A Study of the Catalytically Active Copper Species in the Synthesis of Methanol on Cu–ZnO by X-Ray Photoelectron Spectroscopy

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X-Ray photoelectron spectroscopic studies on reduced Cu–ZnO catalysts have revealed that Cu^{1+} is present in low Cu content catalysts together with two distinct types of Cu metal species, one of which is preferentially reoxidized to Cu^{1+} on exposure to air at room temperature and is proposed as the catalytically active species together with Cu^{1+} for the synthesis of methanol from CO and H_2.

Cu–ZnO Catalysts promoted by Al_2O_3 or Cr_2O_3 are very active and selective in the synthesis of methanol at low temperature and pressure. Recently, Herman *et al.*[1-4] have investigated Cu–ZnO catalysts by means of diffuse reflectance, X-ray diffraction (XRD), and electron microscopy. On the basis of their results, they proposed that Cu^{1+} dissolved in the ZnO lattice was the catalytically active species in the synthesis of methanol from CO and H_2. However, their conclusions were based on the characterization of the catalysts by bulk techniques. Detailed surface analysis is required to obtain informa-

tion about the Cu species accessible to the reactants and to determine the catalytically active Cu species. The active Cu species found in Cu–ZnO catalysts is considered to be essentially the same as that in promoted catalysts, since Herman *et al.*[3] have shown that Al_2O_3 is merely a structural promoter in Cu–ZnO–Al_2O_3 catalysts which stabilizes the active Cu–ZnO phase. In this communication, Cu–ZnO catalysts of various compositions, which have been reduced at 250 °C for 2 h in an atmospheric H_2 stream, were studied by X-ray photoelectron spectroscopy (XPS).
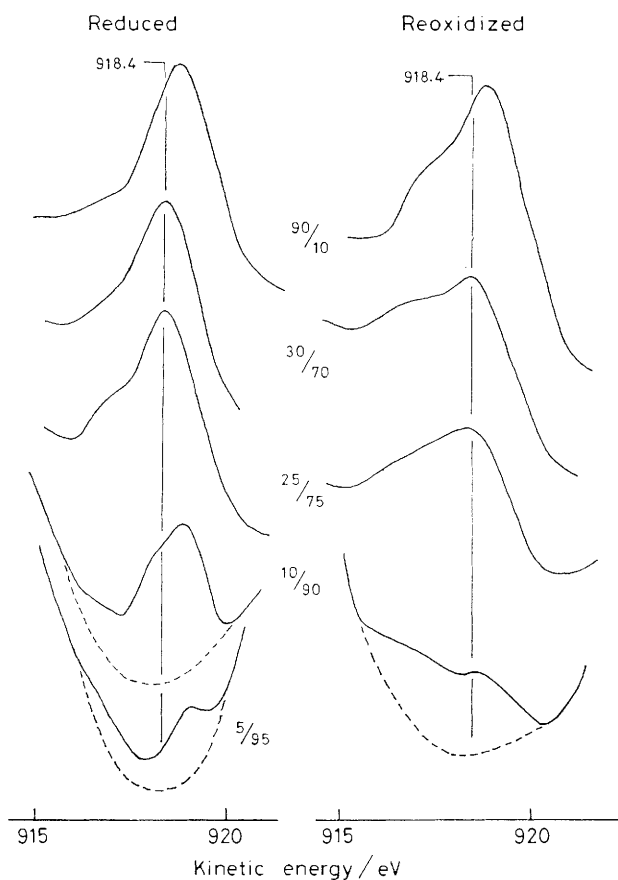
Figure 1. $Cu(L_3M_{4,5}M_{4,5})$ X-Ray induced Auger spectra for the Cu–ZnO catalysts reduced at 250 °C for 2 h in an atmospheric H_2 stream [ca. 500 ml min^{-1} g(cat)$^{-1}$] and for the catalysts subsequently reoxidized in air for 5 min at room temperature. The catalyst composition is shown by the CuO/ZnO ratio expressed as weight per cent. Dashed lines indicate the background spectra due to ZnO.

CuO–ZnO Catalysts were prepared by coprecipitating Cu and Zn nitrates with Na_2CO_3 at 80 °C (final pH was 8.0—8.3). The precipitates were dried at 110 °C for 16 h and calcined at 350 °C for 4 h in air. The catalyst composition is represented by the CuO/ZnO ratio expressed as weight per cent. The XP spectrometer has been described in detail elsewhere (Al anode).[5] The reduced catalyst was mounted on double-sided adhesive tape in a N_2-filled glovebox attached to the spectrometer. The detailed procedures have been reported previously.[6] The binding (BE) and kinetic (KE) energies of the $Cu(2p_{3/2})$ and $Cu(L_3M_{4,5}M_{4,5})$ levels were referenced to the $Zn(2p_{3/2})$ band at 1021.7 eV, whose position was originally determined with reference to the C(1s) line at 285.0 eV due to carbon contaminants. Both Cu levels were sandwiched between the reference level and the measurements were repeated until the BE and KE calculated from the preceding and subsequent reference levels were within ±0.1 eV, in order to correct a slightly time-dependent charging effect. This procedure assures the reproducibility of the energies of the Cu levels to be better than ±0.1 eV even for separate samples. After XPS measurements were made for the reduced sample, the sample was exposed to air at room temperature for 5 min while still mounted on the tape. The XP spectra of the reoxidized catalyst were recorded in the same way as for the reduced catalyst.

When the CuO–ZnO catalyst was reduced at 250 °C for 2 h under an atmospheric pressure of H_2, the $Cu(2p_{3/2})$ XP spec-

trum with associated satellite peaks characteristic of Cu^{2+} changed to a single narrow band irrespective of the catalyst composition, indicating the reduction of Cu^{2+} to Cu^{1+} and/or Cu metal. However, the BE of the resultant $Cu(2p_{3/2})$ level depended on the catalyst composition and decreased with decreasing Cu content (932.4 eV for the catalysts with $\geqslant 30$ wt% CuO, and 932.2, 932.1, and 931.9 eV for the 25/75, 10/90, and 5/95 catalysts, respectively).

Since it is not possible to distinguish between Cu^{1+} and Cu metal on the basis of the $Cu(2p_{3/2})$ BE alone,[7] the spectra of the Cu(LMM) level were investigated in detail. Figure 1 shows the Cu(LMM) X-ray induced Auger spectra for both the reduced and subsequently reoxidized catalysts. With the reduced catalysts, the Auger energy of the principal line was 918.7 eV for the catalysts containing >35 wt% CuO, consistent with that for pure Cu metal, whereas it shifted to 918.4 eV for the catalysts with 30—25% CuO. However, a new peak at 919.0 eV appeared for the 10/90 and 5/95 catalysts, the former also showing the peak at 918.4 eV as a shoulder.

The chemical shifts in the $Cu(2p_{3/2})$ and Cu(LMM) Auger bands involve both initial state chemical shift (ΔE) and extra-atomic relaxation shift (ΔR). Assuming that the two-hole relaxation energy is $2\Delta R$, Bahl et al.[8] have presented the correlations, given in equations (1) and (2), between the chemical shifts in the core (ΔBE) and Auger (ΔKE) levels, and ΔE and ΔR. All the shifts are referenced to the pure metal.

$$\Delta BE = \Delta E - \Delta R \qquad (1)$$

$$\Delta KE = -\Delta E + 3\Delta R \qquad (2)$$

It is shown in equations (1) and (2) that ΔE and ΔR, both of which are negative, decrease regularly with decreasing Cu content, including the Cu species corresponding to the shoulder peak found for the 10/90 catalyst. These findings indicate that Cu metal is negatively charged by electron transfer from ZnO, the extent of charge transfer being enhanced as the Cu content in the catalyst decreases. In addition, the regular decrease in ΔR indicates that the Cu metal species found in the high Cu content catalysts have essentially identical properties to the pure metal. An exception is the decrease in the particle size with decreasing Cu content, since it is well established[9] that ΔR or screening effects decrease with decreasing particle size of the metal. However, the Cu species found predominantly in the 10/90 and 5/95 catalysts is characterized by $\Delta R = 0$, which is markedly different from the ΔR values for the metal species in the high Cu content catalysts. Consequently, it is concluded that two distinct types of Cu metal species are present in the reduced Cu–ZnO catalysts.

Another important finding for the reduced catalysts is the presence of a shoulder peak at 916.7 eV, which can be assigned unambiguously to Cu^{1+}. The fraction of Cu^{1+} in total Cu seems to increase with decreasing Cu content, as shown in Figure 1, although the Cu^{1+} content in the 5/95 catalyst is obscured by the relatively strong background spectrum due to ZnO. These results provide direct evidence for the presence of a monovalent Cu species in the reduced catalyst surface. Taking into account both the increased Cu^{1+} fraction and the appearance of the new type of Cu metal exclusively in the low Cu content catalysts, it is suggested that both Cu species are formed from the same precursor, presumably from Cu^{2+} dissolved in the ZnO lattice. The Cu^{2+} ion is the predominant species in these catalysts as will be shown elsewhere.[10] With impregnated catalysts, no Cu^{1+} formation was found in the surface after reduction under the same conditions.

Exposure of the reduced catalysts to air caused a difference in the reactivity of the two types of Cu metal species toward

oxidation. The formation of Cu^{2+} was not detected by XPS. As illustrated in Figure 1, upon exposure to air the amount of Cu^{1+} present is enhanced for all the catalysts, the degree of Cu oxidation being increased with decreasing Cu content. It is particularly noteworthy that in the 10/90 catalyst, the Cu-(LMM) Auger peak at 919.0 eV disappears preferentially on exposure to air, whereas the peak at 918.4 eV remains. This finding clearly indicates the higher reactivity of the Cu metal towards oxidation and the higher stability of Cu^{1+} in low Cu content catalysts. On the basis of these results, it is proposed that the $Cu^{0}-Cu^{1+}$ species, whose properties are markedly different from those found in high Cu content catalysts and from Cu metal particles detectable by XRD, is the active species for the synthesis of methanol from CO and H_2. Further evidence for this proposal is provided by taking into consideration the fact that addition of a small amount of CO_2, H_2O, or O_2 to the syngas causes a marked improvement in the synthesis by retarding the over-reduction of the catalyst.[11]

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