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Physicochemical surface and catalytic properties of CuO–ZnO/Al₂O₃ system

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Abstract

A series of CuO–ZnO/Al₂O₃ solids were prepared by wet impregnation using Al(OH)₃ solid and zinc and copper nitrate solutions. The amounts of copper and zinc oxides were varied between 10.3 and 16.0 wt% CuO and between 0.83 and 7.71 wt% ZnO. The prepared solids were subjected to thermal treatment at 400–1000°C. The solid–solid interactions between the different constituents of the prepared solids were studied using XRD analysis of different calcined solids. The surface characteristics of various calcined adsorbents were investigated using nitrogen adsorption at –196°C and their catalytic activities were determined using CO-oxidation by O₂ at temperatures ranged between 125°C and 200°C.

The results showed that CuO interacts with Al₂O₃ to produce copper aluminate at ≥600°C and the completion of this reaction requires heating at 1000°C. ZnO hinders the formation of CuAl₂O₄ at 600°C while stimulates its production at 800°C. The treatment of CuO/Al₂O₃ solids with different amounts of ZnO increases their specific surface area and total pore volume and hinders their sintering (the activation energy of sintering increases from 30 to 58 kJ mol^{–1} in presence of 7.71 wt% ZnO). This treatment resulted in a progressive decrease in the catalytic activities of the investigated solids but increased their catalytic durability. Zinc and copper oxides present did not modify the mechanism of the catalyzed reaction but changed the concentration of catalytically active constituents (surface CuO crystallites) without changing their energetic nature. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

γ-Al₂O₃ is considered as the most convenient support for a big variety of catalysts especially those used in oxidation–reduction reactions. However, the catalytic activities of γ-Al₂O₃-supported solids decrease progressively as a function of time of use due to an enhanced formation of metal aluminate which exhibits a lower catalytic activity as compared with the metal

oxide itself [1,2]. It has been reported by Bolt et al. [2] that the reaction between the transition metal oxide and Al₂O₃ to produce metal aluminate is strongly dependent upon the nature of the transition metal element. According to these authors the rate of reaction between the metal oxide and Al₂O₃ decreases in the following order: Cu>Co>Ni>>Fe.

The preparation of technical catalysts that having high activity and durability requires the presence of what is called catalyst stabilizer whose function is to prevent or to inhibit metal–support interaction. MoO₃

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is added to $\text{CoO}/\text{Al}_2\text{O}_3$ to suppress the formation of cobalt aluminate by preventing cobalt ions from entering the $\gamma\text{-Al}_2\text{O}_3$ lattice [3,4]. It has been reported by El-Shobaky et al. [5,6] that the doping of Al_2O_3 either with Li_2O or with Na_2O hinders the CuAl_2O_4 formation due to the formation of Li or Na-aluminates films covering the surface of Al_2O_3 particles and suppress the diffusion of copper species through the interior of the Al_2O_3 particles [5].

Zinc oxide acts as catalyst stabilizer in $\text{CuO-ZnO}/\text{Al}_2\text{O}_3$ solids employed in low-temperature water–gas shift reaction [1,6,7], in CO-oxidation by O_2 [8], in methanol synthesis [9] and dimethyl ether synthesis from methanol [10]. The mechanisms of stabilization process have been tentatively investigated in recently published work [8].

The present investigation reports a study on the effects of CuO, ZnO contents and precalcination conditions on physicochemical, surface and catalytic properties of $\text{CuO-ZnO}/\text{Al}_2\text{O}_3$ solids. The techniques employed were XRD, nitrogen adsorption at -196°C and oxidation of CO by O_2 125–200°C over various catalyst specimens.

2. Experimental

2.1. Materials

$\text{CuO-ZnO}/\text{Al}_2\text{O}_3$ samples were prepared by treating a known mass of finely powdered $\text{Al}(\text{OH})_3$ solid with a solution containing a calculated amount of zinc nitrate drying at 100°C followed by calcination at 500°C for 5 h. The obtained solid was treated with copper nitrate dissolved in the least amount of distilled water, dried at 100°C and heated in air at temperatures varying between 400°C and 1000°C for 5 h. The concentration of copper oxide was varied between 10.3 and 16.0 wt% CuO and that of zinc oxide was changed between 0.83 and 7.71 wt% ZnO. Aluminium hydroxide was prepared by precipitation from aluminium nitrate solution using 0.2 M NH_4OH at 70°C and $\text{pH}=8$, the precipitate was washed with distilled water till free from NH_4^+ and NO_3^- ions then dried at 100°C till constant weight. The chemicals used were of analytical grade supplied by Prolabo company. Table 1 includes the nominal chemical compositions of the various prepared mixed solids, which should be

Table 1
Chemical compositions of various prepared solids

Solid molecular formula	Symbols	CuO (wt%)	ZnO (wt%)
0.25 $\text{CuO}:\text{Al}_2\text{O}_3$	CuAl	10.3	0.00
0.25 $\text{CuO}:0.0125 \text{ ZnO}:\text{Al}_2\text{O}_3$	CuZnAl-I	16.2	0.83
0.25 $\text{CuO}:0.03 \text{ ZnO}:\text{Al}_2\text{O}_3$	CuZnAl-II	16.0	1.96
0.25 $\text{CuO}:0.06 \text{ ZnO}:\text{Al}_2\text{O}_3$	CuZnAl-III	15.7	3.86
0.25 $\text{CuO}:0.125 \text{ ZnO}:\text{Al}_2\text{O}_3$	CuZnAl-IV	15.1	7.71

close to the real compositions because the chemicals used were of analytical grade and the catalysts samples were prepared by impregnation method.

2.2. Techniques

The X-ray powder diffraction patterns of the various solids precalcined at $400\text{--}1000^\circ\text{C}$ were carried out using a Philips diffractometer (type PW 1390). The patterns were run with nickel-filtered copper radiation ($\lambda=1.5405 \text{ \AA}$) at 36 kV and 16 mA with a scanning speed of 2° in 20 min^{-1} .

The surface properties namely, BET-surface area, total pore volume (V_p) and mean radius (\bar{r}) were determined from nitrogen adsorption isotherms measured at -196°C using conventional volumetric apparatus. Before carrying out the measurements each sample was degassed under a reduced pressure of 10^{-5} Torr at 200°C for 3 h.

The catalytic oxidation of CO by O_2 on different catalyst samples was conducted at temperatures between 125°C and 200°C using a static method. A stoichiometric mixture of CO and O_2 at a pressure of 2 Torr was used. This method is simple and permits to follow up the kinetics of catalytic reaction by measuring the drop in pressure of reacting gases as a function of time. A fresh 200 mg catalyst sample, activated by heating under a reduced pressure of 10^{-6} Torr at 300°C for 2 h., was employed in each kinetic experiment.

3. Results and discussion

3.1. Solid–solid interactions in $\text{CuO-ZnO}/\text{Al}_2\text{O}_3$ system

XRD diffractograms of the various prepared mixed solids subjected to heating in air 400, 600, 800 and

1000°C were measured. The XRD patterns of different mixed solids preheated in air at 400°C, not given, are similar to each other and show the presence of well crystallized CuO phase and poorly crystalline γ -Al₂O₃. The diffractograms of the mixed solids subjected to heating in air at 600°C, not given here, revealed that these solids consist of a mixture of well crystallized CuO phase and CuAl₂O₄ phase with moderate crystallinity besides poorly crystalline γ -Al₂O₃. The comparison between the diffractograms of different solids reveals that:

1. The presence of ZnO decreases the intensity of diffraction lines of CuO phase to an extent proportional to its amount present.
2. ZnO leads to a decrease in the diffraction lines of CuAl₂O₄ phase.
3. The addition of 7.71 wt% ZnO prevents completely the formation of copper aluminate besides the presence of a portion of ZnO as a separate phase.

It can thus be concluded that zinc oxide hinders the solid–solid interaction between CuO and Al₂O₃ at 600°C and decreases the crystallinity of copper oxide crystallites which may be taken as evidence for higher degree of dispersion in CuO on γ -Al₂O₃.

The possible interaction between ZnO and Al₂O₃ to form ZnAl₂O₄ might decrease the possibility of the reaction $\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4$. However, this assumption could not account for the observed role of ZnO in inhibiting the formation of CuAl₂O₄ simply because the amount of ZnO is small (0.83–7.71 wt%) and the calcination temperature (600°C) are not favourable for ZnAl₂O₄ formation which needs thermal treatment at $\geq 600^\circ\text{C}$ [11]. The hinderance of CuAl₂O₄ formation due to ZnO-treatment of CuO/Al₂O₃ followed by heating in air at 600°C might result from coating of the top surface layers of Al₂O₃ particles by ZnO species that inhibited the diffusion of CuO species in the alumina matrix to form copper aluminate.

Fig. 1 shows XRD diffractograms of the investigated solids preheated at 800°C. Inspection of this figure reveals that:

1. ZnO-free sample consists of CuO, CuAl₂O₄ and poorly crystalline γ -Al₂O₃.
2. The addition of ZnO (0.83–7.71 wt%) results in a progressive increase in the intensity of the diffraction lines of CuAl₂O₄ phase to an extent proportional to its amount present.

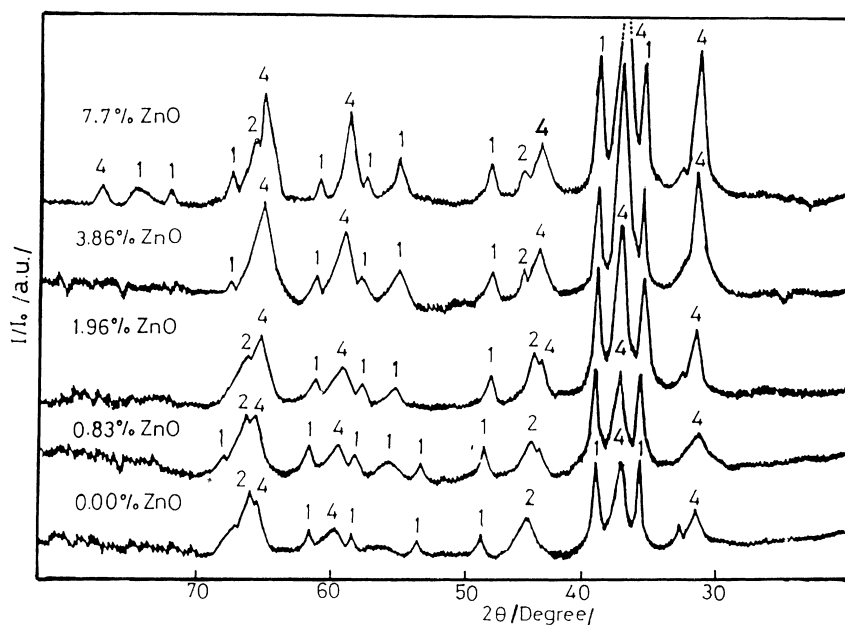


Fig. 1. X-ray diffractograms of CuO/Al₂O₃ containing different amounts of ZnO and preheated in air at 800°C: (1) CuO, (2) γ -Al₂O₃, and (4) CuAl₂O₄.

These results indicate that ZnO stimulates the solid–solid interaction between CuO and Al₂O₃ forming CuAl₂O₄ by heating the mixed oxides in air at 800°C. So, ZnO behaves in a manner opposite to that manifested by thermal treatment at 600°C. The enhancement of copper aluminate formation at 800°C due to ZnO, to our knowledge, has not been reported before. These findings point out to the role of calcination temperature in solid–solid interaction between CuO and Al₂O₃ in presence of small amounts of ZnO.

The rise in calcination temperature of different mixed solids to 1000°C resulted in a complete conversion of copper oxide into CuAl₂O₄ and transformation of γ -Al₂O₃ to α -Al₂O₃ (corundum). This conclusion comes from inspection of XRD patterns, not given here, for the various mixed solids calcined at 1000°C. The addition of ZnO to CuO/Al₂O₃ brought

about a progressive decrease in the intensity of diffraction lines of the crystallization of α -Al₂O₃ by heating CuO/Al₂O₃ solids at 1000°C similar effect has been reported in the case of Li₂O and Na₂O-treatment of CuO/Al₂O₃ solids [5]. Details of solid–solid interactions in pure and Li₂O-treated CuO–ZnO/Al₂O₃ solids subjected to thermal treatment at 400–1000°C have been reported in our recent investigation [12].

3.2. Surface properties of different adsorbents

The different surface characteristics namely, specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (\bar{r}) of the various adsorbents were determined from nitrogen adsorption isotherms measured at –196°C. The results obtained are give in Table 2.

Table 2

Some surface characteristics of different investigated solids precalcined at various temperatures

Sample	Calcined temperature (°C)	S_{BET} (m ² g ^{–1})	S_t (m ² g ^{–1})	V_p (cm ³ g ^{–1})	\bar{r} (Å)	BET-C
Al ₂ O ₃	400	235	213	0.372	32	38
	600	194	180	0.282	29	45
	800	180	166	0.340	37	47
	1000	136	130	0.307	45	64
CuAl	400	249	257	0.319	26	25
	600	189	200	0.242	25	29
	800	128	122	0.223	34	28
	1000	117	113	0.161	28	6
CuZnAl-I	400	270	281	0.264	19	32
	600	172	175	0.233	27	32
	800	136	156	0.242	35	11
	1000	128	125	0.233	36	8
CuZnAl-II	400	236	238	0.242	20	37
	600	199	214	0.285	27	16
	800	147	144	0.233	31	13
	1000	95	94	0.194	41	11
CuZnAl-III	400	273	278	0.279	21	27
	600	161	163	0.217	26	23
	800	131	126	0.226	34	18
	1000	94	89	0.155	33	12
CuZnAl-IV	400	286	263	0.288	20	38
	600	233	243	0.310	27	45
	800	147	150	0.202	27	47
	1000	91	94	0.136	29	64

Another series of specific surface area S_t was calculated from the V_{1-t} plots of the different investigated adsorbents. These plots were constructed using suitable standard t -curves depending on the C -constant in the BET-equation.

Inspection of Table 2 reveals that the values of S_{BET} and S_t are close to each other, within the experimental errors which indicates the correct choice of the reference t -curves for analysis and shows the absence of ultramicropores.

The determination of activation energy of sintering (ΔE_s) for the various investigated adsorbents can throw more light about the effect of ZnO in the sinterability of CuO–ZnO/Al₂O₃ system. ΔE_s can be readily determined from the data of S_{BET} as a function of calcination temperature for the various investigated adsorbents adopting the method proposed by one of the authors [13]. The relationship between ΔE_s and S_{BET} can be given by the equation:

$$S_{\text{BET}} = A \exp(-\Delta E_s/RT),$$

where A is a constant and ΔE_s is the approximate activation energy of sintering. When $\log S_{\text{BET}}$ is plotted against $1/T$ a straight line is obtained, the slope of which determines the value of ΔE_s .

Fig. 2 shows plots of $\log S_{\text{BET}}$ against $1/T$ for different solids preheated in air at 400–1000°C. The computed ΔE_s values are 30, 34, 42, 47, 48 and

58 kJ mol⁻¹ for Al₂O₃, CuAl, CuZnAl-I, CuZnAl-II, CuZnAl-III and CuZnAl-IV samples, respectively. Inspection of these results shows that:

1. The presence of CuO (16.2 wt%) causes an increase in the value of ΔE_s .
2. ZnO increases progressively the activation energy of sintering to an extent proportional to its amount present, i.e. the addition of CuO and ZnO to Al₂O₃ support material suppress the sintering of the treated mixed solids. The suppression of sintering process and the increase of specific surface area of CuO–ZnO/Al₂O₃ system due to treatment with ZnO (0.83–7.71 wt%) are expected to be accompanied by an improvement in its catalytic activity.

3.3. Catalytic activity of CuO–ZnO/Al₂O₃ system

3.3.1. Effect of ZnO

The catalytic oxidation of CO by O₂ was conducted over CuO/Al₂O₃ solids treated with ZnO (0.83–7.71 wt%) and subjected to heating in air at 400°C, 600°C and 800°C. First-order kinetics were found in all cases, the slope of each first-order plot determines the values of reaction rate constant (k).

Fig. 3 shows representative first-order plots of CO-oxidation by O₂ carried out at 125°C over zinc-free catalyst sample calcined at 400°C and those containing different amounts of ZnO and heated at 400°C. The catalytic reaction was done over the various investigated catalyst samples calcined at 400°C, 600°C and 800°C and the reaction was carried out at 125–200°C. The reaction rate constant (k) was calculated for each sample at different reaction temperatures. Table 3 includes the values of k for different samples. It can be seen from Table 3 that ZnO decreases the catalytic activity of CuO/Al₂O₃ precalcined at 400°C and 600°C to an extent proportional to its amount present. The decrease is, however, more pronounced for the catalysts calcined at 400°C. On the other hand, ZnO exerts no significant change in the catalytic activity of the catalysts precalcined at 800°C. The observed decrease in the activity to ZnO-treatment followed by heating at 400°C and 600°C could not be attributed to the induced modifications in the surface characteristics of the treated catalysts simply because the catalyst sample containing 7.71 wt% ZnO measures the highest specific surface area and exhibits

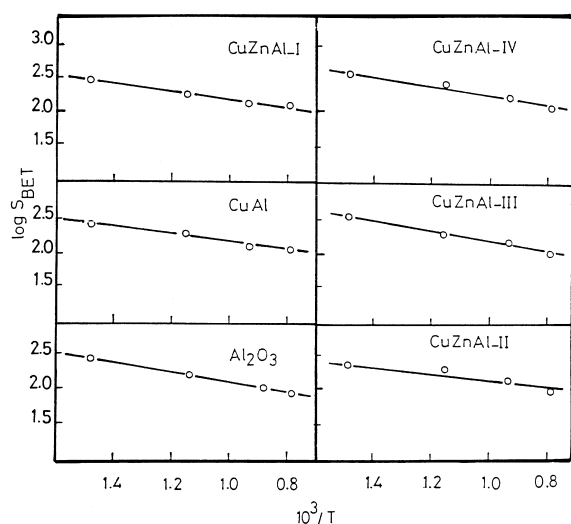


Fig. 2. Variation of $\log S_{\text{BET}}$ versus $1/T$ for different solids.

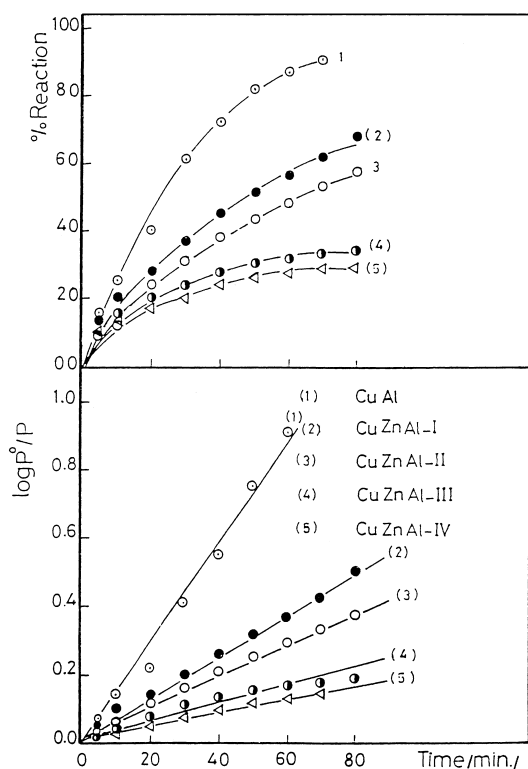


Fig. 3. First order plots of CO oxidation reaction carried out at 125°C over various catalysts preheated at 400°C.

the lowest catalytic activity (c.f. Tables 2 and 3). Indeed, the XRD analysis of different solids precalcined at 600°C showed that ZnO hinders the solid–solid interaction between CuO and Al₂O₃ to produce CuAl₂O₄ of lower catalytic activity compared with CuO phase(11). In the light of the textural properties and solid–solid interaction between CuO and Al₂O₃ of the investigated solids containing different amounts of ZnO, one might expect an increase in the catalytic

activity of CuO/Al₂O₃ catalysts. However, opposite effect was observed.

The enhancement of CuAl₂O₄ formation due to ZnO-treatment of CuO/Al₂O₃ solids, followed by calcination at 800°C, might be expected to be followed by a measurable decrease in the catalytic activity of the treated solids. This expectation has not been verified experimentally because no significant change in the catalytic activity was found.

The observed change in the catalytic activity of CuO/Al₂O₃ solids due to the treatment with ZnO and calcination at 400°C and 600°C should be discussed in terms of the concentration of catalytically active constituents (CuO crystallites) in the uppermost surface layers of the treated catalysts. The induced decrease in the catalytic activity due to ZnO-treatment suggests that this treatment effects a decrease in the surface concentration of CuO crystallites. The zinc oxide-treated CuO–Al₂O₃ solids were prepared by impregnating the support material with Zn(NO₃)₂ solution prior to treating with Cu(NO₃)₂ solution. It seems that this method of preparation might cause a preferential absorption of zinc species on the uppermost surface layers of the catalyst's support. Consequently, the area available for copper species decreases.

The fact that the extent of decrease in the catalytic activity due to ZnO-treatment of CuO/Al₂O₃ solids diminishes by increasing the calcination temperature from 600°C to 800°C suggests that the rise in the calcination temperature of the treated solids might enhance the diffusion of ZnO from the top surface layers towards the interior of the treated solids. The diffusion process might result from a concentration gradient of ZnO in surface and bulk of the treated catalysts [14]. The diffusion of ZnO from surface towards the bulk might be accompanied by more

Table 3

Effect of ZnO content on the values of k measured at different temperatures over various catalysts calcined at 400°C, 600°C and 800°C

Catalyst	ZnO (wt%)	Calcination temperature (°C)		
		400 [$k_{125} \times 10^{-3}$] (min ⁻¹)	600 [$k_{175} \times 10^{-3}$] (min ⁻¹)	800 [$k_{200} \times 10^{-3}$] (min ⁻¹)
CuAl	0.00	14.6	24.5	16.7
CuZnAl-I	0.83	6.3	22	14.2
CuZnAl-II	1.96	4.6	16.3	16.0
CuZnAl-III	3.86	2.8	14.4	16.0
CuZnAl-IV	7.71	2.0	12.7	16.0

chances for CuO to be located on the uppermost surface layers of the treated solids. In other words, the increase in calcination temperature of ZnO-treated solids from 600°C to 800°C might increase the concentration of CuO crystallites on the uppermost surface layers of these solids.

The enhanced formation of CuAl₂O₄ due to ZnO-treatment of CuO/Al₂O₃ solids calcined at 800°C should be accompanied by an important decrease in their catalytic activity which has not been found. One might expect an enhanced diffusion of CuO from the interior of the catalysts towards their outermost surface layers increasing thus the concentration of the catalytically active constituents in the ZnO-treated catalysts calcined at 800°C. The diffusion of CuO and formation of copper aluminate exert opposite effects on the catalytic activity of the treated solids. The confirmation of an enhanced diffusion of CuO due to ZnO-treatment needs to be verified by XPS-analysis which permits an accurate determination of the copper species on the top surface layers of the treated catalysts [14–16]. However, it is plausible to argue that Cu/Al₂O₄ formation takes place via migration of CuO on the outermost surface layers towards the interior of the Al₂O₃ support material forming CuAl₂O₄. The progressive diffusion of CuO might lead to formation of increasing amounts of copper aluminate. It follows

that the concentration of copper on the top surface layers of the treated solids calcined at 800°C might be smaller than that in the bulk of these solids i.e. a concentration gradient exists from bulk to the surface and the heating process at 800°C resulted in migration of CuO species from the interior of the catalysts towards the outermost surface layers. The fact that ZnO-treatment of CuO/Al₂O₃ solids calcined at 800°C did not much change the catalytic activity of the treated solids suggests that the effect of an enhanced formation of CuAl₂O₄ was counteracted by diffusion of CuO from the interior of the catalysts towards their top surface layers.

The determination of the activation energy (ΔE) of CO-oxidation by O₂ over different ZnO-treated solids can throw more light on the role of zinc oxide in changing the mechanism of the catalyzed reaction. This has been done by determining the catalytic reaction rate constant (k) at different temperatures on various catalyst samples via applying the Arrhenius equation. The computed ΔE values are given in Table 4. Inspection of Table 4 shows that:

1. ΔE increases progressively by increasing the amount of ZnO in CuO/Al₂O₃ solids calcined at 400°C. These results express the observed decrease in their catalytic activity due to this treatment.

Table 4

Apparent activation energies ΔE , ΔE^* and frequency factor (A) of the catalytic reaction conducting over different catalysts

Catalyst	Calcination temperature (°C)	Temperature ranged for ΔE (°C)	ΔE (kJ mol ⁻¹)	ln A	ΔE^* (kJ mol ⁻¹)
CuAl-I	400	125–175	10.4	–1.31	10.4
CuZnAl-I		125–175	26.3	2.33	12.6
CuZnAl-II		125–175	30.6	1.93	12.9
CuZnAl-III		125–175	50.9	8.66	13.5
CuZnAl-IV		125–175	45.9	7.18	13.9
CuAl	600	125–175	58.3	11.17	58.3
CuZnAl-I		125–175	41.8	10.71	59.1
CuZnAl-II		125–175	49.5	8.63	58.1
CuZnAl-III		125–175	39.2	5.85	59.1
CuZnAl-IV		125–175	12.7	–1.22	59.1
CuAl	800	150–200	16.0	–0.08	16.0
CuZnAl-I		150–200	14.0	–0.83	16.9
CuZnAl-II		150–200	71.0	4.3	15.3
CuZnAl-III		150–200	38.0	5.76	16.0
CuZnAl-IV		150–200	43.0	7.11	16.0

2. ZnO-treatment of the investigated solids at 600°C decreases the values ΔE . This decrease in the values of ΔE does not express the observed decrease in the catalytic activity of the treated solids.
3. ZnO-treatment changes ΔE in a complex manner for the investigated solids calcined at 800°C.

These findings do not also express the observed change in the catalytic activity of these solids. This discrepancy has been solved by recomputing ΔE values taking into consideration the possible changes in the values of the pre-exponential factor (A) in the Arrhenius equation. Column 5 of Table 4 includes the values of $\ln A$ calculated for different solids. It is seen, that the observed change in the values of ΔE due to ZnO-treatment of the solids calcined at 400°C, 600°C and 800°C results mainly, from a corresponding change in the value of A . In fact, the recalculation of ΔE values adopting the (A) value of ZnO-free catalyst calcined at a given temperature to the other ZnO-containing catalyst samples calcined at the same temperature ΔE^* values were obtained and given in the last column of Table 4. The ΔE^* are close for ZnO-free catalyst sample (within the experimental error $\pm 2 \text{ kJ mol}^{-1}$) and those treated with different amounts of ZnO and calcined at 400–800°C. These findings show that ZnO-treatment of CuO/Al₂O₃ solids did not modify the mechanism of the catalytically-active constituents (surface CuO crystallites). This conclusion finds an additional evidence from the plot of the equation $A = a \exp(h \Delta E)$ derived on the basis of the dissipation function of active sites by their energy as a consequence of surface heterogeneity: $F(E_i) = a \exp(h E_i)$, where E_i is the energy of interaction of site “ i ” with the substrate [17]. The plot of $\ln A$ versus ΔE for different ZnO-treated catalyst samples gives a straight line Fig. 4 whose slope and intercept determine the values of (h) and (a) are 0.22 and 0.05; 0.27 and 0.01; 0.27 mol kJ^{-1} and 0.01 min^{-1} for different treated solids calcined at 400°C, 600°C and 800°C, respectively. The constants (h) and (a) values indicate that the ZnO-treatment of CuO/Al₂O₃ solids did not change the dissipation of the active sites i.e. the character of surface heterogeneity. In other words, this treatment did not change the energetic nature of active sites but changes (decreases) their concentration. The commercial catalyst used in low temperature water–gas shift reaction is composed

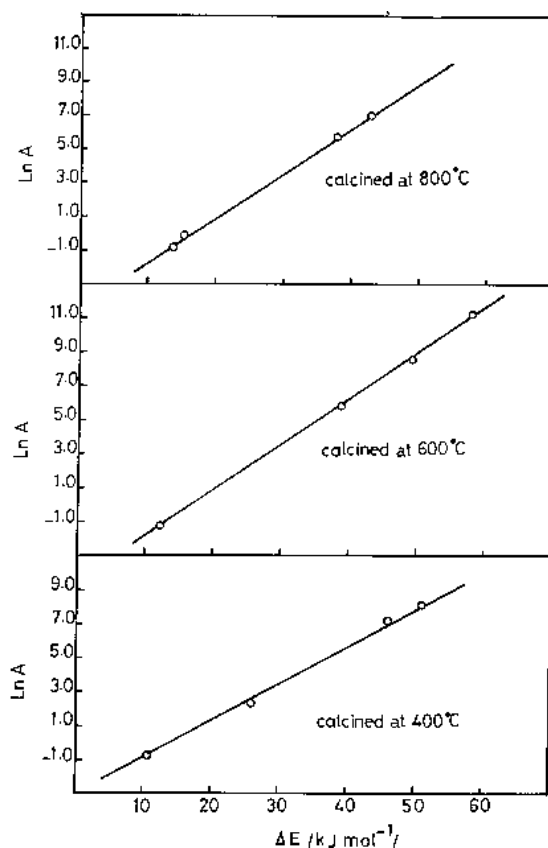


Fig. 4. Relationship between ΔE and frequency factor for the catalytic reaction conducted over different catalysts.

of CuO/Al₂O₃ solids treated with convenient amount of ZnO [1,6,7]. The addition of ZnO although decreases the catalytic activity of the treated solids it increases their durability. This conclusion has been reached at in our recent investigation [8], by following up the reaction of CO-oxidation by O₂ on different regenerated catalyst samples. The catalytic activity of ZnO-containing CuO/Al₂O₃ solids, being regenerated several times is 10-fold that measured for a regenerated sample free ZnO.

3.3.2. Effect of calcination temperature on the catalytic activity of different ZnO-treated CuO/Al₂O₃ solids

The effect of precalcination temperature on the catalytic activity of various CuO–ZnO/Al₂O₃ solids is better investigated by plotting the reaction rate constant per unit surface (\bar{k}) as a function of calcina-

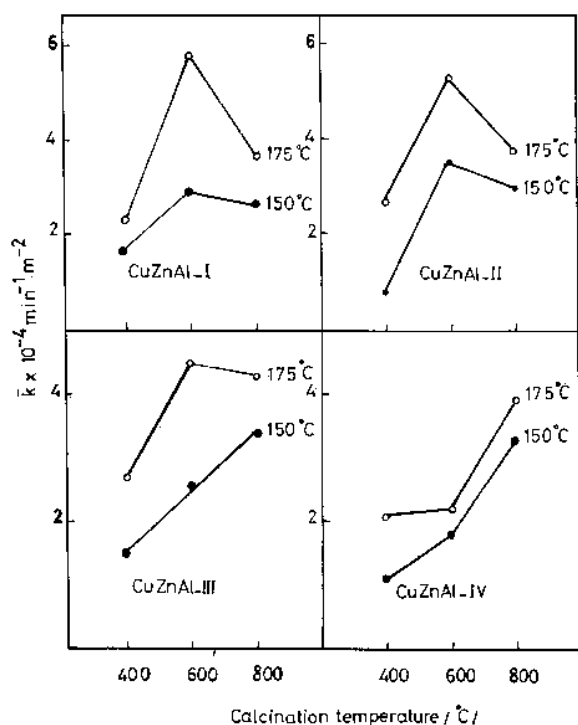


Fig. 5. Relationship between \bar{k} of CO-oxidation reaction conducted at various temperatures, as a function of calcination temperature for different solids.

tion temperature for different solids. Fig. 5 shows the relation between \bar{k} of CO-oxidation by O_2 conducted at various temperatures as a function of calcination temperature for different CuO–ZnO/ Al_2O_3 solids.

It is seen from Fig. 5 that the relation between \bar{k} and calcination temperature of different investigated catalyst samples shows maxima located at 600°C, except the sample containing 7.71 wt% ZnO. The ascending parts of the curves in Fig. 5 can be attributed to an effective removal of OH groups strongly bound to the catalyst surface whose removal needs a prolonged heating at temperature $\geq 450^\circ\text{C}$ [18,19]. These groups occupy a fraction of the catalyst surface preventing it from being involved in chemisorption and catalysis of CO-oxidation reaction. The removal of surface OH groups might be followed by a significant increase in the concentration of catalytically-active sites (surface CuO crystallites) taking part in different processes of the catalytic reaction.

The descending part of the curves in Fig. 5 (600–800°C) can be attributed to inward migration of CuO

from top surface layers of the catalyst towards the interior of its grains [14–16] and to the formation of CuAl_2O_4 which exhibits a catalytic activity lower than that measured for CuO itself [1]. The inward migration of CuO and the formation of copper aluminate can account for the observed decrease in the catalytic activity of CuO–ZnO/ Al_2O_3 solids being calcined at 800°C.

4. Conclusions

These are the main conclusions that can be drawn from the obtained results:

1. CuO interacts with Al_2O_3 to produce CuAl_2O_4 at temperature starting from 600°C, the complete conversion of copper oxide into copper aluminate requires the heating of mixed oxide solids at 1000°C. ZnO hinders the formation of CuAl_2O_4 produced at 600°C and stimulates its formation at 800°C.
2. ZnO-treatment of CuO/ Al_2O_3 solids increases their specific surface area and total pore volume. This treatment increases also the activation energy of sintering due to thermal treatment at temperatures in the range of 400–1000°C.
3. The catalytic activity of CuO–ZnO/ Al_2O_3 solids decreases by increasing the amount of ZnO present. The decrease was, however, more pronounced for the treated solids calcined at 400°C.
4. ZnO-treatment of CuO/ Al_2O_3 solids did not modify the mechanism of catalytic oxidation of CO by O_2 but changes (decreases) the concentration of catalytically-active constituents (CuO crystallites) in the top surface layers of the treated solids without changing their energetic nature.
5. The catalytic activity of CuO–ZnO/ Al_2O_3 solids calcined at 400–800°C increases by increasing the calcination temperatures reaching a maximum limit at 600°C then decreases by increasing the calcination temperatures above this limit.

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