

Effects of Preparation Conditions on Surface and Catalytic Properties of Copper and Zinc Mixed Oxides System

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Abstract: Copper-zinc mixed oxides treated with small amounts of alumina and having the formula 0.5 CuO: 0.5ZnO: 0.05 Al₂O₃ were prepared by coprecipitation of their mixed hydroxides from their mixed nitrates solutions using 1 M NaOH solution. The precipitation was carried out at different pH values varying between 7 to 9.5 and at 50 and 70°C.

The results revealed that the bulk of various solids consisted of CuO and ZnO having ratios varying between 0.91 and 1.20. While the surface Cu/Zn ratio was bigger than those present in the bulk and varied between 1.16 to 1.64 depending on the pH value and calcination temperature. The mixed oxide solids existed as nanocrystalline CuO and ZnO phases. The surface characteristics are strongly dependent on both the pH value and calcination temperature. The computed S_{BET} values varied between 21 and 108 m²/g and all adsorbents are mesoporous solids. The prepared solids showed a good catalytic activity in CO oxidation by O₂ which proceeds *via* first order kinetics in all cases. The activation energy of the catalyzed reaction was determined for various solids and the computed values were very small indicating the big catalytic activity of the investigated solids.

Keywords: CO oxidation, CuO and ZnO catalyst, nanocrystalline.

1. INTRODUCTION

Recent advances in the synthesis and characterization of nanoscale materials have promoted extensive searches describing methods of preparation of highly efficient nanostructured catalysts for the removal of chemical contaminants and harmful gases such as SO₂ and CO [1-8]. CO oxidation is a serious environmental concern, since exposure to few ppm of this odorless invisible gas can be fatal [9]. Therefore, there is a need to develop highly active CO oxidation catalysts to remove even a small amount of CO from the local environment. The catalytic oxidation of CO by O₂ is of environmental and industrial importance and is being used in a wide variety of practical applications [10-14]. CO oxidation catalysts with high activities near room temperature have several applications, including closed cycle CO₂ lasers and air purification devices [15-18].

Most industrialized nations have established environmental regulations to control air emissions. Issues such as the greenhouse effect and ozone layer depletion have received special attention because of dramatic and potentially disastrous consequences being anticipated by environmental scientists. The main sources of air pollution are power plants, industrial plants and automobiles. Automotive transport is very popular and the number of cars in circulation has considerably increased especially in urban areas. Motors vehicles generate more air pollution than any other single

human activity; they are the dominant source of carbon monoxide, oxides of nitrogen and hydrocarbons.

CuO - ZnO- based catalysts are used in water-gas shift reaction at low temperature [19]. Cen Yaqing *et al.* [20] have reported that the pH value was important parameter for the preparation of CuO-ZnO catalyst by adopting coprecipitation method. This study showed that with increasing pH value on alkali side, the activity of the catalyst first increases and then decreases and the catalyst prepared at the pH value on an alkali side of 9.5 has the biggest activity.

The effect of Li₂O- doping on surface and catalytic properties of CuO - ZnO / Al₂O₃ in CO- oxidation by O₂ at 150 - 200 °C has been investigated by El-Shobaky *et al.* [21]. These authors claimed that Li₂O-doping caused a measurable increase in the specific surface area (23-45%) and in the total pore volume (24-43%) of the adsorbents being calcined at 600-700°C. If the doping process was carried out at 600°C, it resulted in a considerable decrease (52%) in the catalytic activity, in CO oxidation by O₂, measured at 175°C. A rise in calcination temperature of the doped catalysts (4.5 mol.% Li₂O) from 600 to 700 or 800°C brought about a significant increase of (125% and 186%, respectively) in the catalytic activity measured at 175°C. This discrepancy was discussed in terms of the effect of Li₂O- doping in decreasing the dispersity of CuO crystallites of the solids calcined at 600°C and the role of Li₂O in hindering CuAl₂O₄ formation upon calcination at 700 or 800°C. The decrease in the degree of dispersion of CuO crystallites due to doping at 600°C is normally followed by a decrease in the catalytic activity while the suppression or hindrance of CuAl₂O₄ formation

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might be followed by an increase in the catalytic activity. The doping process carried out at 600-800°C did not modify the concentration of catalytically active constituents involved in chemisorption and catalysis of the CO oxidation reaction.

The present work reports the results concerning the effect of pH value, coprecipitation and calcination temperatures on surface and catalytic properties of CuO / ZnO prepared by coprecipitation and treated with very small amount of Al₂O₃. The techniques employed were atomic absorption, XRD, EDX, nitrogen adsorption at -196 °C and catalysis of CO oxidation by O₂ at 100-200 °C using a static method.

2. EXPERIMENTAL

2.1. Materials

The chemicals employed were of analytical grade as supplied by Aldrich and Merck companies.

Stock solutions of copper and zinc nitrates containing 0.5 mol per liter were prepared, the required amount of aluminum nitrate was taken as a solid and dissolved in a required volume of zinc nitrate solution.

The mixed hydroxides were prepared from their nitrate solutions using 1M of sodium hydroxide solution. The rate of dropping of mixed nitrates and sodium hydroxide solutions was controlled in order to keep the pH of coprecipitation medium constant at a fixed pH value. The coprecipitation process was carried out at 50 and 70 °C at various pH values namely 7, 8.5 and 9.5. The coprecipitation process was carried out by taking 50 ml of zinc, aluminum mixed nitrates followed by complete coprecipitation of their mixed hydroxides with vigorous stirring followed by dropwise addition of the required volume of copper nitrate (50 ml) with subsequent dropwise addition of copper nitrate till complete coprecipitation of all mixed hydroxides.

2.2. Techniques

Copper, zinc ratio in the bulk of different mixed solids calcined at 400 °C was determined by using Varian Spectra AA atomic absorption spectrometer. The analysis was carried out at 4 mA lamp current, acetylene fuel, nitrous oxide as support, slit width 0.1 nm and 327.4 nm wavelength for determination of copper and 213.9 nm wavelength for determination of zinc. A known weight (200 mg) of each solid was dissolved in a minimum volume of hydrochloric acid followed by dilution by distilled water to 100 ml.

EDX measurements were carried out on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The parameters were as follows : - 15 kV accelerating voltage, 100 s accumulation time, 8 μm window width. The surface molar composition was determined by the Asa method (Zaf-correction, Gaussian approximation)

X- ray powder diffractograms of various investigated solids calcined at 300, 350 and 400 °C were determined using a Bruker diffractometer (Bruker D8 advance target). The scanning rate was fixed at 8° in 2θ min⁻¹ for phase identification and 0.8° in 2θ min⁻¹ for line broadening profile analysis, respectively. The patterns were run with Cu Kα1 with secondly monochromator (λ = 0.15405 nm) at 40 kV and 40 mA. The crystallite size of crystalline phases present in

different solids investigated was calculated from the line broadening profile analysis of the main diffraction lines of the crystalline phases present using the Scherrer equation [22].

$$d = \frac{K\lambda}{\beta_{1/2}\cos\theta}$$

where d is the mean crystallite diameter, λ the X-ray wave length, K the Scherrer constant (0.89), β_{1/2} the full-width at half-maximum (FWHM) of the main diffraction peak of crystalline phases, expressed in radian, and θ is the diffraction angle.

The specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (r̄) of the various adsorbents were determined from nitrogen adsorption isotherms measured at -196 °C using NOVA Automated Gas sorbometer. The values of V_p were computed from the relation

$V_p = 15.45 \times 10^{-4} \times V_{st} \text{ cm}^3/\text{g}$, where V_{st} is the volume of nitrogen adsorbed at P/P⁰ tends to unity. The values of r̄ were determined from the equation

$$\bar{r} = \frac{2V_p}{S_{BET}} \times 10^4 \text{ \AA}$$

The catalytic activities of different prepared solids calcined at 400 °C were determined by following up the kinetics of CO oxidation by O₂ over various catalysts at 100,150 and 200 °C. A 100 mg of catalyst sample, activated by heating at 350 °C under a reduced pressure of 10⁻⁶ Torr, was taken in each kinetic experiment. The reaction was monitored by measuring the pressure of the reacting gas mixture (CO+1/2O₂) at different time intervals till no further change in pressure was attained. The initial pressure of (CO+1/2O₂) was fixed at 2 Torr. The reaction product (CO₂) was removed from the reaction atmosphere by freezing at liquid nitrogen temperature. So, the percentage decrease of the pressure of the reacting gases at a given time interval determines the percentage conversion of the catalytic reaction at that time. The saturation vapour pressure of CO at - 196 °C being 160 Torr makes its liquefaction at that pressure improbable under the employed conditions (2 Torr)[23].

3. RESULTS AND DISCUSSION

3.1. Spectroscopic Determination of Copper: Zinc Ratio

Cu /Zn ratio in the bulk of solids was determined spectroscopically using solids calcined at 400 °C and being prepared under different conditions. The results obtained are given in the last column of Table 1. Examination of Table 1 shows that Cu /Zn ratio in the bulk of the solids investigated, being coprecipitated under different conditions and calcined at 400 °C, varied between 0.91 and 1.20 depending on coprecipitation temperature and pH value. The biggest ratio was obtained for the solids coprecipitated at the smallest pH (7) and highest temperature (70 °C). While the smallest ratio was observed for the solids coprecipitated at the biggest pH (9.5) and highest temperature (70 °C). These findings could be attributed to the amphoteric nature of Zn(OH)₂ leading to a possible dissolution of a small portion of Zn(OH)₂ precipitate in solution having a pH=9.5.

Table1. Surface and Bulk Molar Composition of CuO - ZnO and Al₂O₃ System Prepared at Different pH Values and Preparation Temperature Determined by EDX and Atomic Absorption

Solid	Preparation pH	Preparation Temperature	Calcination Temperature, °C	Element	Atomic Abundance		Surface Cu / Zn Ratio	Bulk Cu / Zn Ratio
					Calculated (Bulk)	Found (Surface)		
Sample 1	8.5	50 °C ageing 1h at 50 °C	300	Cu	22.2	25.6	1.33	0.93
				Zn	22.2	19.3		
				O	51.1	54.4		
				Al	4.5	0.7		
			350	Cu	22.2	24.5	1.28	
				Zn	22.2	19.1		
				O	51.1	54.4		
				Al	4.5	2.0		
			400	Cu	22.2	23.8	1.16	
Zn	22.2	20.6						
O	51.1	53.8						
Al	4.5	1.8						
Sample 2	9.5	50 °C ageing 1h at 50 °C	300	Cu	22.2	24.8	1.26	0.98
				Zn	22.2	19.6		
				O	51.1	53.6		
				Al	4.5	2.0		
			350	Cu	22.2	24.0	1.30	
				Zn	22.2	18.5		
				O	51.1	53.5		
				Al	4.5	4.0		
			400	Cu	22.2	24.4	1.37	
Zn	22.2	17.8						
O	51.1	54.1						
Al	4.5	3.7						
Sample 3	7	70 °C ageing 1h at 70 °C	300	Cu	22.2	27.5	1.64	1.20
				Zn	22.2	16.8		
				O	51.1	53.9		
				Al	4.5	1.8		
			350	Cu	22.2	27.7	1.60	
				Zn	22.2	17.3		
				O	51.1	54.5		
				Al	4.5	0.5		
			400	Cu	22.2	24.6	1.28	
Zn	22.2	19.3						
O	51.1	54.6						
Al	4.5	1.5						
Sample 4	7	70 °C without ageing	300	Cu	22.2	25.0	1.29	1.10
				Zn	22.2	19.4		
				O	51.1	53.7		
				Al	4.5	1.9		
			350	Cu	22.2	24.4	1.23	
				Zn	22.2	19.9		
				O	51.1	54.2		
				Al	4.5	1.5		
			400	Cu	22.2	23.8	1.17	
Zn	22.2	20.3						
O	51.1	54.3						
Al	4.5	1.6						
Sample 5	9.5	70 °C ageing 1h at 70 °C	300	Cu	22.2	23.4	1.16	0.91
				Zn	22.2	20.1		
				O	51.1	54.1		
				Al	4.5	2.4		
			350	Cu	22.2	23.2	1.21	
				Zn	22.2	19.1		
				O	51.1	54.4		
				Al	4.5	3.3		
			400	Cu	22.2	24.7	1.28	
Zn	22.2	19.3						
O	51.1	54.1						
Al	4.5	1.9						

3.2. Energy Dispersive X-Ray (EDX) Analysis of Various Solids

EDX investigation was carried out for CuO / ZnO system treated with 0.05 mol Al₂O₃ / mol solid prepared under different conditions and calcined at 300-400 °C. The relative atomic abundance of Cu, Zn, Al and oxygen species present in the uppermost surface layers of different solids investigated is given in Table 1. It is well known that EDX technique supplies the effective atomic concentration of different constituents of the solids investigated present on their top surface layers. The thickness of these layers is bigger than that measured using XPS technique. This difference is due to the bigger value of the energy of X-ray beam in case of the EDX as compare to that in case of XPS technique. Also, enclosed in Table 1 are the values of atomic abundance of Cu, Zn, Al and oxygen present in the bulk (calculated) of various solids. Examination of Table 1 shows the following: (i) The surface Cu/Zn ratio in the solids prepared under varying conditions and calcined at 300 - 400 °C is strongly dependent on pH values, preparation and calcination temperatures. (ii) The surface concentrations of Cu in all solids investigated is bigger than that in the bulk of these solids. On the other hand, the surface zinc and aluminum concentration are smaller than those present in the bulk of different solids. (iii) The surface copper, zinc ratio in mixed solids prepared at pH = 8.5 at 50 °C (sample 1) and calcined at 400 °C and mixed solids prepared at pH = 9.5 at 70 °C (sample 5) and calcined at 300 °C showed the smallest copper zinc ratio (iv) The surface copper, zinc ratio in the mixed solids prepared at pH = 7 at 70°C (sample 3) and being calcined at 300°C measured the biggest value. (v) The small value of pH gave higher copper/zinc ratio. This finding might be discussed in terms of the difference in solubility product of Cu(OH)₂ and Zn(OH)₂ which measures 4.8×10^{-20} and 1.2×10^{-17} , respectively. These values suggest an earlier precipitation of Zn(OH)₂ prior to Cu(OH)₂. (vi) The rise in calcination temperature of solids prepared at high pH value (pH=9.5) [samples 2,5] within 300 and 400 °C resulted in a progressive increase in surface copper zinc ratio. This increase may express a possible migration of copper species from bulk to surface opposite to the concentration gradient. (vii) The rise in calcination temperature of solids prepared at lower pH value (pH=7 or 8.5) [samples 1,3,4] within 300 and 400 °C resulted in a progressive decrease in surface copper zinc ratio.

3.3. X-Ray Investigation of Different Solids

The X-ray diffractograms of different solids prepared under varying conditions and being calcined at 300, 350 and 400 °C were determined.

Figs. (1, 2) show representative X-ray diffractograms of different calcined solids prepared at pH = 8.5 and 9.5 at 50 °C (sample 1, 2). The different structural characteristics of various investigated solids were determined and the results obtained are given in Table 2. These characteristics include the identification of different phases present, their crystallite size and degree of crystallinity. Examination of this Table shows the following: (i) The different investigated solids calcined at 300 - 400 °C consisted of nanocrystalline CuO, ZnO phases. (ii) The crystallite size of both CuO and ZnO phases prepared at high temperature (70 °C) [samples 3,4,5]

or at high pH values [sample 2] increases progressively as a function of calcination temperature. (iii) The crystallite size of CuO and ZnO phases in the solids prepared at pH=9.5, 50°C and being calcined at different temperatures measured the smallest values. (iv) The crystallite size of both CuO and ZnO phases present in solids prepared at low temperature and at pH = 8.5 [sample 1] decreases progressively as a function of calcination temperature.

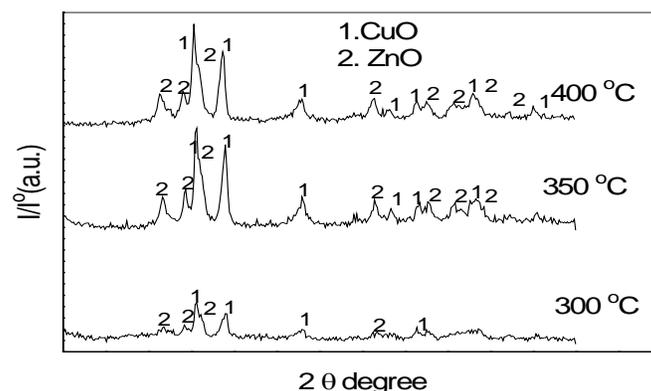


Fig. (1). X-ray diffractograms of sample 1 and being calcined at 300, 350 and 400 °C.

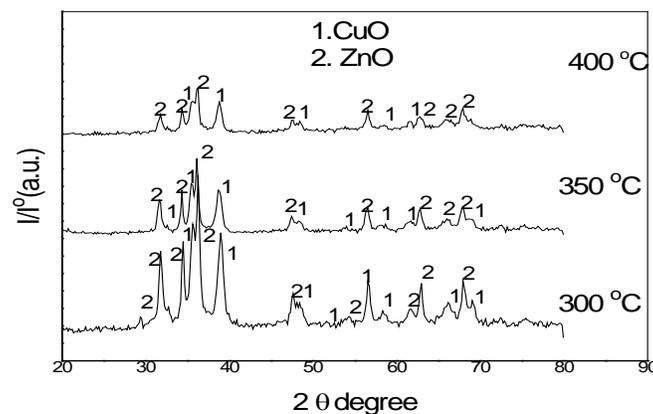


Fig. (2). X-ray diffractograms of sample 4 and being calcined at 300, 350 and 400 °C.

3.4. Surface Characteristics of Different Solids

The different surface characteristics of various solids were determined from analysis of nitrogen adsorption isotherms carried out at - 196 °C over various adsorbents. These characteristics include specific surface areas (S_{BET}), total pore volume (V_p) and mean pore radius (r). The S_{BET} values were determined from linear portion of the BET equation.

Another series of specific surface area (S_i) was determined from $V_i.T$ plots constructed using suitable standard T-curves depending on the values of the BET- C constant.

Figs. (3, 4) depict representative $V_i.T$ plots of mixed solids (samples 1, 5) and being calcined at 300, 350, 400 °C. The $V_i.T$ plots of all solids investigated (not given) showed

Table 2. The Effect of pH and Preparation Temperature on the Crystallite Size and Degree of Crystallinity

Solid	Preparation pH	Preparation Temperature	Calcination Temperature, °C	Major Phase Present	Crystallite Size (nm)		*Degree of Crystallinity (a.u.)	
					CuO	ZnO	CuO	ZnO
Sample 1	8.5	50 °C ageing 1h at 50 °C	300	CuO	19.2	11.8	36.3	25.2
			350	CuO	17.3	10.5	79.2	31.4
			400	CuO	13.1	8.5	93.2	42.7
Sample 2	9.5	50 °C ageing 1h at 50 °C	300	CuO	7.6	3.9	53.3	33.7
			350	CuO	9.0	7.0	61.1	36.8
			400	CuO	11.2	7.9	72.4	48.5
Sample 3	7	70 °C ageing 1h at 70 °C	300	ZnO	9.8	25.7	47.5	128.0
			350	ZnO	12.8	28.0	67.5	106.0
			400	ZnO	16.0	32.0	109.0	102.0
Sample 4	7	70 °C without ageing	300	ZnO	12.9	14.1	155.0	122.0
			350	ZnO	15.3	19.3	72.0	114.0
			400	ZnO	16.5	29.8	51.7	76.2
Sample 5	9.5	70 °C ageing 1h at 70 °C	300	ZnO	9.9	18.5	69.3	69.8
			350	ZnO	14.8	23.8	64.2	71.7
			400	ZnO	12.0	33.0	58.3	85.0

* The peak area of the major line of each phase was taken as a measure for the degree of the degree of crystallinity.

an upward deviation indicating the domination of wide pores. However all adsorbents are considered as mesoporous adsorbents. This conclusion is reached at by comparing the values of r given in Table 3 which shows that the r values of all adsorbent vary between 10 and 158 Å.

Examination of Table 3 shows the following (i) The values of S_{BET} and S_t for all adsorbents investigated are close to each other which justifies the correct choice of standard t-curve used in pore analysis and indicates the absence of ultramicro pores. (ii) The S_{BET} of different solids decreases progressively by increasing the calcination temperature within 300-400 °C. (iii) The mixed solids prepared at pH=7 and 70 °C [sample 3] and being calcined at 300 °C measured the biggest S_{BET} value while the adsorbent prepared at pH=7 at 70 °C [sample 3] and being calcined at 400°C measured the smallest S_{BET} value. (iv)The solids prepared at pH=9.5 and 50°C and being calcined at all temperatures within 300-400 °C measured the biggest total pore volume. While the smallest V_p values were measured for the mixed solids prepared at pH=7 at 70 °C without ageing [sample 4]. (v) The increase in pre-calcination temperature of all solids from 300-400 °C led to a decrease of 14%, 14%, 81%, 60% and 26% for the samples 1,2,3,4 and 5, respectively. So, sample 3 suffered an effective sintering due to increasing its calcination temperature from 300-400 °C. While samples 1 and 2 showed the smallest sinterability by increasing their calcination temperature within 300-400 °C.

3.5. Catalytic Activity of Various Solids

The oxidation of CO by O₂ was carried out over various prepared solids calcined at 400 °C. First order kinetics was observed in all cases ; the slopes of the first order plots determine the values of reaction rate constant(k)measured at a

given temperature over a given catalyst sample. Fig. (5) shows representative first order-plots of CO oxidation by O₂ carried out at 100,150,200 °C over samples 1 and 2. The computed k values measured at 100, 150 and 200 °C for the investigated solids are given in Table 4. Examination of Table 4 shows the following (i) The catalytic activity of various investigated solids, expressed as reaction rate constant is strongly dependent on the conditions of preparation. (ii) The solids prepared at pH=7 and at 70 °C [sample 3] showed the smallest catalytic activity. (iii) The solids prepared at pH = 8.5 and at 50 °C [sample 1] has the biggest catalytic activity at reaction temperature of 100 °C. In fact, the $k_{100}^{\circ C}$ values were between 54 to 96 min⁻¹g⁻¹.

The main factors determining the catalytic activity are surface copper concentration (catalytically active constituent) and its crystallite size. The bigger the surface concentration of copper the bigger will be the catalytic activity and the smaller the crystallite size of CuO the bigger will be the catalytic activity and vice versa. In the light of these two factors the catalyst sample devoted with the biggest catalytic activity measured the smallest surface Cu / Zn ratio [1.16 c.f. Table 1] and crystallite size of 13.1 nm. These values are not in favour of the observed big catalytic activity of this particular sample. It seems that not all the surface copper oxide participates directly in chemisorption and catalysis in CO oxidation reaction. In other words, a portion of surface copper may be involved in the catalytic reaction. However, XRD investigation of the solids investigated showed that this particular sample being calcined at 400 °C consists of nanosized copper oxide as a major phase while the major phase present in other solids was ZnO

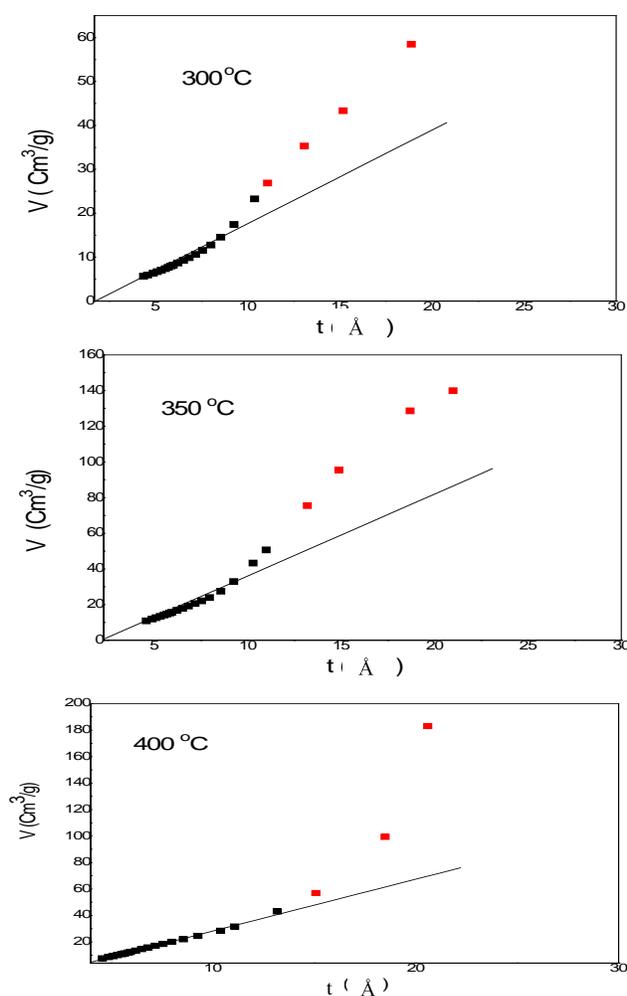


Fig. (3). Volume thickness plots (V_{t-t}) of sample 1 and being calcined at 300,350 and 400 °C

Determination of apparent activation energy (ΔE_a) of CO oxidation by O₂ over the catalysts investigated prepared under different conditions can throw more light on the role of preparation condition of these catalysts in changing the mechanism of the catalyzed reaction. This has been done by determining the catalytic reaction rate constant (k) measured at 100-200 °C over various solids *via* direct application of the Arrhenius equation. The computed ΔE_a values are given in Table 5. Examination of Table 5 shows that ΔE_a values changed from one catalyst to another and the bigger the catalytic activity of the solids investigated the smaller is the activation energy of the catalyzed reaction and vice versa. This finding expresses the observed changes in the catalytic activities of the solids investigated prepared under different conditions. In order to throw more light about the possible heterogeneity of surfaces of the investigated catalysts, the values of $\ln A$ (pre-exponential factor of the Arrhenius equation) were calculated for various catalysts and the data obtained are given in the second column of Table 5. It is shown from this table that ΔE_a and $\log A$ values changed from 1.7 to 10.3 which suggested the heterogeneous nature of surfaces of CuO-ZnO mixed solids prepared at different conditions. So, the observed changes of ΔE_a could result from corresponding changes of $\ln A$ values. This speculation could be

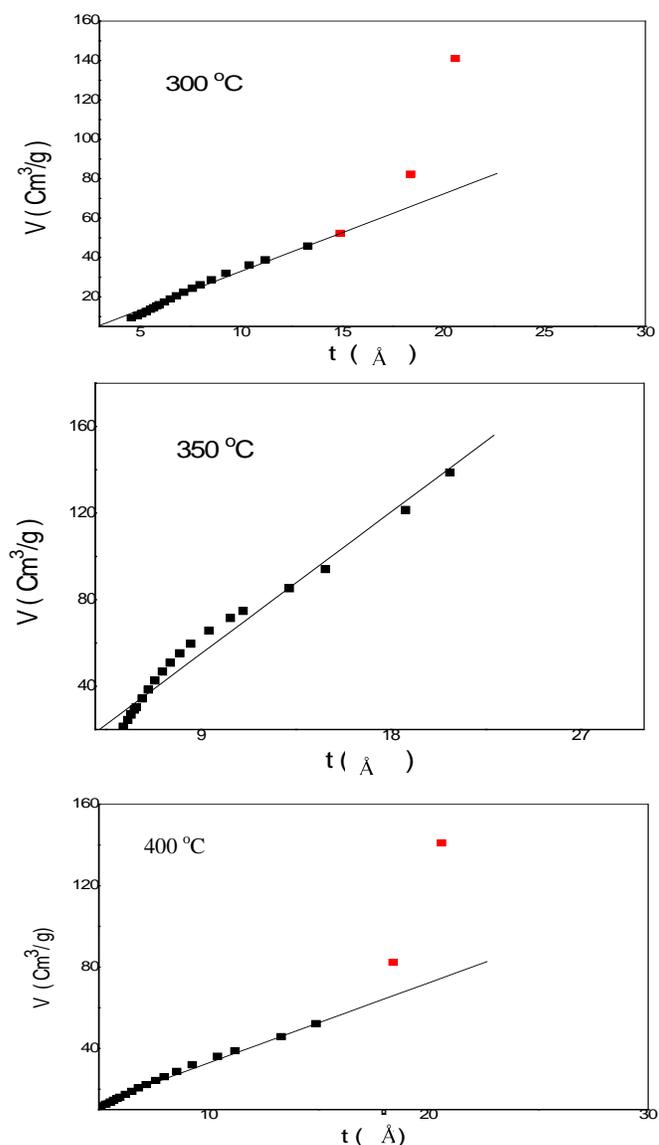


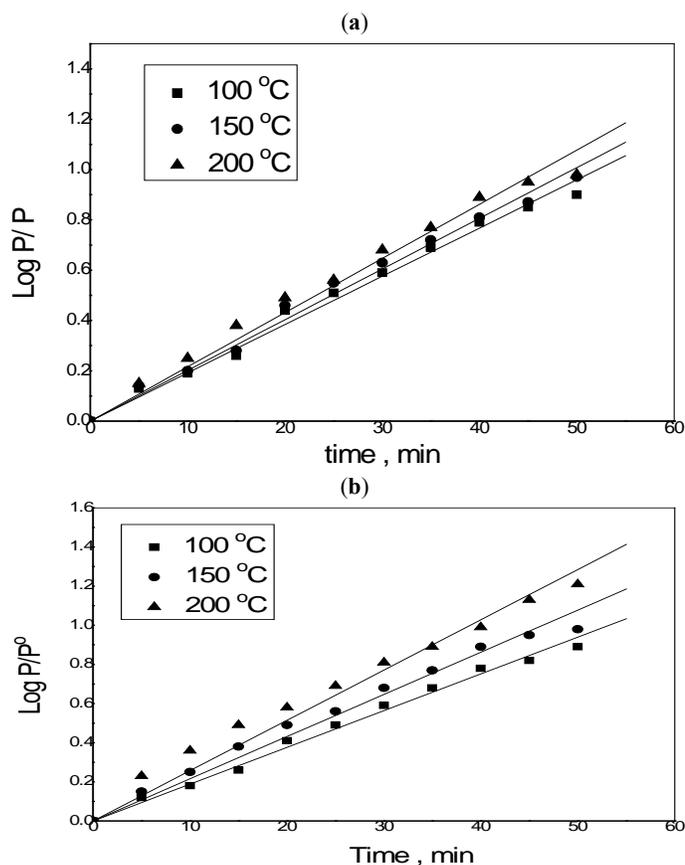
Fig. (4). Volume thickness plots (V of sample 5 and being calcined at 300,350 and 400 °C.

confirmed *via* recalculation of ΔE_a values adopting the value of $\log A$ of the solid prepared at pH=8.5 and at 50 °C [sample 1] to the other sample prepared under the other conditions. The recalculated values of activation energy of the catalyzed reaction (ΔE^*) carried out over various catalysts are given in the last column of Table 5. This column shows clearly that ΔE^* values for different solids are close to each other within the experimental error (2.5 ± 0.3 kJ/mol). These findings suggested that the catalytic oxidation of CO by O₂ over the solids investigated prepared at different conditions follows the same mechanism. Furthermore, all catalysts investigated are devoted with big catalytic activities as being evidenced from the small values of ΔE_a .

The heterogeneity of surfaces of the catalysts investigated may find another evidence from the plot of the equation $A = a \exp(h \Delta E)$ derived on the basis of dissipation function of active sites by their energy as a consequence of surface heterogeneity [24,25]: $F(E_i) = a \exp(h E_i)$, where E_i is the energy of site "i" with the substrate [24]. The plot of $\ln A$

Table 3. Surface Characteristics of 0.5 CuO - 0.5 ZnO - 0.05 Al₂O₃ System Prepared by Coprecipitation at Different pH Values and Calcined at 300-400 °C

Solid	Preparation pH	Preparation Temperature	Calcination Temperature, °C	S _{BET} m ² /g	St m ² /g	Total Pore Volume V _p , cc/g	Mean Pore Radius r- Å	BET-C Constant
Sample 1	8.5	50 °C ageing 1h at 50 °C	300	36	39	0.283	158	43
			350	33	31	0.087	52	1157
			400	31	34	0.016	10	-152
Sample 2	9.5	50 °C ageing 1h at 50 °C	300	81	75	0.314	78	414
			350	63	62	0.301	96	83
			400	70	71	0.298	85	227
Sample 3	7	70 °C ageing 1h at 70 °C	300	108	105	0.215	40	7
			350	26	30	0.073	57	251
			400	21	20	0.067	62	145
Sample 4	7	70 °C without ageing	300	70	74	0.026	16	6
			350	55	57	0.028	10	598
			400	28	31	0.013	19	66
Sample 5	9.5	70 °C ageing 1h at 70 °C	300	47	49	0.218	93	33
			350	30	28	0.196	133	121
			400	29	25	0.072	49	148

**Fig. (5).** First order plots of CO oxidation by O₂ carried out at different temperatures over catalyst being calcined at 400 °C (a) sample 1. (b) sample 2.

versus ΔE_a for the catalysts prepared under different conditions gives a straight line whose slope and intercept are "h" and "a" respectively. Fig (6) shows the linear plot of $\ln A$ versus ΔE_a for the catalyst prepared under different conditions. The computed values of the constant "h" and "a" are 0.28 mol kJ⁻¹ and 4.6 min⁻¹, respectively. The constant "h" and "a" values indicate that the condition of preparation of the system investigated did not change the dissipation of active sites. i.e. the character of surface heterogeneity. In other words, the conditions of preparation did not change the energetic nature of active site but changed their concentration.

3.6. Effect of Ageing on Surface Composition, Surface Characteristics and Catalytic Properties of the System Investigated

The effect of ageing of the mixed solids coprecipitated at a pH = 7 and being aged for 1 h at 70 °C on their structural, surface and catalytic properties were investigated.

Examination of Table 1 concerning the values of atomic abundance of Cu, Zn, Al and oxygen present in upper most surface layers of samples 3 and 4 shows that : Ageing after precipitation led to increase of copper, Zinc ratio from 1.29 to 1.64 for the solids calcined at 300 °C.

The different surface characteristics of samples 3 and 4 were determined (c.f. Table 3) and the results shows that the ageing after precipitation led to: (i) An increase of the degree of crystallinity of CuO crystallites. (ii) A decrease in crystallite size of CuO crystallite from 12.9 nm to 9.8 nm for the solids calcined at 300 °C.

It is seen from Table 2 that the ageing process of sample 3 coprecipitated at a pH = 7 and 70 °C for 1 h led to a measurable increase in its S_{BET} from 70 to 108 m²/g for the sam-

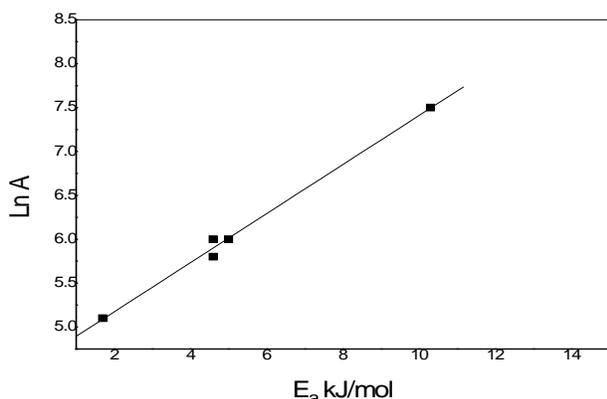
Table 4. Reaction Rate Constant Per Unit Mass ($k \times 10^{-3} \text{ min}^{-1} \text{ g}^{-1}$) for the Catalytic Oxidation of CO by O_2 Conducted at 100-200 °C Over 0.5 CuO- 0.5 ZnO - 0.05 Al_2O_3 System Prepared at Different pH Values at 50 °C and 70 °C

Solid	Preparation pH	Preparation Temperature	k_{100}	k_{150}	k_{200}
Sample 1	8.5	50 °C ageing 1h at 50 °C	96	101	108
Sample 2	9.5	50 °C ageing 1h at 50 °C	94	108	129
Sample 3	7	70 °C ageing 1h at 70 °C	54	99	107
Sample 4	7	70 °C without ageing	92	99	131
Sample 5	9.5	70 °C ageing 1h at 70 °C	74	90	101

Table 5. Activation Energies (ΔE_a and ΔE^*) and $\ln A$ for the Catalytic Reaction Carried Out at 100-200 °C Over 0.5 CuO- 0.5 ZnO - 0.05 Al_2O_3 System Prepared by Coprecipitation and Different pH Values at 50 °C and 70 °C and Being Calcined at 400 °C

Solid	Preparation pH	Preparation Temperature	ΔE (kJ/mol)	$\ln A$	ΔE^* (kJ/mol)
Sample 1	8.5	50 °C ageing 1h at 50 °C	1.7	5.1	2.4
Sample 2	9.5	50 °C ageing 1h at 50 °C	4.6	6.0	2.2
Sample 3	7	70 °C ageing 1h at 70 °C	10.3	7.5	2.5
Sample 4	7	70 °C without ageing	5.0	6.0	2.5
Sample 5	9.5	70 °C ageing 1h at 70 °C	4.6	5.8	2.8

ple calcined at 300 °C. However, the ageing process of this particular sample being calcined at 400 °C exerted an opposite effect, the BET-surface area decreased from 31 to 20 m^2/g . This finding might suggest an effective sintering of the adsorbent subjected to ageing at 70 °C followed by heating at 400 °C. While the ageing for 1 h at 70 °C increased the S_{BET} of the adsorbent being calcined at 300 °C due to an effective departure of most of water of constitution in mixed solids sample being aged at 70 °C followed by calcination at 300 °C. Furthermore, the ageing process brought about a measurable increase in the V_p value of the adsorbents calcined at 300, 350 and 400 °C.

**Fig. (6).** Relationship between E_a and $\ln A$ for the catalytic oxidation of CO by O_2 carried out at 100 °C over different samples.

The comparison between the values of the reaction rate constant measured at 100 °C for catalyst samples 3 and 4 shows that: the ageing process led to a considerable increase in the k_{100} value from 54 to 92 $\text{min}^{-1}\text{g}^{-1}$ (an increase of 41%). This finding could be attributed to the observed improve-

ment in the surface copper zinc ratio and the effective decrease in the crystallite size of CuO phase. These two parameters dominate the possible negative effect of the decrease in the specific surface area due to the ageing process.

4. CONCLUSIONS

The main conclusions derived from the results obtained can be summarized as follows:

1. CuO/ZnO having equimolar ratio and treated with 0.05 $\text{Al}_2\text{O}_3/\text{mol}$ catalysts being calcined at 300-400 °C are composed of nanosized copper and zinc oxides phases.
2. Surface concentration of different atomic species which were strongly dependent on the conditions of preparation and calcination temperatures were bigger than those present in the bulk of different solids.
3. The S_{BET} values varied between 21 and 108 m^2/g depending on the pH value and calcination temperature. All of the investigated adsorbent consists of mesoporous solids.
4. It seems that not all the surface copper oxide participate directly in chemisorption and catalysis in CO oxidation reaction as the catalyst having the biggest catalytic activity measured the smallest surface Cu/Zn ratio.
5. The computed values of activation energy of CO oxidation by O_2 (ΔE) over different solids showed small values indicating a big catalytic activity of these solids. The recalculated values of activation energy of the catalyzed reaction (ΔE^*) are close to each other within the experimental error (± 0.3 kJ/mol) showing that the catalytic reaction proceeded *via* almost the same mechanism over the solids investigated.

6. The conditions of preparation did not change the energetic nature of active site but change their concentrations.
7. The ageing process of mixed solids coprecipitated at pH = 7 and being ageing 1 h at 70 °C improved its catalytic performance.

REFERENCES

- [1] Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.*, **1989**, *115*, 301
- [2] Moser, W. R. *Advanced Catalysts and Nanostructured Materials* Academic press, **1996**.
- [3] Xu, X.; Goodman, D.W. *J. Phys. Chem.*, **1993**, *97*, 771.
- [4] Valden, M.; Lai, X.; Goodman, D.W. *Science*, **1998**, *281*, 1647.
- [5] McCrea, K.R.; Parker, J.S.; Somorjai, G.A. *J. Phys. Chem. B*, **2002**, *106*, 10854.
- [6] Scott, R.W.J.; Datye, A.K.; Crooks, R.M. *J. Chem. Soc.*, **2003**, *125*, 3708.
- [7] Scott, R.W.J.; Wilson, O.M.; Kenik, E.A.; Crooks, R.M. *J. Am. Chem. Soc.*, **2004**, *126*, 15583.
- [8] Scott, R.W.J.; Sivadinarayana, C.; Wilson, O.M.; Yan, Z.; Goodman, D.W.; Crooks, R.M. *J. Am. Chem. Soc.*, **2005**, *127*, 1380.
- [9] World Health Organization, Carbon monoxide, Environmental Health Criteria 213, World Health Organization, Geneva, **1999**.
- [10] Gardener, S.D.; Hoflund, G.B.; Upchurch, B.T.; Schryer, D.R.; Kielin, E.J.; Schryer, J. *J. Catal.*, **1991**, *129*, 114.
- [11] Kobayashi, T.; Haruta, M.; Sauno, H.; Nakone, M. *Actuators Soc. Auto. Wing.*, **1988**, *3*, 339.
- [12] Kobayashi, T.; Haruta, M.; Sauno, H. *Chem. Express* **1989**, *4*, 217.
- [13] Harrison, P.G.; Willett, M.J. *Nature*, **1988**, *332*, 337.
- [14] Stark, D.S.; Crocher, A.; Steward, G.J. *J. Phys. E: Sci. Instrum.*, **1983**, *16*, 126.
- [15] Schryer, D.R.; Upchurch, B.I.; Van Norman, J.D.; Brown, K.G.; Schryer, J. *J. Catal.*, **1990**, *122*, 193.
- [16] El-Shobaky, G.A.; Ghozza, A.M. *Mater Lett.*, **2004**, *58*, 699-705.
- [17] El-Shobaky, G.A.; Radwan, N.R.E.; El-Shall, M.S.; Turky, A.M.; Hassan M.A. Hassan. *Appl. Surf. Sci.*, **2008**, *254*(6), 1651.
- [18] El-Shobaky, G.A.; Radwan, N.R.E.; El-Shall, M.S.; Turky, A.M.; Hassan M.A. Hassan. *Colloids. Surf. A: Physicochem. Eng. Asp.*, **2007**, *311*(1-3), 161.
- [19] Gines, M.J.L.; Amadeo, N.; Laborde, M.; Apesteguia, C.R. *Appl. Catal. A*, **1995**, *131*, 283.
- [20] Can, Y.; Li, X.; Liu, H. *Chin. J. Catal.*, **2006**, *27*(3), 210-216.
- [21] El-Shobaky, G.A.; Fagal, G.A.; Ghozza, A.M.; Mokhtar, M. *Colloids. Surf. A: Physicochem. Eng. Asp.*, **1998**, *142*, 17.
- [22] Cullity, B.D. *Elements of X-ray Diffraction*, Addison-wesely Publishing Cos, 2nd ed, Addison-Wesley, Reading, MA, **1978**, p. 102.
- [23] El-Shobaky, G.A.; El-Khouly, S.M.; Ghozza, A.M.; Mohamed, G.M. *Appl. Catal. A*, **2006**, *302*, 296.
- [24] Balandin, A.A.; Doki. Akad. Nauk. SSSR **1953**, *93*, 55.
- [25] El-Shobaky, G.A.; Fagal, G.A.; Mokhtar, M. *Appl. Catal. A*, **1997**, *155*, 167.

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