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# Structural Changes in a $Cu/Al_2O_3$ Catalyst when Used for Oxidation of Carbon Monoxide

It has been found when copper is deposited on high surface area alumina using loadings below about 4 wt% Cu and calcined below 773 K that a "surface spinel $CuAl_2O_4$" forms, in which most of the $Cu^{2+}$ is located in a distorted octahedral geometry (*1, 2*). Previous results in our laboratories (*3*) have indicated that, for such loadings, the most active catalysts for CO oxidation at 473 K are obtained by prereduction with pure CO; however, the initial active state was found to be affected by a significant deactivation. The present study was undertaken to elucidate the structural changes accompanying deactivation during CO oxidation.

A 2 wt% $Cu/Al_2O_3$ catalyst was prepared by wet impregnation of $\gamma$-alumina of high purity (BDH, 95 $m^2/g$) with copper nitrate solution followed by evaporation of excess water, drying at 383 K and calcining at 773 K. Activity, defined as CO conversion by oxidation with air at 473 K, was measured in a flow reaction system as described elsewhere (*3*). Catalyst prereduction was carried out by flowing CO (or $H_2$) at 573 K for 3 h.

As has been found previously (*3*), activity was higher for the catalyst prereduced with CO than for the nonprereduced sample (Fig. 1). The most active catalyst also displayed a significant deactivation for the first hours on-stream, and a less marked decay for longer periods. The activity level was also affected by the type of reducing agent: reduction with CO produced a more active catalyst than did reduction with $H_2$. It is also seen in Fig. 1 that partial reoxidation with air after prereduction with CO produced a less pronounced decay in initial activity.

The presence of red particles, most probably metallic copper, was detected by optical microscopy in samples used for different periods of time (5, 24, and 48 h). Red aggregates up to about 50 $\mu$m were observed at 160× magnification.

Samples (fresh, prereduced and used) handled to avoid contact with air, were prepared for characterization by XPS and FTIR of adsorbed CO. The fresh and used samples presented the $Cu_{2p}$ doublet with binding energies of 934.4 and 954.4 eV, together with elevated satellite signals, which is typical of $Cu^{2+}$ (*4, 5*). Reduction with CO caused the disappearance of satellite peaks and a displacement (ca. 0.6 eV) of $Cu_{2p}$ doublet to a lower value. While a 1.2-eV decrease would be expected if all CuO were reduced to metal (*6, 7*), other authors (*8, 9*) have pointed out that small metallic clusters may also exhibit a peak at higher binding energy than does bulk metal. Therefore, it can be assumed that the catalyst reduced with CO most likely contained copper species on the surface with oxidation states lower than +2, either a mixture of $Cu^0$ and $Cu^{+1}$ or only $Cu^0$.

The values obtained from XPS and IR (Table 1) suggest that the fraction of exposed copper is maximal in the fresh sample, decreases after prereduction with CO, and further decreases after use for 5 h. However, longer operation (24 h) produces a significant increase in exposed copper, even though the activity decreased (Fig. 1).

Such deactivation may be caused in part

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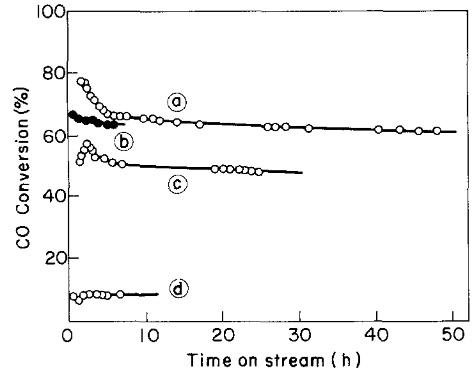

FIG. 1. Catalytic activity for CO oxidation on 2 wt% $Cu/Al_2O_3$ catalyst after different pretreatments: (a) prereduced with CO at 573 K for 3 h; (b) a + reoxidized with air at 573 K for 3 min; (c) prereduced with $H_2$ at 573 K for 3 h; (d) fresh oxidized. Reaction conditions: 473 K, 150 cc/min air + 30 cc/min CO, 0.5 g sample diluted with 1.5 g alumina.

by formation during reaction of aggregates of the metallic $Cu^0$ seen under microscopy. Sintering of $Cu^0$ during reaction may account for a decrease in surface concentration of copper seen in both the XPS and IR measurements for the prereduced sample and that used 5 h. However, the increase in exposed copper found for the sample used for 24 h was unexpected and contrary to the trend followed by the catalyst in previous states. In this case it seems unlikely that redispersion of the $Cu^0$ occurred because optical microscopy showed the presence of large $Cu^0$ aggregates at longer operation (24 and 48 h).

Accordingly, an increase in dispersion accompanied by a decrease in activity (Table 1, Fig. 1) most likely arises from the slow formation during reaction of a highly dispersed but less active phase, possible a $CuAl_2O_4$ "surface spinel," by means of migration of copper from bulk spinel (where copper is inaccessible to XPS or IR of adsorbed CO) and/or migration of copper from the active centers. If the latter is considered as the most predominant source of copper for the surface spinel formation, then the active copper should be present as small clusters, less dispersed than the surface spinel. Consequently, the slow formation of the less active $CuAl_2O_4$ was probably accelerated by the initial reoxidation carried out after prereduction (full circles in Fig. 1).

Two interesting phenomena could be inferred after reduction in a $H_2$ atmosphere (Table 2), namely the formation of metallic centers $Cu^0$, and the crystallization of the reduced phase $Cu^0$. It is probable that as a result of the exothermic character of the reduction, and the refractory properties of the solid, local temperatures increased considerably, so producing crystallization. As observed in Table 2, the spectrum of adsorbed CO following $H_2$ reduction showed a major absorption band at 2114 $cm^{-1}$, which is typical for CO adsorption on metallic copper (*10*). Further oxidation of the

TABLE 1

XPS and FTIR Results

| Sample treatment | ICu2p/IAl2p[a] | Absorbance[b] at at ca. 2120 $cm^{-1}$ |
|---|---|---|
| Fresh: a | 1.17 | 0.346 |
| a + CO-reduced: b | 0.71 | 0.177 |
| b + Used 5 h | 0.51 | 0.143 |
| b + Used 24 h | 0.98 | 0.347 |

[a] In this calculation both $Cu_{2p3/2}$ signal and its satellite were considered. X-ray source: Mg*Kα*. $Al_{2p}$ signal at 74.7 eV was employed as reference.

[b] Using self-supported wafer with 10.2–11.9 mg $cm^{-2}$ pressed at $10^3$ kg $cm^{-2}$. Adsorption pressure: 30 Torr CO.

TABLE 2

FTIR of Adsorbed CO on $H_2$ Prereduced Samples

| Sample[a] treatment | Wavenumber $cm^{-1}$ | Absorbance |
|---|---|---|
| $H_2$-Reduced: c | 2114 | 0.049 |
| c + reoxidized with 0.01 Torr $O_2$: d | 2122 | 0.035 |
| d + reoxidized with 1.6 Torr $O_2$ | 2128 | 0.042 |

[a] Temperature for reduction and reoxidation was 523 K. Other details are in Table 1.

$H_2$-reduced catalyst by small oxygen pulses shifted the CO stretching band toward higher wavenumbers up to 2128 $cm^{-1}$, which corresponds closely to CO adsorbed on CuO surfaces (*6, 10*).

Comparing absorbances after CO or $H_2$ reduction (Tables 1 and 2) led us to conclude that the appearance of $Cu^0$ upon $H_2$ reduction is accompanied by a significant decrease in the copper dispersion. Therefore, we draw the conclusion that the higher activity achieved upon CO prereduction (Fig. 1) is mostly related to a lesser sintering of copper particles than that which occurs when $H_2$ is the reducing agent.

The exothermic heat for complete reduction when using CO (68 kcal/mol) is somewhat higher than when using $H_2$ (58 kcal/mol). This implies, contrary to our observations, that more $Cu^0$ crystallization takes place in the former case. Therefore, the species formed after reduction with CO must be different in nature than just the bulk metallic $Cu^0$ formed by $H_2$ reduction. A possible explanation of this phenomenon is the formation of certain $Cu^0$-carbonyl species, perhaps as small clusters (*11*).

The induction period observed after prereducing with $H_2$ (Fig. 1) could be due to the formation of more active $Cu^0$-carbonyl species as suggested above. Indeed, the formation of large aggregates of $Cu^0$ seen under microscopy may reflect enhanced surface diffusion of $Cu^0$ during reaction as a result of the volatile character of $Cu^0$ carbonyls (*12*). This suggestion receives support from the appearance of a red-transparent film seen on the Pyrex reactor wall around the catalyst bed after the activity test.

In summary, the results discussed suggest that the active—CO prereduced—copper on alumina catalyst is deactivated during CO oxidation by the formation of two species: bulk $Cu^0$ and $CuAl_2O_4$ surface spinel.

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