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ABSTRACT: In order to investigate the effect of Na_2O doping (0.75-4.5 mol%) on metal oxide-support interactions, the surface and catalytic properties of the $CuO–ZnO/Al_2O_3$ system have been studied using XRD, nitrogen adsorption at $-196°C$ and the catalytic oxidation of CO by O_2 at 150–200°C. Pure and doped mixed oxide solid samples were prepared via the wet impregnation method using $Al(OH)_x$, $NaNO_3$, $Zn(NO_3)_2$ and $Cu(NO_3)_2$ solutions, followed by drying and calcination at 600°C and 700°C. The nominal composition of the solids thus prepared was $0.25CuO:0.06ZnO:Al_2O_3$.

The results obtained showed that Na_2O doping followed by heating in air at 600°C leads to enhanced crystallization of the CuO crystallites to an extent proportional to the amount of dopant present, while doping followed by heating in air at 700°C hinders the solid-solid interactions between CuO and Al_2O_3 and leads to the production of $CuAl_2O_4$. The specific surface area was found to increase progressively as a function of the dopant concentration for the solid calcined at 700°C. The catalytic activity was also found to increase progressively on increasing the amount of dopant added. The maximum increase in the catalytic activity measured at 150, 175 and 200°C over solids calcined at 700°C was 114, 102 and 82%, respectively. The doping process did not modify the mechanism of the catalyzed reaction but rather increased the concentration of catalytically active constituents (surface CuO crystallites) involved in the chemisorption and catalysis of the CO oxidation reaction without affecting their energetic nature.

INTRODUCTION

Alumina is often employed as a convenient support for the wide variety of catalysts used in different chemical reactions. Examples of such reactions are provided by the low-temperature water-gas shift reaction (Andreev *et al.* 1991; Molt 1986) and the oxidation of CO by O_2 (El-Shobaky and Al-Noami, 1987; El-Shobaky and Ibrahim 1989a; El-Shobaky *et al.* 1989b,c, 1995, 1996a, 1997a). The role of the support material is to increase the degree of dispersion of the catalytically active constituents, thereby hindering their grain growth and leading to an increase in the thermal stability and service lifetime of the supported catalysts. However, these catalysts undergo deactivation due to the formation of the corresponding aluminate via metal oxide-alumina interactions (Bolt *et al.* 1993, 1994a). The rate of reaction between the catalytically active constituents (transition metal oxide) and Al_2O_3 has been reported to vary in the following order: CuO > CoO or Co_3O_4 > NiO >

Fe_2O_3 (Bolt *et al.* 1994b). Suppression of aluminate formation is therefore most important for the preparation of technical catalysts. Thus MoO_3 is added to CoO in the preparation of $CoO \cdot MoO_3/Al_2O_3$ to hinder the access of cobalt ions into the γ-Al_2O_3 lattice and thereby suppress the formation of $CoAl_2O_4$ (Ramaswamy *et al.* 1985; Bolt *et al.* 1993), while ZnO is added to CuO/Al_2O_3 to hinder copper aluminate formation (El-Shobaky *et al.* 1997a).

The doping of transition metal oxides loaded on γ-Al_2O_3 with certain foreign oxides might also suppress the formation of aluminate. In fact, we have reported in a recent investigation that Li_2O doping of CuO–ZnO/Al_2O_3 catalyst hinders the formation of $CuAl_2O_4$ (El-Shobaky *et al.* 1997b). The present work reports a study of Na_2O doping of the CuO–ZnO/Al_2O_3 system on solid-solid interactions between CuO and Al_2O_3 and thence on the surface and catalytic properties of the treated solids. The techniques employed were XRD, nitrogen adsorption studies at -196°C and the oxidation of CO by O_2 at 150–200°C over various catalyst specimens.

EXPERIMENTAL

Materials

Pure CuO–ZnO/Al_2O_3 samples were prepared by treated a known mass of finely powdered $Al(OH)_3$ solid with a calculated amount of zinc nitrate dissolved in the least amount of distilled water. The paste thus obtained was dried at 100°C and then calcined for 5 h at 500°C. The resulting solid was treated with copper nitrate dissolved in the least amount of distilled water, dried at 100°C and then heated in air at 600°C or 700°C, respectively. The nominal composition of the calcined samples thus obtained was $0.25CuO:0.06ZnO:Al_2O_3$.

The doped mixed solids were prepared by treating a known mass of $Al(OH)_3$ with $NaNO_3$ solution, drying at 100°C and then treating the dried solid with $Zn(NO_3)_2$ solution followed by impregnation with $Cu(NO_3)_2$ solution. The resulting materials were then dried at 100°C and calcined for 5 h in air at 600°C or 700°C, respectively. The concentrations of $NaNO_3$ solution employed corresponded to the addition of 0.75, 1.5 and 4.5 mol% Na_2O, respectively.

Techniques

X-Ray investigations of the pure and doped mixed solids, preheated in air at 600°C or 700°C as described above, were carried out using a Philips diffractometer (type PW 1390) employing Ni-filtered Cu radiation ($\lambda = 1.5405$ Å) at 36 kV and 16 mA with a scanning speed of 2° in 29 min^{-1}. Phase identification was achieved by matching the diffraction lines obtained for the various solids with appropriate ASTM cards (JCPDS 1979).

The surface properties of the solids, i.e. the values of S_{BET}, V_p and r for the various adsorbents, were determined from nitrogen adsorption isotherms measured at -196°C using a conventional volumetric apparatus. Before carrying out measurements, each sample was degassed by heating for 2 h at 200°C under a reduced pressure of 10^{-5} Torr.

The catalytic oxidation of CO by O_2 over the various adsorbents as catalysts was carried out at various temperatures between 150°C and 200°C using a static method and employing a stoichiometric mixture of CO and O_2 at a total pressure of 2 Torr. A fresh 200 mg catalyst sample was employed for each kinetic experiment, the sample being activated by heating for 2 h at 300°C at a reduced pressure of 10^{-6} Torr.

RESULTS AND DISCUSSION

X-Ray diffraction studies

X-Ray diffractograms of the pure and doped solids preheated at 600°C or 700°C were determined and are depicted in Figures 1 and 2, respectively. The results shown in Figure 1 indicate that calcination of the pure mixed solids at 600°C led to very poorly crystalline γ-alumina and a poorly crystalline CuO phase. The addition of Na₂O as a dopant resulted in a progressive increase in the relative intensity of the diffraction lines corresponding to the CuO phase. Thus, the height of the main diffraction line corresponding to the CuO phase was 5 arbitrary units for the pure mixed oxide sample and 10, 17 and 25 arbitrary units for the samples treated with 0.75, 1.5 and 4.5 mol% Na₂O, respectively, suggesting that Na₂O doping leads to an increase in the degree of crystallinity of the CuO phase to an extent proportional to the amount of dopant present. Such behaviour may be attributed to the location of Na^+ ions within tetrahedral and octahedral sites on the Al_2O_3 surface, leading to an effective decrease in the capacity of the Al_2O_3 phase towards the surface monolayer dispersion of CuO (Leyrer *et al.* 1986; El-Shobaky and Ibrahim 1989a; El-Shobaky *et al.* 1996b).

The results for the various solids calcined at 700°C depicted in Figure 2 indicate that an increase in the calcination temperature of the pure mixed oxides led to complete conversion of the CuO phase into a $CuAl_2O_4$ phase possessing moderate crystallinity. In contrast, the Na₂O-doped materials calcined at the same temperature consisted of a mixture of unreacted CuO and $CuAl_2O_4$ phases,
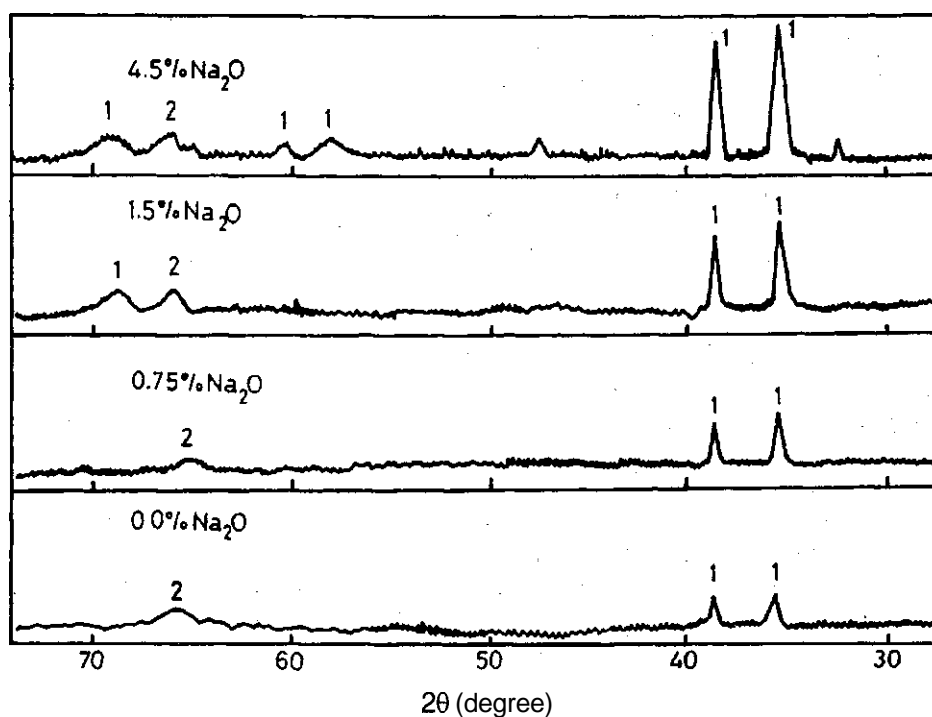

Figure 1. **X-Ray diffractograms for pure and doped CuO–ZnO/Al₂O₃ solids precalcined in air at 600°C. Peaks 1 correspond to the CuO phase; peaks 2 correspond to the γ-Al₂Oₓ phase.**
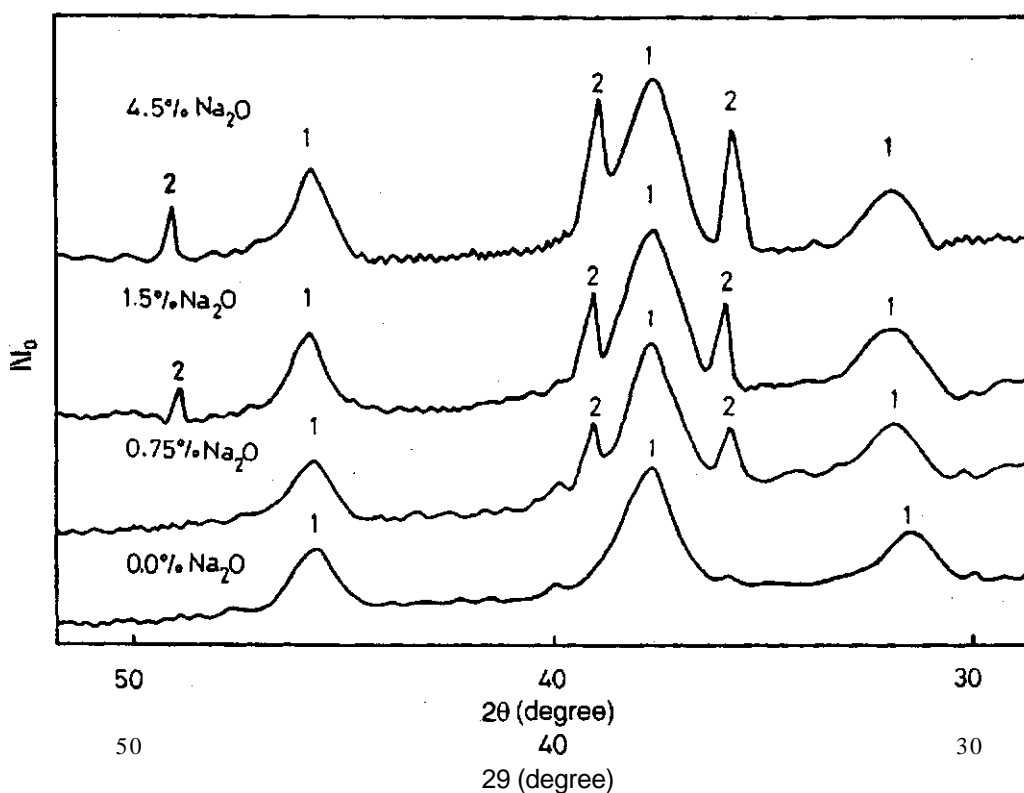
Figure 2. **X-Ray diffractograms for pure and doped CuO–ZnO/Al$_2$O$_3$ solids precalcined in air at 700°C. Peaks 1 correspond to the CuAl$_2$O$_4$ phase; peaks 2 correspond to the CuO phase.**

with the height of all the diffraction lines corresponding to the CuO phase increasing progressively as the dopant concentration increased. This finding clearly indicates that doping with Na$_2$O leads to a progressive hindering of the solid–solid interaction between CuO and Al$_2$O$_3$ which produces CuAl$_2$O$_4$. Such inhibition may be attributed to the formation of sodium aluminate during the thermal diffusion of Cu^{2+} ions into the Al$_2$O$_3$ matrix, thereby creating an energy barrier which must be overcome before the formation of CuAl$_2$O$_4$ can commence (El-Shobaky et al. 1989c). This explains why complete conversion of CuO into CuAl$_2$O$_4$ requires thermal treatment of the doped solids at temperatures above 700°C.

Surface properties of the pure and doped solids

The various surface properties of the pure mixed and doped solids were obtained from the corresponding nitrogen adsorption isotherms measured at −196°C. Figure 3 depicts the isotherms obtained for the various solids calcined at 700°C and indicate that all belong to type II of the classification advanced by Brunauer et al. (1967). The values of S$_{BET}$ for these various solids were computed from the linear plots derived from the BET equation. Such values are listed in Table 1 together with those of V$_p$ and r which were also computed from the isotherm data.

An additional set of specific surface areas, S$_t$, was obtained from the volume-thickness curves (V, versus t plots). Such plots were constructed using appropriate standard t-curves based on the magnitude of the C constant in the BET equation (Brunauer et al. 1940; Delleys 1963; Lippens and de Boer 1965). The corresponding plots for the samples calcined in air at 700°C are shown in

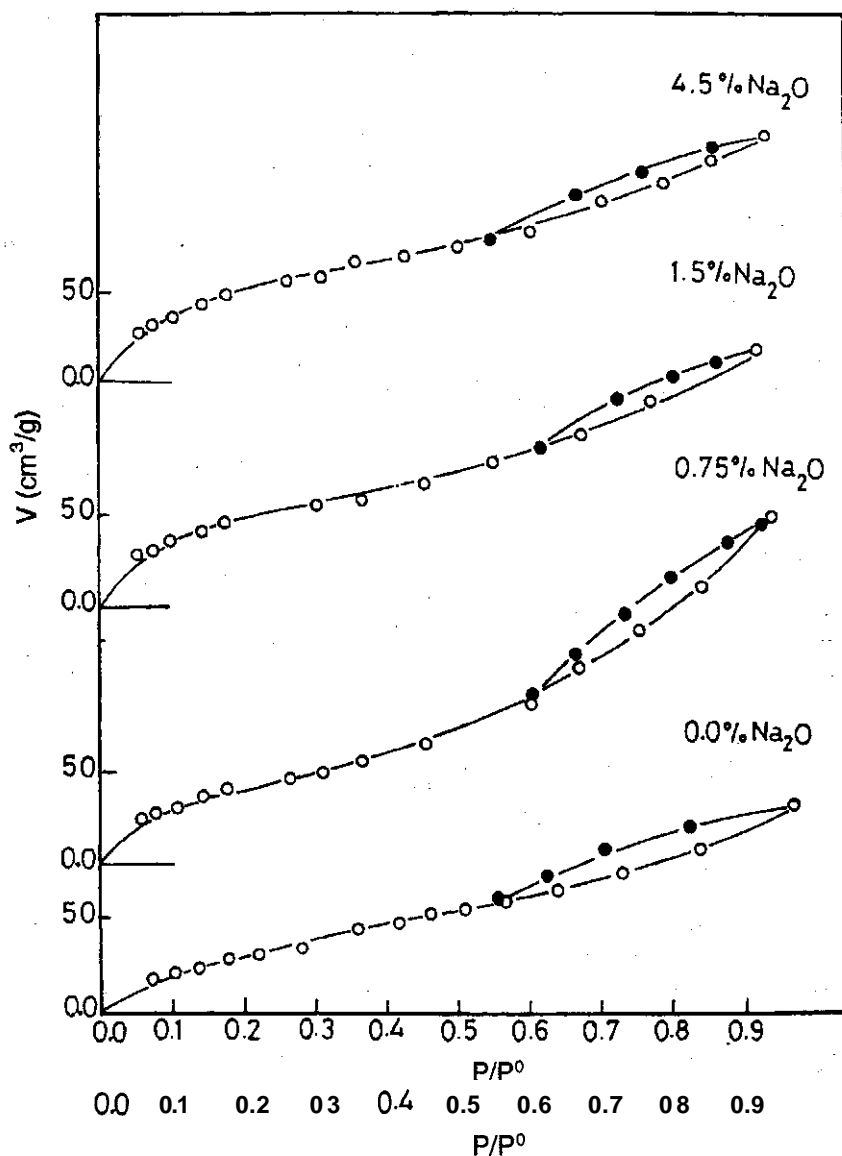Figure 3. **Nitrogen adsorption isotherms measured at −196°C for pure and doped CuO–ZnO/Al₂O₃ solids precalcined in air at 700°C.**

TABLE 1. Some Surface Characteristics of Pure and Na₂O-doped CuO–ZnO/Al₂O₃ Solids Calcined in Air at 700°C

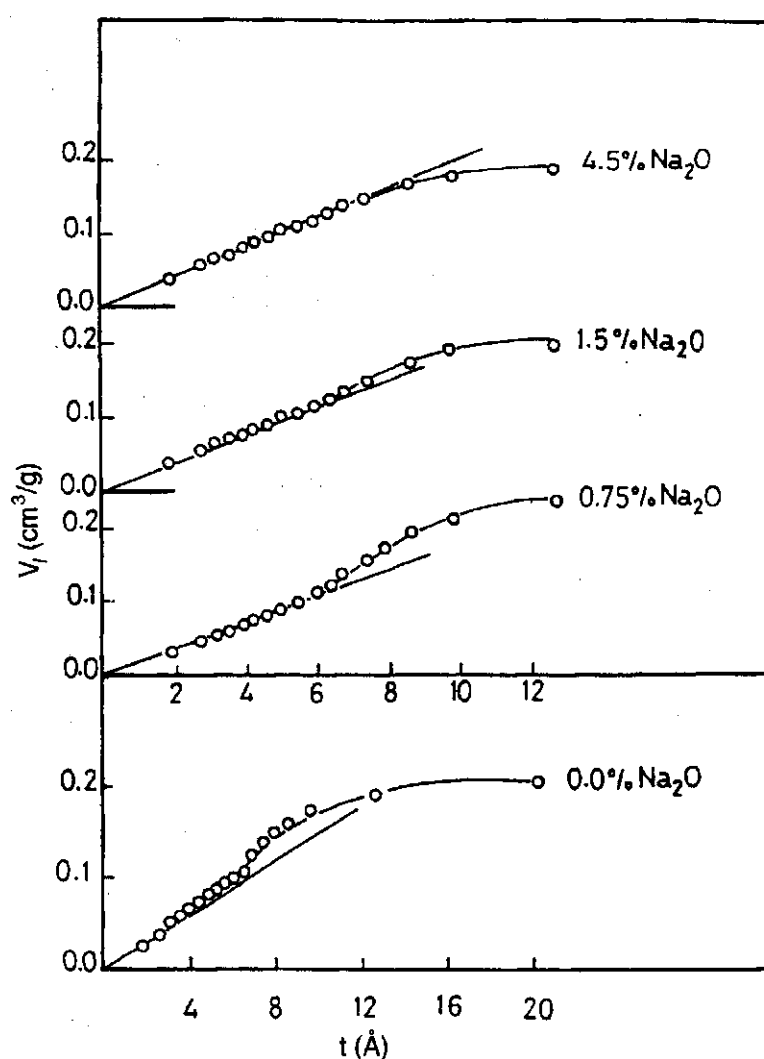| Na₂O content of solid (mol%)	S_{BET} (m²/g)	S_t (m-7g)	V_p (ml/g)	$\bar{r}$ (Å)	BET C constant
0.00	141	150	0.208	37	21
0.75	175	178	0.203	29	25
1.50	184	186	0.226	31	24
4.50	208	200	0.226	27	21

Figure 4. Volume versus thickness $(V_f - t)$ plots for pure and doped CuO–ZnO/Al$_2$O$_3$ solids precalcined in air at 700°C.

Figure 4 from which it is seen that, with the exception of the sample doped with 4.5 mol% Na$_2$O, all the solids exhibit similar V$_f$ versus t plots whose initial upward deviation indicates the existence of mainly wide pores. In contrast, the sample doped with 4.5 mol% Na$_2$O shows an initial downward deviation indicating that this solid contained mainly narrow pores.

Inspection of the data listed in Table 1 indicates the following for the pure mixed and doped solids calcined at 700°C.

1. The values of S$_{BET}$ and S$_t$ for the various samples studied are close to each other thereby justifying the choice of standard t-curves used for pore analysis as well as the absence of ultramicropores in the materials.

2. The addition of Na$_2$O as a dopant leads to an increase in the BET specific surface area, S$_{BET}$, for the solids studied.
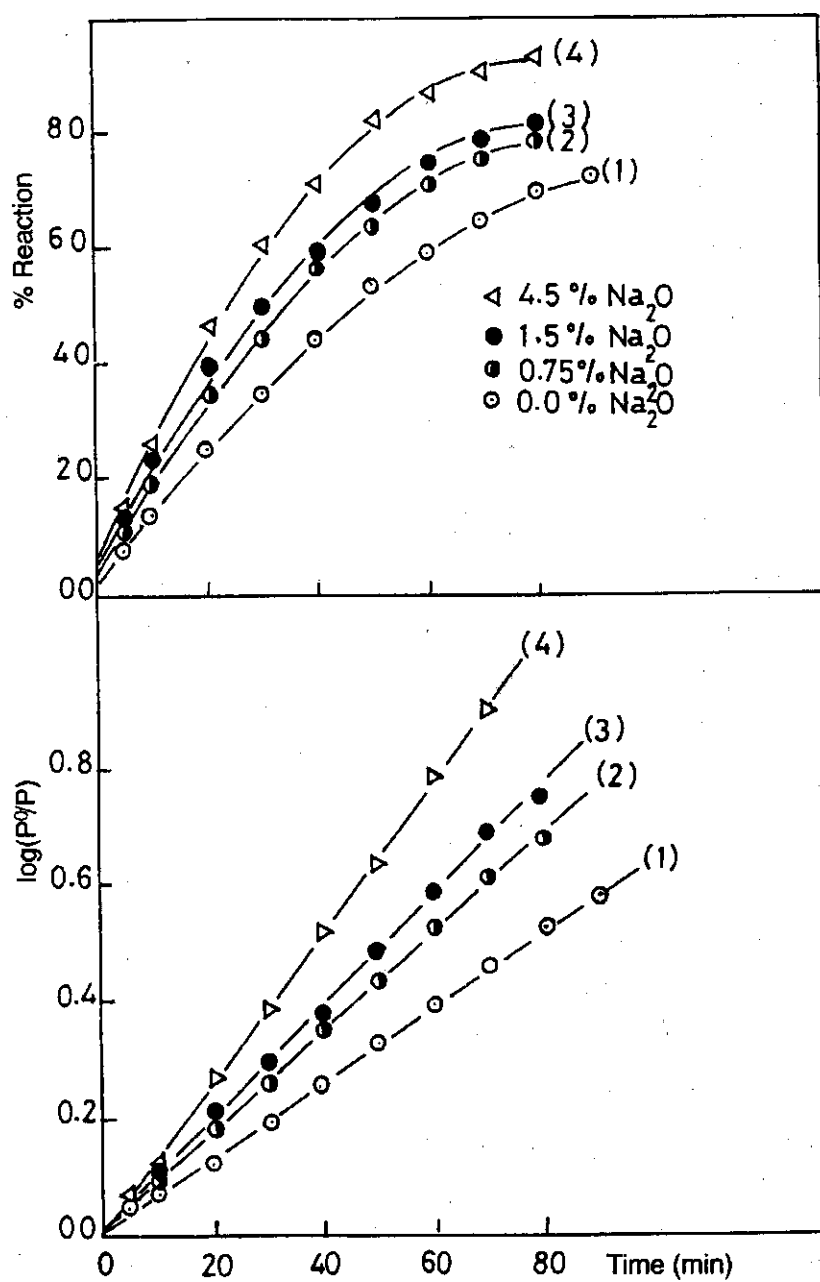
Figure 5. Kinetic curves and first-order plots for CO oxidation by O, conducted at 175°C over pure and doped CuO–ZnO/Al₂O₃ solids precalcined in air at 700°C.

3. The maximum increase in the value of S_{BET} for the doped materials was 67 m^2/g (48%), observed on the addition of 4.5 mol% Na_2O. This may be attributed to the creation of new pores arising from the liberation of nitrogen oxide gases during the thermal decomposition of $NaNO_3$.

4. However, it should be noted that doping with 4.5 mol% Na_2O also resulted in a decrease in the value of the mean pore radius $(\bar{r})$ from 37 A for the pure material to 27 A for the doped material, i.e. such addition led to pore narrowing. Hence, the increase in BET specific surface area could also be attributed to such pore narrowing as well as the creation of new pores.

Catalytic oxidation of CO over the pure and doped solids

The catalytic oxidation of CO by O_2 was studied at three different temperatures, i.e. 150, 175 and 200°C. First-order kinetics were observed in all cases. Figure 5 depicts representative first-order plots for the catalytic reaction carried out at 175°C over the pure and doped solids calcined in air at 700°C. This figure clearly shows that doping with Na_2O led to a considerable increase (ca. 100%) in the catalytic activity of the treated solids. Even the addition of the smallest amount of Na_2O studied (0.75 mol%) effected a ca. 30% increase in the catalytic activity of the resulting doped solid. The increase in the catalytic activity measured at 150, 175 and 200°C arising from the addition of 4.5 mol% Na_2O was 114%, 102% and 82%, respectively.

The increase in the catalytic activity observed on doping the various solids and calcining in air at 70Q°C suggests a corresponding increase in the concentration of catalytically active constituents taking part in the chemisorption/catalysis process involved in the CO oxidation reaction. In fact, the results reported above regarding the XRD investigations of the corresponding solids indicate that doping hinders the solid-solid interactions at 700°C between CuO and Al_2O_3 to produce $CuAl_2O_4$, the extent of such hindrance being proportional to the amount of Na_2O added. Hence, the observed increase in the catalytic activity can be related directly to the hindrance of $CuAl_2O_4$ formation, i.e. to the proportion of unreacted CuO present in the doped materials. This deduction is in line with previous observations that CuO exhibits a higher catalytic activity towards oxidation/reduction reactions than $CuAl_2O_4$ (El-Shobaky and Al-Noaimi 1987; Bolt et al. 1994a).

Activation energy (AE) for the catalyzed reaction over the pure and doped solids

The computed values of AE for the various solids investigated are listed in Table 2, which also includes the value of log A (the frequency factor) calculated for these materials. The data listed indicate that the addition of only 0.75 mol% Na_2O resulted in a decrease in the value of AE from 22.9 kJ/mol to 16 kJ/mol, with the latter value remaining constant as the dopant concentration was increased further to 4.5 mol%.

Recalculating the value of AE for the various concentrations of dopant added using the value of log A for the pure material (0.555) gave the values of ΔE^* listed in Table 2. These latter corrected values indicate that the addition of Na_2O to the pure material, followed by calcination at 700°C, had little effect on the activation of the catalyzed reaction whose value remained constant at 22 ± 1 kJ/mol irrespective of the amount of dopant added. In other words, the addition of Na_2O to the system did not modify the mechanism of CO oxidation in the presence of O_2 but merely increased the concentration of catalytically active constituents by hindering the solid-solid interaction between CuO and Al_2O_3 and thereby increasing the content of CuO in the system.

TABLE 2. Activation Energies (AE, ΔE^*) and Frequency Factor (A) for the Catalytic Oxidation of CO by O_2 over Pure and Na_2O-doped CuO–ZnO/Al₂O₃ Solids Calcined in Air at 700°C

Na_2O content of solid (mol%)	AE (kJ/mol)	log A	AE* (kJ/mol)
0.00	22.9	0.555	22.9
0.75	16.1	-0.108	21.8
1.50	16.1	-0.058	21.6
4.50	16.1	-0.086	21.2

CONCLUSIONS

The main conclusions arising from the present study may be summarized as follows:

1. The use of Na_2O as a dopant in the CuO–ZnO/Al₂O₃ system enhances the crystallization of the CuO phase at 600°C and hinders the formation of $CuAl_2O_4$ at 700°C.

2. When Na_2O-doped samples were calcined at 700°C, this led to an increase in the value of S_{BET} (48%), with the dominant porosity of the heavily doped solids arising from the presence of narrow pores.

3. The catalytic activity of Na,0-doped CuO–ZnO/Al₂O₃ solids calcined at 700°C increased as the dopant concentration increased. The increase observed may be attributed to the dopant hindering the formation of $CuAl_2O_4$ at this temperature.

4. Such doping of solids calcined at 700°C did not modify the activation energy of the catalyzed CO/O_2 reaction but rather increased the concentration of catalytically active constituents participating in the process.

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