

Catalytic activity of pure copper oxide and samples containing different concentrations of aluminium oxide in heterogeneous decomposition of hydrogen peroxide

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The catalytic activities of pure CuO and of CuO samples containing different concentrations of Al^{3+} ions have been determined using the heterogeneous catalytic decomposition of H_2O_2 . The activity has been correlated with various physicochemical properties. Experimental evidence shows that Al^{3+} is responsible for lowering the charge carrier concentration (positive holes) which affects the capability of the surface for oxygen adsorption. This has a decisive role in the decomposition reaction. A suitable mechanism has been proposed to explain the observed results.

Catalysts containing copper have generated considerable interest^{1,2} because of their general performance as oxidation catalysts, e.g. in the synthesis of glyoxal from glycol³, as promoters for the redox behavior of supported transition metal oxide catalysts (e.g. in the reduction of NiAl_2O_3)⁴ and as principal components of many of the base metal formulations for automobile exhaust emission control⁵. Various studies have also been conducted for the elucidation of the role of copper in the catalytic reactions such as in partial and stereoselective hydrogenation of alkenes⁶ and hydrogen transfer in aldehyde to ketones over hydroxyapatites⁷.

The heterogeneous decomposition of hydrogen peroxide catalyzed by copper and nickel ferrites has been investigated and the data have been discussed in terms of the redox behaviour of the base metal ions⁸. Also, addition of Cu(II) to MnO_2 catalyst enhances the H_2O_2 decomposition reaction owing to the increased capacity of manganese cations for electron exchange process⁹.

Presently we have studied the structural properties of CuO containing different amounts of Al^{3+} ions in the form of Al_2O_3 employing DTA and IR techniques, and the catalytic activity of the samples towards H_2O_2 decomposition. The results have been correlated with the non-stoichiometry of different samples and electrical conductivity measurements.

Materials and Methods

All reagents used were of AR grade. Doped and mixed catalysts were prepared by the impregnation method. Solutions containing calculated

amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in doubly distilled water were mixed with basic copper carbonate in different ratios ranging from 0.5 up to 50 mol % with continuous stirring and heated over a water-bath till a homogeneous mixture was formed on complete dryness. The resulting samples were calcined in a muffle furnace in a system of dry air from 200 to 700°C for 3 hr.

Differential thermal analyses (DTA) of pure basic copper carbonate and the mixed oxides were studied employing an automatic recording thermobalance, type Li 160 KS (West Germany) at a heating rate of 5°C/min.

The IR spectra were recorded in KBr matrix in the range of 1700-200 cm^{-1} on a Perkin-Elmer 599 B infrared spectrophotometer.

Electrical conductivity was measured by adopting the method previously discussed¹⁰. The sample temperature was controlled using Gallen-Kamp temperature controller. The voltage was obtained via a 240 A Keithley power supply and the current was measured with a 410 A picoammeter. Variation of σ values with the experimental conditions was recorded using a Linseis LS4 recorder.

Catalytic activity and non-stoichiometry of the different catalysts were measured using heterogeneous catalytic decomposition of H_2O_2 and N_2H_4 in aqueous media. The evolved volume of either O_2 or N_2 gas liberated at atmospheric pressure was measured using the gasometric technique¹¹.

Results and Discussion

(a) DTA and IR analysis of pure and mixed basic copper carbonates

The differential thermal analysis curves for pure basic copper carbonate and of mixed samples containing Al^{3+} ions are presented in Fig. 1. In thermogram (a) an endothermic peak is located at 282°C , which corresponds to the thermal decomposition of the carbonate to copper oxide. The small endothermic peak located at 672°C is due to the transformation of some CuO to Cu_2O with creation of oxygen anion vacancies.

The DTA curves of host carbonate containing 1, 5, 10, and 50 mol % Al^{3+} ions are also shown in Fig. 1. It is clear that addition of Al^{3+} ions enhances the thermolysis process. The existence of a small endothermic peak at around 720°C is attributed to the spinel formation of CuAl_2O_4 (ref. 12).

The IR spectrum of the products obtained by heating basic copper carbonate at 200°C indicates that the basic copper carbonate is partially decomposed. The IR spectra of the products obtained on increasing calcination temperature exhibit bands at 520 and 580 cm^{-1} which may be attributed to the different tetrahedrally and octahedrally coordinated Cu^{2+} ions with lattice oxygen¹³ (Fig. 2). The band located at 1100 cm^{-1} corresponds to the O_2^- species which is in accord with data obtained using XPS analysis¹³.

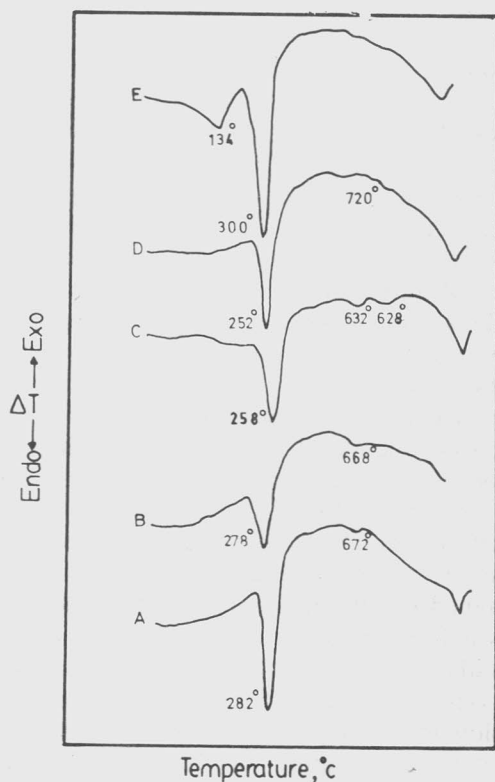


Fig. 1—DTA curves of parent basic copper carbonate (A) and that containing 1, 5, 10 and 50 mol % Al^{3+} (B-E)

The IR spectra of basic copper carbonate containing different concentrations of Al_2O_3 and calcined at 500°C did not show any change in the location of the vibrational bands of the coordinated Cu^{2+} ions with its lattice oxygen for samples containing 5 to 10 mol % Al^{3+} ions. When 50 mol % Al^{3+} ions were admixed, the intense bands disappeared and instead a broad band appeared at around 500 cm^{-1} . This feature is attributed to occupation of interstitial spaces in the host lattice by Al^{3+} ions instead of replacement of Cu(II) to form a solid solution. It also appears that calcination at 500°C does not lead to spinel formation.

(b) Electrical conductivity measurements

Variation of $\log \sigma$ against $1/T$ for the parent basic copper carbonate and the mixed samples, shown in Fig. 3, indicates a decrease in σ in the

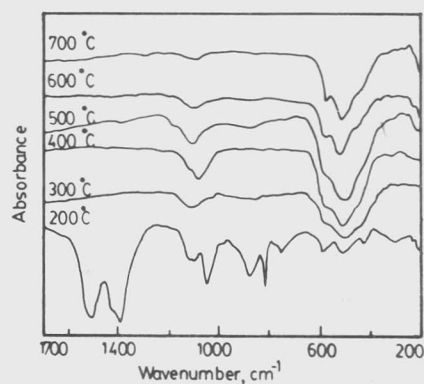


Fig. 2—IR spectra of products obtained by isothermal decomposition of the basic copper carbonate in air at various temperatures

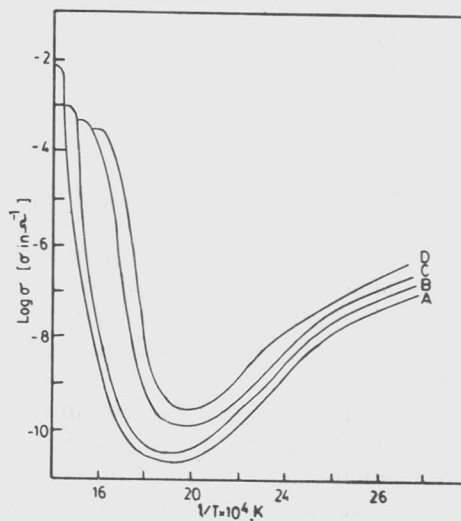


Fig. 3—Electrical conductivity variations versus $1/T$ plots of pure basic copper carbonate (A) and the samples containing 0.5, 1 and 5 mol % Al^{3+} ions (B-D)

initial stage of decomposition followed by an increase in the inversion temperature, when the material was fully decomposed to the oxide lattice structure. It is well known that decomposition of solids is an endothermic process. Hence increasing temperature causes rupturing of lattice bonds thereby consuming some more of energy. Thus the charge carriers will not have enough energy to be more mobile up to the inversion temperature at around 282°C. Addition of Al^{3+} ions to the host solid influences the variation of σ value and the trend is similar to that shown by pure basic copper carbonate, but slightly higher conductivity values as compared to that of the pure salt.

The resistivities for samples containing 0.0, 0.5, 1.0, 5.0, 10.0 and 50.0 mol % Al^{3+} and calcined at 500°C are 18.0, 31.0, 5.6, 2.2, 1.5 and 1.7×10^{-8} ohm cm^{-2} respectively. This data show that Al^{3+} ions when diffuse in the matrix of CuO cause eventually a reduction in the resistivity. This can be attributed to a reduction of charge carrier concentration. Since the electrical conductivity of CuO is entirely due to positive holes associated with negative defects (cation vacancies) the mechanism outlined in Eq. (1) can be proposed to interpret such a phenomenon



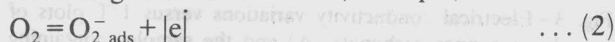
This mechanism is responsible for lowering the charge carrier concentration. In order to provide support to this idea activation energy (E_a) of charge carriers in samples containing 0.0, 0.5, 1.0, 5.0, 10.0 and 50.0 mol % Al^{3+} (calcined at 500°C) were measured and the values are 0.16, 0.19, 0.24, 0.28, 0.35 and 0.55 kcal/mol respectively.

The E_a values show a fermi potential of higher activation energy when Al^{3+} ions concentration is increased. This is in agreement with the mechanism given above (see Eq. 1).

(c) Non-stoichiometry and catalytic activity measurements

Measurement of the amount of surface excess oxygen can manifest the non-stoichiometry of the lattice structure of either pure CuO or of CuO containing Al^{3+} ions. The results are given in Tables 1 and 2.

Results presented in Table 1 show an increase in the amount of surface excess oxygen up to 400°C. Non-stoichiometry is related directly to O_2 chemisorption via creation of more acidic surface according to the mechanism (see Eq. 2)



(where $|e|$ is a defect electron). Therefore, activa-

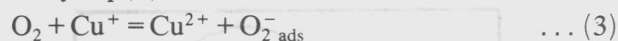
Table 1—Variation of amount of surface excess oxygen with calcination temperature of pure CuO catalysts

Calcination temp (°C)	Surface excess oxygen (meq/g. cat) 10^2	Calcination temp (°C)	Surface excess oxygen (meq/g. cat) 10^2
200	5.0	500	6.2
300	7.5	600	1.8
400	8.6	700	0.35

Table 2—Variation of surface excess oxygen with mol % of Al^{3+} ions (samples were calcined at 500°C for 3 hr in air)

Al^{3+} concentration (mol %)	Surface excess oxygen (meq/g. cat) 10^2	Al^{3+} concentration (mol %)	Surface excess oxygen 10_2 (meq/g cat)
Pure	6.2	5.0	1.6
0.5	2.4	10.0	1.35
1.0	2.0	50.0	1.10

tion of CuO at 400°C seems to have more non-stoichiometry. The noticeable decrease after 400°C is caused by lattice shrinkage. The remarkable increase beyond 600°C is mainly attributed to the phase transition to Cu_2O , resulting in higher chemisorption of O_2 by the mechanism represented by Eq. (3)



Addition of Al^{3+} ions to CuO calcined at 500°C for 3 hr shows a monotonic decrease in the amount of surface excess oxygen with increase in Al^{3+} ion concentration. Resistivities of such samples show the same effect, i.e. a relation parallel to their conductance and the measured amount of excess surface oxygen where Al^{3+} ions can interstitially substitute or form CuAl_2O_4 spinel structure. This leads to strengthening the oxygen bond and eventually leads to lower reactivity as detected by Barker *et al.*¹⁴.

The reactivities of the catalysts under investigations were measured using H_2O_2 decomposition reaction. The kinetic runs were carried out at 30°C. The plot of $\log V_{\text{O}_2}$ against time for the various catalysts is linear indicating a first order reaction in the region of time of about 30 min. The determined specific rate constants have been plotted as a function of catalyst calcination temperature, either for pure CuO or catalysts containing Al^{3+} ions in different concentrations (see Fig. 4). The plots in Fig. 4 show a maximum in (k) around calcination temperature of 400°C, followed by decrease at higher temperatures up to 700°C. For CuO containing Al^{3+} ions, a similar trend is observed, but the magnitude of k values decreases

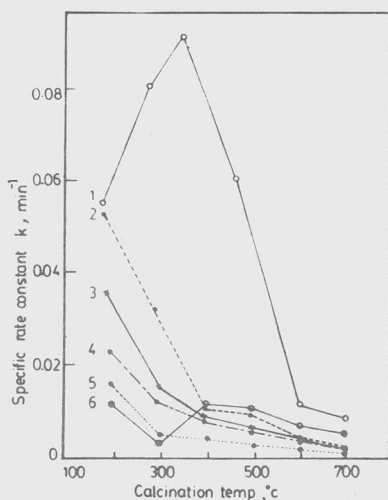


Fig. 4—Specific rate constants for H_2O_2 decomposition against catalyst calcination temperature for pure CuO and CuO mixed with 0.5, 1, 5, 10 and 50mol % Al^{3+} (1-6) respectively [Experiments were conducted at 30°C]

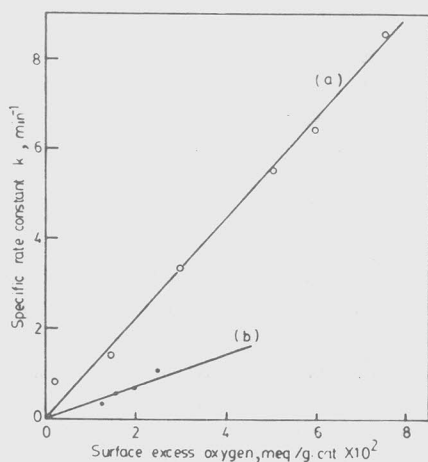
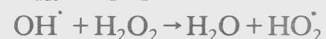


Fig. 5—Specific rate constants (k) for H_2O_2 decomposition over different catalysts against the amount of excess surface oxygen [Catalysts used were (a) thermal products of basic copper carbonate, and (b) CuO containing different concentrations of Al^{3+} and calcined at 500°C for 3 hr in air]

with increase of Al^{3+} ion concentration. The plots of surface excess oxygen concentration against the k values (Fig. 5) are linear. However, the results confirm that the surface adsorbed oxygen either in the form of O_2^- or O^{2-} has a decisive role in the decomposition reaction. Consequently, the decomposition steps shown in Scheme 1 may be suggested.



Scheme 1

where OH^\cdot and HO_2^\cdot are free radicals.

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