monohydrate,7) and an axially symmetric signal (termed signal B) with parameters of $g_{/\!/}$ = 2.34, $g_{\perp}$ = 2.06 and four hyperfine lines of $A_{/\!/}$ = 138G, which are due to the nuclear spin of copper, has been attributed to the isolated Cu^{2+} ions in the distorted octahedral symmetry. These results indicate that the dimeric structure of cupric acetate monohydrate changed partly into the monomeric structure on silica. The spin concentrations of the signals show that ca. 50 % of copper loaded on the catalyst A retains the dimeric structure. On outgassing and calcining the sample, the signal A disappeared and the axially symmetric signal was changed to an anisotropic signal with the parameters of g_1 = 2.50, g_2 = 2.09 and g_3 = 2.04, which has been attributed to the isolated Cu^{2+} ions in the distorted tetrahedral symmetry.2)

When the calcined sample A was exposed to the vapor of acetic acid at room temperature, the ESR signals obtained on the fresh sample were recovered (Fig. 2b), indicating that the dimeric structure of the Cu^{2+} ions was kept on the catalyst A even after the calcination in O_2 at 300°C. Also, when the sample A was reduced with CO at 300°C for 1 h and subsequently was exposed to the vapor of acetic acid, the signal A was found to be weakened to one-twelfth of the original intensity, even though the signal B was not changed in its intensity. Furtheremore, it is interesting to observe that the signal A was weakened to ca. 80 % of the original intensity after the CO oxidation with N_2O at 150°C. Therefore the Cu^{2+} ions of the dimeric structure was confirmed to be reduced in the course of this reaction.

The fresh sample of B, on the other hand, gave an axially symmetrical signal shown in Figure 3a which can be assigned to that of the cupric ammine complex. It was changed on outgassing at 300°C into the signal due to the isolated cupric ions in the distorted tetrahedral symmetry, as reported in literature,$^{2)}$ and no change was observed by the calcination in O_2 at 300°C. When the calcined sample was exposed to the vapor of acetic acid at room temperature, the signal A due to the dimeric structure of the Cu^{2+} ions was developed simultaneously with the change of the anisotropic signal of the isolated Cu^{2+} ions into the signal B, as shown in Figure 3b. However, it should be noted that the intensity of the signal A was one-tenth of that obtained on the catalyst A.

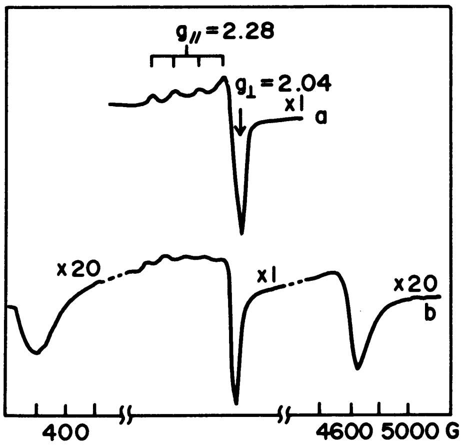

Figure 3
ESR spectra of catalyst B
a) fresh sample, b) calcined sample exposed to acetic acid

On the basis of these kinetical and ESR spectroscopic results, it is suggested that the high activity of this novel copper catalyst for the CO oxidation with N_2O results from the structure of the Cu^{2+} ions derived from cupric acetate monohydrate, which are reduced to the cuprous ions under the steady state of the reaction.

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6) The spectra in Figure 2a were recorded after exposure of the fresh sample A to the vapor of acetic acid, because the part of cupric acetate monohydrate on the fresh sample may be decomposed by drying it at 100°C after the impregnation. The characteristic cupric acetate monohydrate signal was less intense before exposure to the vapor of acetic acid.
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