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BRIEF COMMUNICATION

Creation of Defect Cu^+ Sites in $CuO–ZnO–Al_2O_3$ Ternary Catalyst

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In a previous communication (1), it was shown that the precipitate obtained from mixed nitrate solution of Cu, Zn, and Al is more or less monophasic in which Al^{3+} ions have been incorporated in the aurichalcite $(Cu, Zn)_5(CO_3)_2(OH)_6$ structure, causing appreciable distortion. In the present investigation, calcined Cu, Zn, and Al oxide catalyst has been studied with a view to find out to what extent the defect structure of the oxide is modified by the inclusion of Al^{3+} ion. The samples of Cu/Zn/Al oxide were prepared by coprecipitation from the mixed metal nitrate solution (1). The dry precipitate was calcined in air at 623 K for 5 h. The calcined oxide contained 30% CuO and O–15% Al_2O_3 and 70–55% ZnO. The samples were marked A_0, A_2, A_6, A_{10}, and A_{15}, where the subscript indicates percentage of Al_2O_3 by weight. A sample of Cu–Zn oxide was also prepared by mechanically mixing oxides of copper and zinc obtained by calcination of respective precipitates (prepared from nitrates using ammonium bicarbonate as before) in the ratio 30 : 70 by weight. X-ray diffraction studies indicate that both copper and zinc oxide are present in highly dispersed state, but free aluminium oxide could not be detected.

A Varian X-band superheterodyne spectrometer was used for ESR measurements. In each case, an equal amount of the sample (about 100 mg) was taken, and all the measurements were carried out at room temperature.

A Perkin–Elmer FTIR Spectrometer Model 1725X was used for recording the absorption spectra. The samples were evacuated in a grease-free system at 573 K for 2 h to remove surface adsorbed species such as CO_3^{2-} and water molecules. A liquid-nitrogen trap was placed between the pump and the sample tube to prevent any contamination by oil and grease vapors. After evacuation, the sample tubes were sealed off. Just before taking the measurements, the seal was broken, and the sample was quickly mixed with KB_r and pelleted.

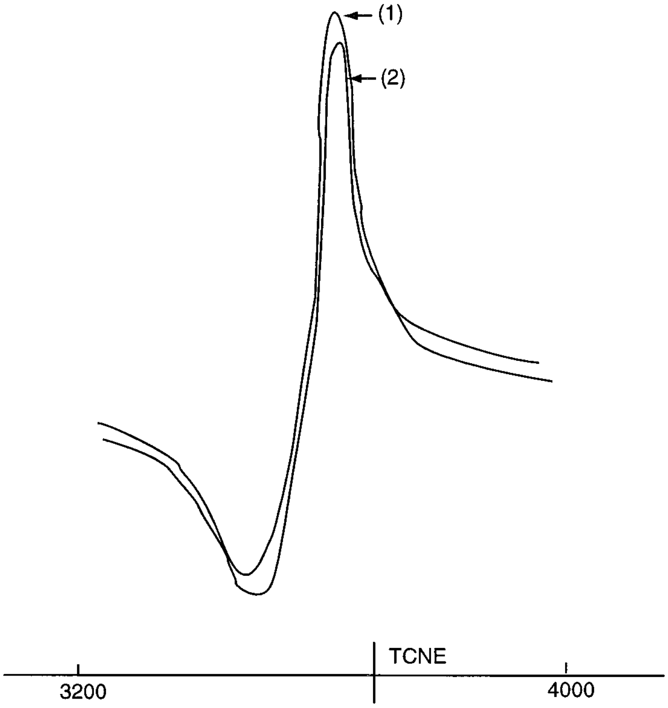

FIG. 1 ESR Spectra of (1) sample A_0 and (2) sample A_2.

DTA and TG studies were carried with a Stanton Redcroft Model STA 780. The samples were heated in a flow

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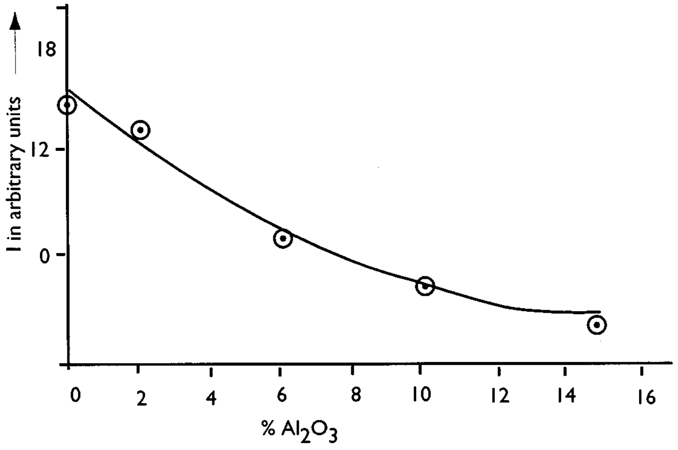

FIG. 2. Change of ESR signal intensity (1) with Al^{3+} content of the $CuO–ZnO–Al_2O_3$ catalyst.

TABLE 1
ESR Studies of the $CuO–ZnO–Al_2O_3$ System

Sample	g_I	g_{II}
A_0	2.05	2.23
A_2	2.05	2.23
A_6	2.05	
A_{10}	2.05	2.23
A_{15}	2.07	2.16

Note. Reference TcNE g = 2.00025.

of O_2 up to 623 K, held at this temperature for 10 min, cooled to 323 K, flushed with dry N_2 for 10 min. Then N_2 was replaced by oxygen-free dry H_2. The H_2 flow rate was kept at 2 liter/h. After flushing for 10 min, the sample was heated at the rate of 5 K/min. The temperature was increased up to 623 K for completion of reduction, as indicated by TG.

For studying chemisorption of carbon monoxide, about 2 g of the catalyst was taken in a sample tube and subjected to the following pretreatment:

1. Evacuation at 523 K for 2 h to 10^{-5} Torr.
2. Treatment with 750 Torr of O_2 for 2 h at 523 K.
3. Evacuation at 373 K for 1 h to 10^{-5} Torr.

The sample was cooled to 273 K for $\frac{1}{2}$ h and then CO was admitted at different pressures. After completion of the adsorption, the sample was again evacuated for 5 min at 273 K and a second adsorption run was carried out as before.

In a previous communication (2), it was shown that in the case of mixed oxides of copper and zinc prepared from aurichalcite, Cu^{2+} ions are incorporated in the octahedral sites of the zinc oxide matrix represented by Cu^{2+}_{ZnO}, giving rise to ESR spectra with anisotropy in the "g" value. In the present investigation, all the samples also exhibited

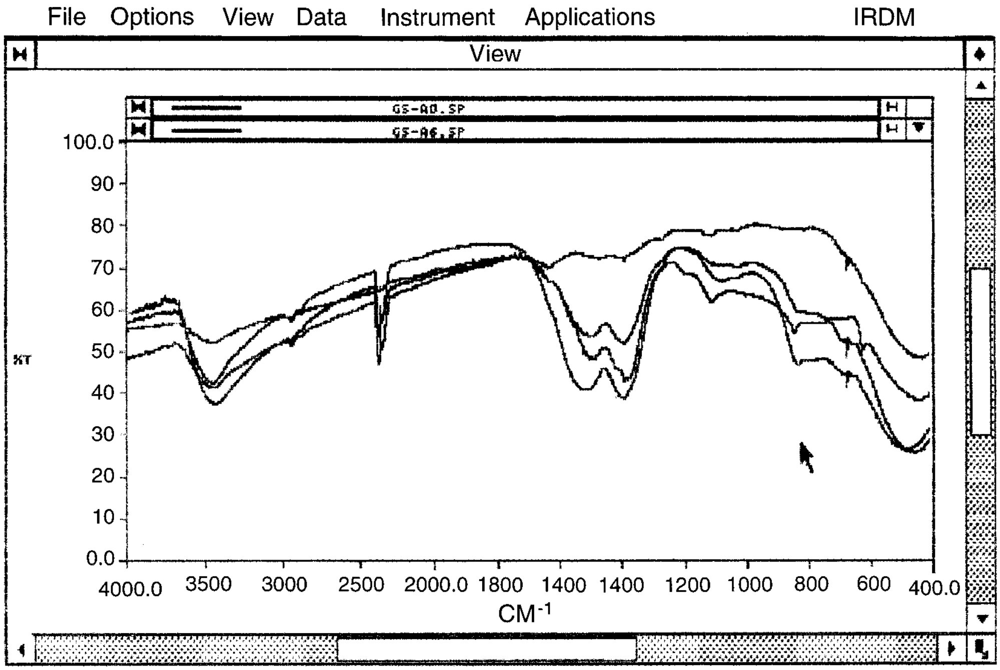

FIG. 3. FTIR absorption spectra of $CuO–ZnO–Al_2O_3$ catalyst: (1) A_0, (2) A_6, (3) A_{10}, and (4) A_{15}.

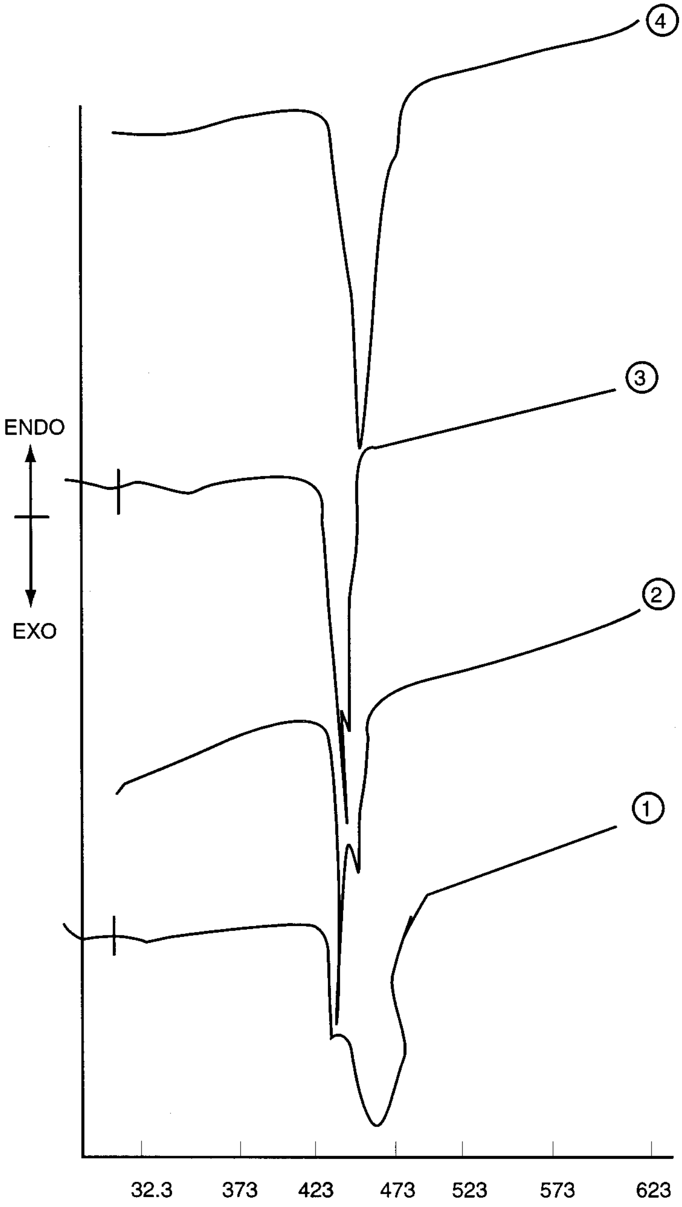

FIG. 4. DTA thermogram of the CuO–ZnO–Al_2O_3 catalyst: (1) CuO–ZnO (mech. mix.), (2) A_6, (3) A_0, and (4) A_{10}.

paramagnetic behavior, as shown in Fig. 1. The *g* values (Table 1) agree fairly well with these reported for distorted octahedral complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ SO_4^{2-} (3). From Fig. 2, it can be seen that with increasing amounts of Al^{3+} the intensity of the ESR signal decreases, indicating a gradual reduction in the concentration of paramagnetic Cu^{2+} ions due to incorporation of Al^{3+}. This may occur in two ways, either by transfer of dissolved Cu^{2+} ions from ZnO matrix to bulk CuO or by conversion of Cu^{2+}_{ZnO} ions to Cu^{+}_{ZnO} through electron trapping.

The FTIR spectra of the samples presented in Fig. 3 show typical absorption bands at 1400 and 1450 cm^{-1} for Al^{3+}-containing samples. It is suggested that the observed absorption bands are due to electron transition from Cu^{+}_{ZnO} sites to the conduction band of ZnO. According to Muller (4), the distance of the energy level of dissolved Cu^{+} ions from the conduction band of zinc oxide is about 1500 cm^{-1}, which is close to the observed absorption band. In view of this, it can be suggested that the observed decrease in the concentration of paramagnetic Cu^{2+}_{ZnO} can take place through trapping of free electrons. These free electrons can be created by incorporation Al^{3+} ions in ZnO in accordance with the following equilibria (5):

$$Al_2O_3 + Zn^{\cdot} \rightarrow 2\,Al/Zn/^{\cdot} + e + 3\,ZnO. \qquad [1]$$

Every Al^{3+} ion introduced displaces two Zn^{2+} ions from the lattice point forming a substitutional defect site of single + ve charge in the ZnO lattice. Two of the three oxygen ions introduced with two Al^{3+} ions react with the displaced Zn^{2+} ions while the third react with an interstitial Zn^{+} ion, leading to the formation of ZnO. The free electron (*e*) generated by reaction [1] converts the Cu^{2+}_{ZnO} ion to Cu^{+}_{ZnO} through trapping. A similar type of phenomenon occurs for In^{3+} and Cu^{2+} doped ZnO, where it has been reported that the presence of In^{3+} converts almost the whole of Cu^{2+} (6). The observed splitting of the absorption band in the FTIR spectra indicates the presence of two different type of donors. According to Muller (4), copper donors in ZnO can exist both as isolated Cu^{+} as well as $(Cu^{2+}Cu^{2+})^{-}$ associates. The formation of the copper associates is favored at copper concentration $\approx 10^{17}$ Cu atom/cm ZnO. Owing to the presence of more positive charges in the $(Cu^{2+}Cu^{2+})^{-}$ associates, the energy level of these donors will be lower than that of Cu^{+} donors.

From Fig. 4, it can be seen that in case of sample A_0 the DTA spectra is made up of two peaks, the larger one appearing at 438–440 K and the smaller one at about 446 K, as reported earlier (2). The Cu–Zn oxide mechanical

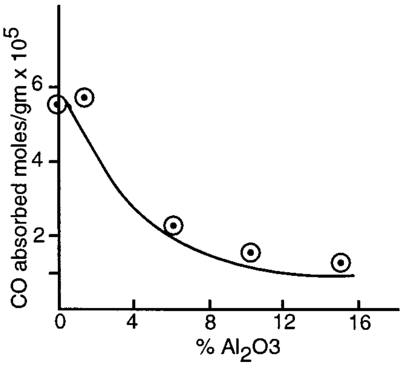

FIG. 5. Dependence of the amount of irreversibly adsorbed CO on Al^{3+} content of the CuO–ZnO–Al_2O_3 catalyst.

mixture also exhibit similar behavior, but in this case the position of the peaks are reversed. Moreover, the temperature of reduction has also been found to be shifted to higher temperature. Addition of Al^{3+} blurs the twin nature of the DTA peak, as can be seen from the spectra of sample A_6. However, in the case of samples A_{10} and A_{15}, a single peak is obtained at still higher temperatures, similar to the one reported earlier (5) for the $CuO–Al_2O_3$ system.

From the difference between the amounts of CO adsorbed in the two cycles at a given pressure, the amount of irreversibly adsorbed CO at 273 K can be calculated. On pure ZnO, no irreversible adsorption could be detected, but in samples A_0 to A_{15} it was found to be quite appreciable, decreasing with increasing Al^{3+} content. In order to explain this, it is assumed that CO is adsorbed as CO^+ (7) on Cu^{2+} ions dissolved in the ZnO matrix. However, Parris and Klier have shown (8) that Cu/ZnO catalysts show an enhanced irreversible CO chemisorption compared to pure copper after reduction with 2% H_2/N_2 gas at 523 K. They have attributed this CO chemisorption to Cu^+ ions in the zinc oxide matrix as the hydroxyl group induced by the presence of copper interacts with CO to make surface formate. According to the ionic-type CO chemisorption proposed in the present investigation, since Cu^{2+}_{ZnO} sites act as adsorption sites for CO on oxidized catalysts, transformation of Cu^{2+}_{ZnO} to Cu^{+}_{ZnO} by incorporation of Al_2O_3 will cause inhibition of CO chemisorption, as shows in Fig. 5.

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