# Relationship between Stable Monovalent Copper in Copper–Chromia Catalysts and Activity for Methanol Formation

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The activity for methanol formation of copper–chromia catalysts is sensitive to the temperature of calcination pretreatment; *X*-ray photoelectron spectroscopic studies of the reduced catalysts showed a correlation between the amount of stable surface $Cu^+$ and the activity for methanol formation.

Copper in Cu–ZnO and Cu–$Cr_2O_3$ catalysts is postulated to be the active site for the synthesis of methanol, at low temperature and pressure, from CO and $H_2$. Herman *et al.*,[1] on the basis of diffuse reflectance, proposed that $Cu^+$ dissolved in the ZnO lattice is the catalytically active species. Okamoto *et al.*,[2] using *X*-ray photoelectron spectroscopy (XPS), proposed that both $Cu^+$ and an electronically altered $Cu^0$ species are the active sites. Using the conclusions made by Herman *et al.* for Cu–ZnO, Courty *et al.*[3] postulated that copper in the IFP (Institute Francais du Pétrole) cobalt-modified copper–chromia linear alcohol catalyst yields an active phase of $Cu^+$-chromite. We show here that the activity for methanol formation of Cu–$Cr_2O_3$ catalysts calcined in air at various temperatures can be related to the amount of surface stable $Cu^+$ detected by XPS.

Cu–$Cr_2O_3$ catalysts were prepared by the decomposition of a homogeneous citrate complex. Citric acid was added to an aqueous solution of equimolar $Cu^{2+}$ and $Cr^{3+}$ acetates to form the corresponding $Cu^{2+}$–$Cr^{3+}$ citrate precipitate. This slurry was evaporated to dryness on a steam bath to form a glassy solid, which was vacuum dried at 150 °C for 2 h. The resulting powder was ground to 20—40 mesh and divided into four samples, which were air-calcined at 300, 350, 400, and $\geqslant$500 °C to yield the mixed oxides. Each catalyst was then reduced at 270 °C for 2 h in flowing $H_2$ diluted to 20% in He at 1 atm pressure before kinetic evaluation or XPS study.

After $H_2$ treatment, catalytic activities were evaluated in a single-pass high-pressure flow reactor maintained at 850 lb in$^{-2}$ (gauge) and 270 °C. The feed gas was supplied from a premixed cylinder of 67% $H_2$ and 33% CO. Under these conditions CO conversions were $\leqslant$2%.

Samples which had undergone identical calcination and reduction treatments were mounted on a resistively heated boat and reduced for an additional hour at 270 °C in a preparation chamber attached to an ultrahigh-vacuum XPS analysis chamber. XPS data were obtained with unmonochromatized Mg-$K_\alpha$ radiation ($h\nu$ 1253.6 eV) and an analyser resolution of 0.4 eV. Binding energies for selected support peaks were determined for the untreated catalysts by assigning the carbon 1s peak of the adventitious carbon to have a binding energy of 284.6 eV. Thereafter the Cu peaks were referenced to the support peaks used as internal standards.

Upon reduction of the catalysts in $H_2$, the XPS spectrum showed that the oxidation state of copper changed from $Cu^{2+}$, characterized by a Cu $2p_{3/2}$ binding energy of 933.6 eV and its associated satellite peak, to $Cu^+$ and/or $Cu^0$. Because $Cu^+$ and $Cu^0$ cannot be distinguished on the basis of the Cu $2p_{3/2}$ binding energy alone, the Cu $L_3M_{4,5}M_{4,5}$ *X*-ray-induced Auger level was investigated. Figure 1 shows the Cu(LMM) Auger spectra for the $H_2$-reduced catalysts as a function of calcination temperature. The principal peak at 918.6 eV can be assigned to $Cu^0$ from studies of spectra of clean Cu metal.[4] A shoulder at *ca.* 916.6 eV is due to $Cu^+$ species, as identified from studies of $Cu_2O$ and other $Cu^+$ compounds.[4] The fraction of $Cu^+$ relative to the total Cu changes as a function of calcination temperature, with its highest concentration resulting from 350 °C air calcination. $Cu^0$ and $Cu^+$ contributions to the XPS data were determined by comparison with reference spectra which were generated by adding together Cu(LMM) Auger spectra from copper metal and copper(I) chromite in various ratios. Quantitative results were derived from peak heights measured above a linear background (from kinetic

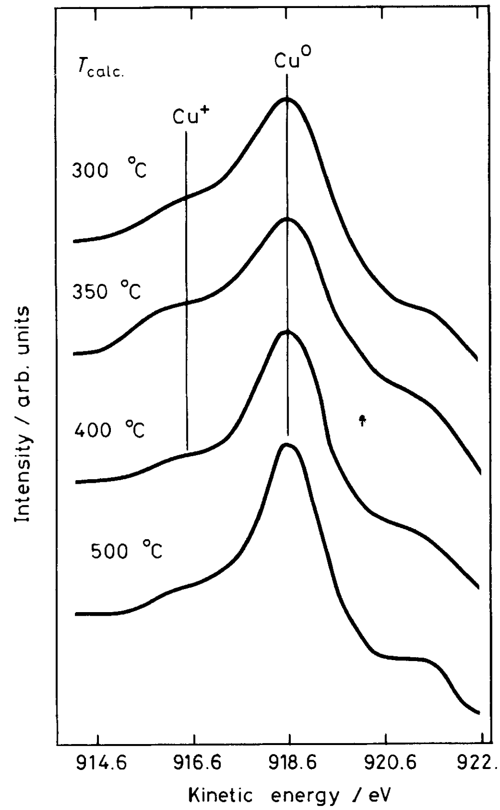

**Figure 1.** Cu $L_3M_{4,5}M_{4,5}$ *X*-ray-induced Auger spectra for 1 : 1 Cu–$Cr_2O_3$ catalysts calcined at various temperatures ($T_{calc}$), then reduced at 270 °C for 3 h in an atmospheric hydrogen stream [30 cm$^3$ (S.T.P.)/min].

**Table 1.** Steady-state activities for methanol formation as a function of calcination temperature ($T_{calc.}$).

| $T_{calc.}$/°C | μmol MeOH$^a$/ s m$^2$ catalyst | XPS [$Cu^+/(Cu^0 + Cu^+)$]$^b$ |
|---|---|---|
| 300 | 0.017 | 0.17 |
| 350 | 0.020 | 0.21 |
| 400 | 0.010 | 0.05 |
| *ca.* 500 | 0.007 | 0.04 |

[a] Uncertainty ± 0.002. [b] Uncertainty ± 0.02.

energy 914.5 to 920 eV) which was identical for the experimental and reference spectra.

The steady-state catalytic activities for methanol formation (Table 1) are also sensitive to calcination pretreatment conditions and vary in parallel with the surface concentration of $Cu^+$ stable to $H_2$ reduction. The existence of a considerable amount of $Cu^+$ from a 350 °C air calcination substantiates the proposal that $Cu^+$–chromite may be the active alcohol site.[3]

These results provide direct evidence for the existence of a monovalent Cu species that is stable to $H_2$ reduction at 270 °C. In addition, the correlation of the surface $Cu^+$ concentration with the activity for methanol formation establishes for the first time direct evidence for $Cu^+$ as the associative CO (*i.e.*, alcohol producing) site on these catalysts.

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