

Low-Temperature Formation of Cu^+ in Evaporated Cu-Cr Oxide Films: Application to Methanol Synthesis

There is increasing evidence that higher oxidation states of transition and noble metals are important for the activation of CO and CO_2 toward oxygenate formation. One example is the role of copper in copper-containing zinc oxide and chromium oxide catalysts for the selective low-pressure synthesis of methanol. The nature of active Cu sites in this reaction has been a subject of considerable interest (1). Recent studies of Cu-ZnO catalysts by Klier and co-workers (2-4) and Okamoto *et al.* (5, 6) provide evidence for Cu^+ stabilization; however, evidence to the contrary also exists, e.g., Fleisch and Mieville (7) and Friedrich *et al.* (8). Studies of Cu-Cr oxide catalysts (9, 10) show additional evidence that Cu^+ is a necessary component for methanol synthesis. A better understanding of the mechanisms responsible for the stabilization of Cu^+ ions will help elucidate the nature of the active site in these catalysts.

We report data showing that vacuum heating of Cu/ Cr_2O_3 evaporated films produces surface-stabilized Cu^+ ions, the concentration of which can be varied with treatment temperature. Catalytic evaluation of an analogous powdered Cu-Cr oxide methanol catalyst that had a similar vacuum heat treatment also showed enhanced activity for methanol synthesis compared to a catalyst without this treatment

Model catalyst samples were prepared by sequential electron-beam evaporation of copper and hot-pressed pellets of Cr_2O_3 . The oil-free evaporation chamber was evacuated by a cryopump and an ion pump. The base pressure was in the low 10^{-7} Torr range but rose as high as 2×10^{-6} Torr during depositions. Composite catalyst

films consisted of four layers of ($10 \text{ \AA} \text{ Cr}_2\text{O}_3 + 6.2 \text{ \AA} \text{ Cu}$) covered by a top layer of $10 \text{ \AA} \text{ Cr}_2\text{O}_3$ to form a sandwich configuration. Film thicknesses of Cr_2O_3 and Cu were determined from bulk densities so as to produce equal atomic percentages of Cu and Cr. The actual Cu/Cr ratio as determined by neutron activation was 1.12. All samples were subsequently calcined in air at 350°C for ~ 4 h to completely oxidize the copper component. Films for surface analysis were evaporated onto aluminum foil. Identical structures were also prepared on self-supporting SiO_2 film 100 \AA thick. These preparations could be treated and analyzed by TEM and electron diffraction (11).

Vacuum heating, hydrogen reductions, and surface analyses were done in a combined reactor/UHV analysis chamber described previously (9). Vacuum heating was carried out at $\sim 2 \times 10^{-6}$ Torr, and reducing conditions were 1 atm flowing hydrogen for ~ 1 h. The X-ray photoemission (XPS) experiments utilized a $\text{MgK}\alpha$ X-ray source. Because the catalyst was a thin film, sample charging did not occur and a flood gun was not required. Binding energies of the photoemission and Auger peaks have been referenced to the copper metal ($\text{Cu } 2p_{3/2}$) peak at a binding energy of 932.4 eV. Catalyst activity was evaluated as previously described (10).

The as-prepared samples contained copper in several oxidation states whose concentrations varied with aging in air at ambient temperature (Fig. 1). Calcination in air at 350°C stabilized the Cu^{2+} oxidation state so that subsequent experiments could be referenced to a common set of initial conditions. Reduction (H_2 , 270°C) of the calcined

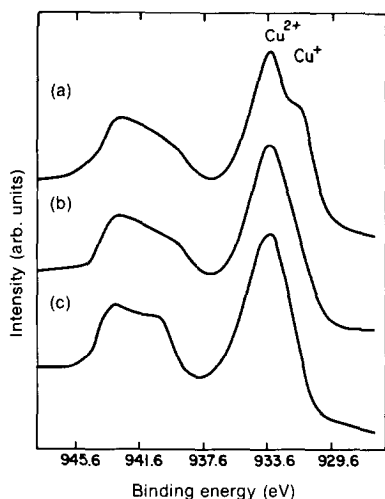


FIG. 1. Cu $2p_{3/2}$ spectra for 1:1 Cu-Cr₂O₃ evaporated films: (a) aged in air at ambient temperature for 2 weeks; (b) aged in air at ambient temperature for several months; (c) calcination in air at 350°C for 4 h to fully stabilize the Cu²⁺ oxidation state. Auger spectra (not shown) verified that the peak labeled Cu⁺ did not contain Cu⁰ species.

samples fully reduced the Cu component (9). This was verified by the XPS spectra of the Cu $2p$ core levels and the Cu $L_3M_{4,5}M_{4,5}$ X-ray-induced Auger levels, which were identical to those of Cu metal. Figure 2a shows the Cu LMM spectrum for this reduced sample. The weak intensity features at lower kinetic energy to the main Cu⁰ Auger peak are also attributable to Cu⁰.

The thin-film catalysts that were merely calcined produced no Cu⁺ that was stable to H₂ reduction. This is in contrast to the catalysts made by the decomposition of homogeneous citrate complexes (see Fig. 1 of Ref. (9a)). If the calcined thin oxide film was heated under vacuum, a significant fraction of the Cu⁺ became stable to reduction (see Fig. 2b). The additional feature at ~916.6 eV kinetic energy is attributable to Cu⁺ ions, as identified from studies of Cu₂O and other Cu⁺ compounds (12, 13). Observation of only one Cu $2p_{3/2}$ peak further supports this assignment.

Calcined Cu-Cr oxide films containing only Cu²⁺ reduced totally to Cu⁺ upon vacuum heating. The XPS spectra of the Cu $2p$

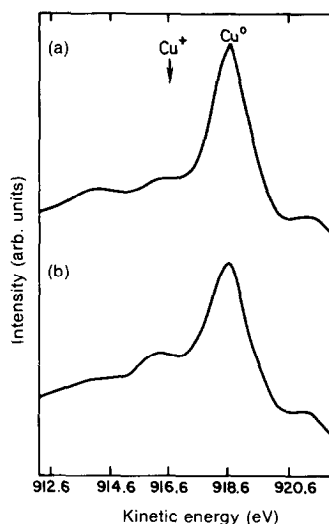


FIG. 2. Comparison of the Cu $L_3M_{4,5}M_{4,5}$ X-ray-induced Auger spectra for 1:1 Cu-Cr₂O₃ evaporated films that had different pretreatments before the hydrogen reduction: (a) calcination in air at 350°C followed by H₂—1 atm at 270°C; (b) calcination in air at 350°C plus heating under vacuum at 425°C followed by H₂—1 atm at 270°C.

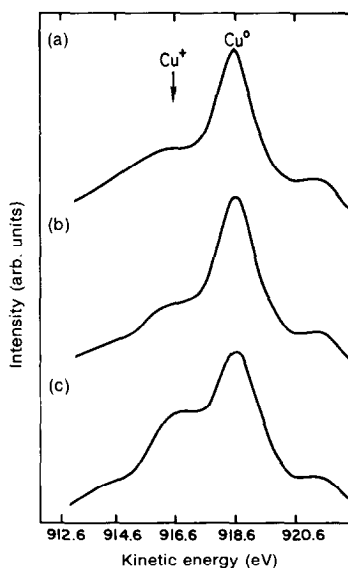


FIG. 3. Cu $L_3M_{4,5}M_{4,5}$ X-ray-induced Auger spectra for hydrogen-reduced 1:1 Cu-Cr₂O₃ evaporated films that had been heated under vacuum at various temperatures: (a) 375°C; (b) 425°C; and (c) 475°C. The preceding calcination conditions and subsequent reduction conditions were kept constant as in Fig. 2. A linear background has been removed.

core levels for vacuum-treated films show no shake-up satellites indicative of Cu^{2+} . The Cu *LMM* Auger spectrum (not shown) shows that the surface region is predominantly Cu^+ . The peak maximum occurs at ~ 916.6 eV, also indicative of Cu^+ ions.

Previous results have demonstrated that although CuO is rapidly transformed to Cu_2O under vacuum at 250°C (14, 15), the resulting Cu^+ is easily reduced (H_2 at 270°C). In contrast, the vacuum-heated Cu–Cr oxide films produce a Cu^+ species that is stable to hydrogen reduction. Figure 3 shows a sequence of Auger spectra from the X-ray-induced Cu *LMM* transition for vacuum heating at several temperatures followed by identical H_2 reduction treatments. The spectra show a growth in Cu^+ signal

intensity on the low kinetic energy side of the Cu^0 Auger peak. Vacuum treatment temperatures $\geq 375^\circ\text{C}$ appear necessary for the formation of the Cu^+ species stable to H_2 reduction. However, vacuum heating above 500°C produced larger quantities of Cu^+ with respect to Cu^0 (not shown).

Figure 4 illustrates both electron diffraction and TEM of a typical vacuum-heated film (supported on 100 \AA SiO_2 instead of Al foil). The typical crystallite size, as seen in the micrograph, is $\sim 500 \text{ \AA}$. The diffraction data compare the experimental *d* spacings for the vacuum-treated film (top) with a known X-ray diffraction pattern for CuCrO_2 (JCPDS No. 26-1113), verifying the formation of the delafossite structure during vacuum treatment.

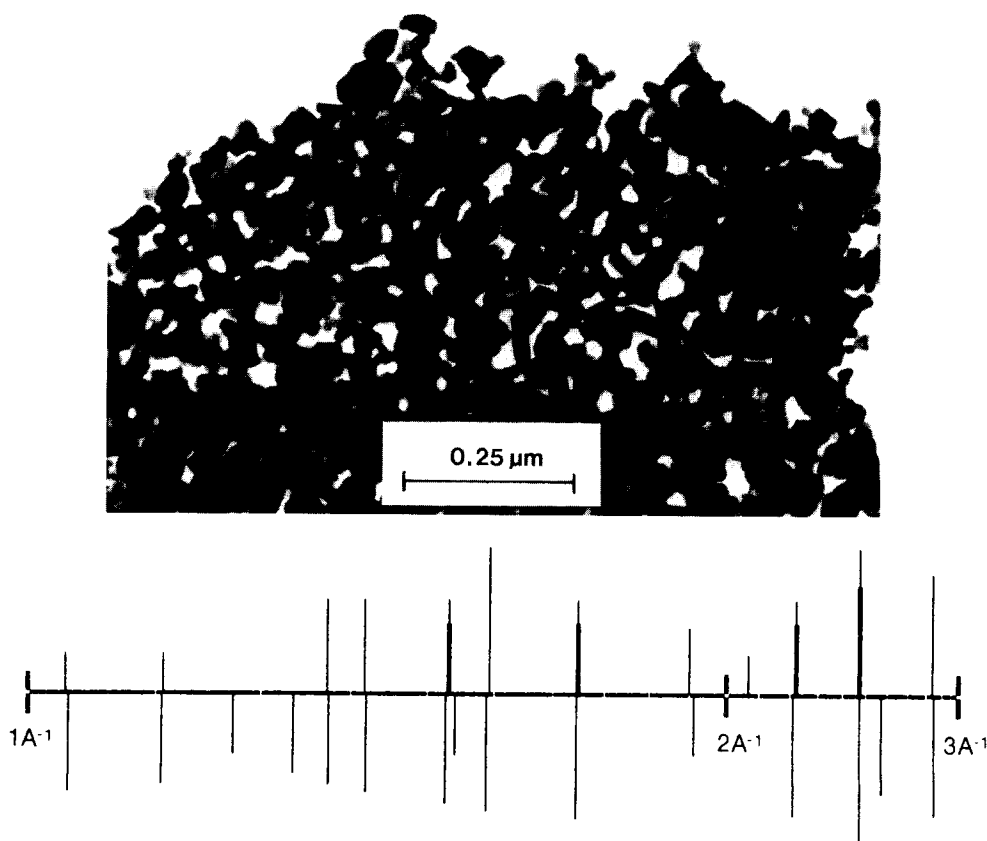


FIG. 4. Top: TEM micrograph of Cu– Cr_2O_3 thin film on 100 \AA SiO_2 (support not visible) after calcination and vacuum heating. Bottom: electron diffraction data for film pictured above. Experimental data are shown above the axis; X-ray data for CuCrO_2 (JCPDS No. 26-1113) are shown below the axis. Intensities and line widths are subjective.

In an attempt to relate specific activity for methanol formation with the Cu^+ species formed by vacuum heating, we compared two powdered Cu–Cr oxide catalysts prepared by the decomposition of homogeneous citrate complexes and calcined identically as described previously (9). One sample was directly reduced at 270°C in flowing H_2 at 1 atm for ~ 2 h; the other was heated to 375°C under mechanical-pump vacuum ($\sim 4 \times 10^{-2}$ Torr) for ~ 4 h and then reduced in H_2 . Table 1 shows the effects of such a treatment upon the catalytic activity for methanol formation. The steady-state rates of methanol formation were made by using a single-pass flow reactor after the catalyst had been on stream for 4 h. The catalysts typically underwent $\sim 10\%$ deactivation during the first hour of reaction, before reaching steady-state activity. In all cases, CO conversion levels were maintained at $< 5\%$. The specific activity for methanol formation increased ~ 4 times for the sample with vacuum pretreatment. The surface area remained constant during these low-temperature treatments. Cu L_{MM} Auger spectra (Fig. 5), and a single Cu $2p_{3/2}$ peak, confirm the enhancement of Cu^+ for the powdered Cu–Cr oxide catalyst with vacuum treatment.

The above observations are consistent with the formation of the CuCrO_2 delafossite phase during vacuum heating. Published results and our own experiments show that the simple copper oxides such as CuO and Cu_2O are readily reduced by hy-

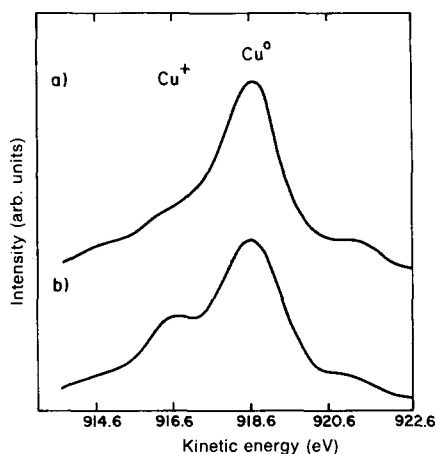


FIG. 5. Cu $L_{3M_{4,5}M_{4,5}}$ X-ray-induced Auger spectra for powdered 1:1.3 Cu–Cr oxide catalysts formed from the decomposition of homogeneous citrate complexes via controlled calcination (see Ref. (9)) followed by: (a) H_2 —1 atm, 270°C ; (b) heating under vacuum at 375°C followed by H_2 —1 atm, 270°C . A linear background has been removed.

drogen at $\leq 270^\circ\text{C}$ (13, 16). XPS results have also shown that CuO is reduced to Cu_2O by vacuum heating to 250°C (14, 15), and more recently a transition from Cu^+ to Cu^{2+} was reported to occur at 400°C via charge transfer between bulk and surface layers (14). In either circumstance the simple oxides formed are easily reduced in hydrogen. Thus we can conclude that chromium is directly responsible for the stability of Cu^+ in the evaporated Cu–Cr oxide system.

Previous studies (9, 10) of Cu–Cr oxide powder catalysts formed by controlled decomposition of a homogeneous citrate complex or by heating to high temperatures in air to preferentially form CuCrO_2 show a correlation between methanol activity and the Cu^+ component of the delafossite compound CuCrO_2 . In the former case, variations in calcination temperature of the citrate precursors affected the stability of the copper oxidation state at the catalysts surface after H_2 reduction, the optimum treatment producing at most 20% Cu^+ . For the latter case, high-temperature air calcinations (900 – 1000°C) are required to stabilize the delafossite phase (CuCrO_2), as opposed

TABLE 1

Pretreatment Effects on Catalytic Activity of Powdered Cu–Cr Oxide

Pretreatment conditions	CH_3OH activity ^a ($\mu\text{mole}/(\text{m}^2\text{-sec})$)	Surface area (m^2)
H_2 , 270°C , 1 atm, 2 h	0.015	52.9
vac, 375°C , 4×10^{-2} Torr, 4h	0.056	49.9
H_2 , 270°C , 1 atm, 2 h		

^a Catalyst activities evaluated at 2:1 H_2/CO , 850 psig, 270°C .

to the spinel phase (CuCr_2O_4) formed near 600–700°C. The major complication is that the surface areas rapidly collapse at high temperature. However, mild vacuum heating of Cu–Cr oxide systems appears to provide a unique way to control the concentration of Cu^+ ions in a copper-containing methanol catalyst without the severe loss of surface area. It also allows surface studies of model evaporated Cu–Cr oxide films to be more directly applicable to studying the possible interaction between Cu^0 and Cu^+ , both of which exist on the active catalyst surface.

In summary, low-temperature vacuum heating of calcined $\text{Cu}/\text{Cr}_2\text{O}_3$ evaporated layers $\geq 375^\circ\text{C}$ forms a surface Cu^+ phase that is stable to reduction by hydrogen at 270°C. Cuprous chromite is the compound responsible for the surface-stabilized Cu^+ ions. The advantage of the vacuum-heating preparation is that it is possible to produce controlled concentrations of Cu^+ sites that have a direct effect on methanol synthesis.

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