

# Influence of ZnO doping and calcination temperature of nanosized CuO/MgO system on the dehydrogenation reactions of methanol

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**Abstract** Pure and doped catalysts were prepared with ZnO dopant concentration (0.04–0.08 mol) by wet impregnation method followed by calcination at 350–650 °C. The prepared solids were characterized by X-ray diffraction, N<sub>2</sub>-adsorption at –196 °C and the methanol conversion as the catalytic probe reaction. The results revealed that the crystallite size and ordering of CuO phase decrease by ZnO-doping for samples calcined at 350–550 °C. Opposite trends were observed by increasing ZnO amount to 0.08 mol (i.e. 9.21 wt%). The specific surface area ( $S_{\text{BET}}$ ) and the catalytic activity of pure catalyst increase by increasing the calcination temperature to 550 °C and/or increasing the amounts of ZnO up to certain extent reaching to a maximum at 7.07 wt% ZnO; above this concentration catalytic activity of doped samples decreases. But at calcination temperature above 550 °C, the catalytic activity and selectivity decrease. The prepared catalysts are selective towards formaldehyde and methyl formate formation.

**Keywords** ZnO-doping · CuO/MgO system · Methanol dehydrogenation · Conversion · Selectivity

## Introduction

Methanol has been considered as an important raw material in the synthesis of various chemicals. Dehydrogenation of methanol was expected as a promising process to synthesize formaldehyde and methyl formate [1]. Formaldehyde is an industrial chemical that is widely used to manufacture numerous household products [2]. Formaldehyde and methyl formate are produced in large quantity by the coal chemical industry and natural gas chemical industry [3], both of them are important organic chemical materials usually used as the raw material of medicines [4]. Methanol is also considered as a candidate for the chemical carrier to transport hydrogen [5]. Copper-based catalysts appeared to be active towards the dehydrogenation of methanol. The activity and selectivity of catalyst were strongly influenced by both reaction conditions and surface structure. On reduced copper surface, CH<sub>3</sub>O species decomposed near 370 K to form formaldehyde and methyl formate [6]. Over the past two decades, there has been considerable interest in the adsorption and decomposition mechanism of methanol over solid surfaces such as Cu, Pt, Ni, TiO<sub>2</sub> and other oxides [7–11].

Improving the catalytic activity and selectivity of metal oxides employed in some important industrial reactions is achieved using suitable support, exposure to radiation and doping with certain foreign cations [12, 13]. Doping of single or multicomponent metal or metal oxide system with certain foreign oxides was efficient approach for bringing about significant modifications in their thermal stability, electrical, optical, magnetic, surface and catalytic properties [14]. The addition of small amounts of certain foreign cations such as Li<sup>+</sup>, Zr<sup>4+</sup> and K<sup>+</sup> to CuO/MgO has influenced the mutual solid–solid interaction between constituents [15, 16]. This influence may be accompanied by

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significant changes in the catalytic and physicochemical properties of the doped catalysts [14]. Doping CuO/MgO system with K<sub>2</sub>O decreased the degree of ordering of CuO and MgO phases [16]. Li<sub>2</sub>O-doping of CuO/MgO solid enhanced its catalytic activity towards conversion of isopropanol [15, 17]. ZnO is a well-known dopant for many catalytic systems such as NiO and Co<sub>3</sub>O<sub>4</sub>, in which ZnO brought about measurable changes in their specific surface areas and the crystallite sizes of their phases [18]. Doping Ni–Al<sub>2</sub>O<sub>3</sub> system with ZnO affected on the range of reduction temperature of NiO due to formation of ZnAl<sub>2</sub>O<sub>4</sub> spinel-like structure [19]. It was reported that the reactivity of Fe<sub>2</sub>O<sub>3</sub> to interact with MO (M = Mg, Ni, Co and Mn) yielding the corresponding MFe<sub>2</sub>O<sub>4</sub> had been found to be much stimulated by doping with ZnO [20, 21]. Zn<sup>2+</sup> had a high activity to diffuse into Co<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> solids at about 600 °C [22]. Doping CuO/TiO<sub>2</sub> with ZnO brought about a measurable decrease in the crystallite size of both anatase and CuO phases to an extent proportional to the amount of dopant added [23].

The present work aimed at studying the role of calcination temperature and ZnO doping of CuO/MgO system was prepared by impregnation method on its structural, surface characteristics, catalytic activity and selectivity. The techniques employed were X-ray-diffraction, N<sub>2</sub>-adsorption at –196 °C.

## Experimental

### Materials

A known amount of magnesium hydroxide (previously prepared [24]) was impregnated with a solution containing a known amount of copper nitrate dissolved in the least amount of distilled water. The CuO content in all solid samples was fixed at 23 mol%. The solutions prepared contained different proportions of Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The obtained pastes were dried at 110 °C and then calcined at 350–650 °C for 4 h. The amount of zinc oxide expressed in mole was 0.04, 0.05, 0.06 and 0.08. The undoped sample was nominated as CuMgO, but doped solids were determined and nominated as 0.04, 0.05, 0.06, 0.08 ZnO-doped CuMgO.

### Techniques

X-Ray diffractograms of various prepared solids were determined using a Bruker diffractometer (Bruker D8 Advance). The scanning rate was fixed at 8° in 2θ/min and 0.8° in 2θ/min for phase identification and line broadening analysis, respectively. The patterns were run with CuKα1 with secondly monochromator, λ = 0.15005 nm at 40 kV

and 40 mA. The crystallite size of the phases present was calculated using Scherrer equation [25].

The specific surface areas of the solid catalyst samples were determined from nitrogen adsorption desorption isotherms measured at –196 °C using a Quanta chrome NOVA 2000 automated gas-sorption apparatus model 7.11. All samples were degassed at 200 °C for 2 h under a reduced pressure of 10<sup>–5</sup> Torr before undertaking such measurements.

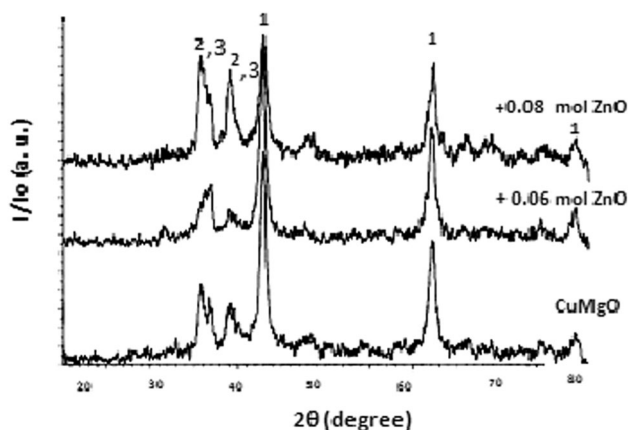
The catalytic activities of pure and variously ZnO doped-CuMgO solid catalyst samples towards methyl alcohol dehydrogenation were determined at reaction temperatures 125–275 °C, the catalytic reaction being conducted in a flow reactor under atmospheric pressure. Thus, a 50 mg catalyst sample was held between two glass wool plugs in a Pyrex glass reactor tube 20 cm long and 1 cm internal diameter packed with quartz fragments 2–3 mm length. The temperature of the catalyst bed was regulated and controlled to within ±1 °C. Argon gas was used as the diluents and the methyl alcohol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 26 °C. The flow rate of the carrier gas was maintained at 15 ml/min. Before carrying out such catalytic activity measurements, each catalyst sample was activated by heating at 300 °C in a current of argon for 1 h then cooled to the catalytic reaction temperature. The injection time of the reaction products and the unreacted methyl alcohol was fixed after 15 min, and GC control at *t* = constant was performed until achieving a steady state process. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. Stainless steel chromatographic columns were used, 4 m length, packed with 10 % squalane supported on chromosorp. The reaction products were analyzed at a column temperature of 40 °C in all conversion runs. Detector temperature was kept at 250 °C.

## Results and discussion

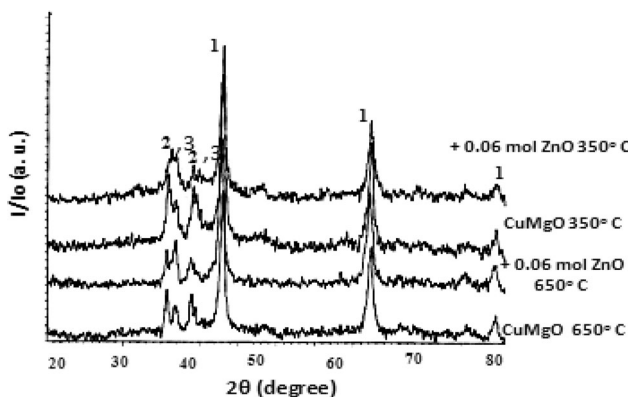
### XRD investigation of pure ZnO-doped CuMgO solids calcined at different temperatures

X-Ray diffractograms of pure and variously ZnO-doped solids precalcined at 350–650 °C were determined and illustrated in Figs. 1 and 2. The values of crystallite sizes of different phases were calculated using Scherrer equation [25], are given in Table 1. Inspection of Figs. 1 and 2 and Table 1 revealed that: (1) all investigated solids precalcined at 350, 550 °C consisted of MgO as a major phase, CuO as a minor thereof together with Cu<sub>2</sub>O phase in

nanocrystalline nature. The presence of  $\text{Cu}_2\text{O}$  phase was evidenced from the brown color of the calcined solids beside presence of diffraction line at  $d = 2.44 \text{ \AA}$  (at  $I/I > 10$  c/o). (2) Doping  $\text{CuMgO}$  system with 0.06 mol ZnO (i.e. 7.07 wt%) brought about a measurable decrease in both of ordering and crystallite sizes of MgO and CuO phases, further increase in ZnO amount to 0.08 mol (i.e.



**Fig. 1** XRD diffractograms of pure and ZnO doped  $\text{CuMgO}$  solids precalcined at 550 °C. Lines 1 refer to MgO, lines 2 refer to CuO phases, lines 3 refer to  $\text{Cu}_2\text{O}$  phase



**Fig. 2** XRD diffractograms of pure and ZnO-doped  $\text{CuMgO}$  solids precalcined at 350 and 650 °C. Lines 1 refer to MgO, lines 2 refer to CuO phases, lines 3 refer to  $\text{Cu}_2\text{O}$  phase

**Table 1** Intensity count, crystallite sizes of various phases present in pure and ZnO-doped  $\text{CuMgO}$  solids calcined at 350, 550 and 650 °C

Solid	Calcination temp. (°C)	Intensity count (a.u.)			Crystallite size (nm)			$I/I_0$ Cu <sub>2</sub> O
		MgO	CuO	ZnO	MgO	CuO	ZnO	
Pure solid	350	131	52	–	17	11	–	27
0.06 ZnO	350	81	36	36	13	4.7	4.7	39
Pure solid	550	114	43	–	12	14.6	–	31
0.06 ZnO	550	109	30	30	12.4	8.7	8.7	30
0.08 ZnO	550	73	61	45	8.6	16.5	13.6	55
Pure solid	650	93	32	–	14	21	–	23
0.06 ZnO	650	94	25	–	14	25	–	33

9.21 wt%) resulted in an increase in the degree of ordering of CuO phase while opposite result was found in case of MgO phase. (3) Calcination at 350 and 550 °C of the doped solids resulted in the formation of nanocrystalline ZnO phase, its crystallite size increases with increasing ZnO content. (4) The rise in calcination temperature of pure and ZnO-doped solids to 650 °C causes decreasing the degree of ordering of CuO, MgO and ZnO phases, but led to increasing the crystallite size of CuO (4.7–25 nm).

These obtained results can be explained in the role of ZnO-doping in increasing the degree of dispersion of active phase [26, 27] via decreasing its crystallite sizes. The mechanism of this action had been tentatively attributed to coating the copper oxide crystallites by ZnO film that may hinder the particle adhesion of the doped oxide solids [26]. The re-increase of degree of crystallinity of CuO phase in the highly doped sample (0.08 mol) at 550 °C could be due to the presence of maximum limit for ZnO to hinder the grain growth of CuO. Increasing ZnO content to 0.06 mol at 650 °C led to dissolving ZnO in MgO and forms solid solution; this interaction led the finally divided CuO crystallites to grow on the top surface layer of MgO. This speculation was based on the effective increase in the crystallite size of CuO as shown in Table 1.

### Specific surface areas of pure and ZnO-doping $\text{CuMgO}$ calcined at different temperatures

The surface characteristics of pure adsorbent sample and those treated with small amounts of ZnO precalcined in air at 550 and 650 °C were determined from nitrogen adsorption isotherms conducted at  $-196 \text{ °C}$ . The dopant concentrations were 0.06 and 0.08 mol ZnO per mol MgO corresponding to 7.07 and 9.21 wt%, respectively. The surface characteristics, namely  $S_{\text{BET}}$ ,  $V_p$  “total pore volume” and  $r^-$  “mean pore radius” calculated for various adsorbents are listed in Table 2. Inspection of the results in Table 2 shows that (1) addition of ZnO resulted in a progressive increase in the specific surface areas of the treated solids. The maximum increase in the  $S_{\text{BET}}$  due to treatment with 0.06 and 0.08 mol ZnO attained about 33 and 52 %

**Table 2** The specific surface areas of pure and ZnO-doped 0.3CuO/MgO adsorbents precalcined at 550 and 650 °C

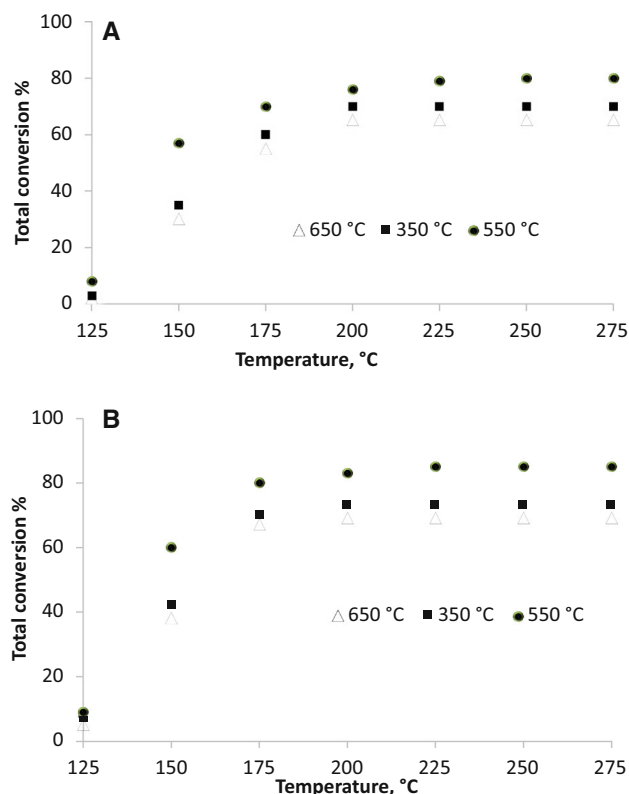
Moles of ZnO	Calcination temp. (°C)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$r^-$ (Å)
0	550	21	0.108	103
0.06	550	28	0.109	78
0.08	550	32	0.102	64
0	650	16	0.052	65
0.06	650	22	0.048	44

for the solids calcined at 550 °C. The observed increase in the specific surface areas of ZnO-doped solids may be attributed to formation of new pores. The formation of these pores may be due to liberation of gaseous nitrogen oxides in the course of the heat treatment of zinc nitrate added. (2) Increasing the calcination temperature from 550 to 650 °C decreases the specific surface areas of the treated solids. The decrease in the  $S_{\text{BET}}$  by increasing calcination temperature to 650 °C attained 24 and 21 % for pure and doped solid with 0.06 mol ZnO, respectively. This decrease in specific surface areas of the treated solids may be attributed to collapse of the pore structure and/or the particle adhesion process (grain growth). In fact, the BET-surface area of CuMgO treated with 0.06 mol ZnO conducted at 650 °C measured 22 m<sup>2</sup>/g while the ZnO-free sample calcined at the same temperature measured 16 m<sup>2</sup>/g. These findings might suggest that ZnO acted as convenient stabilizer against thermal sintering process of the treated solids.

The extension in the surface area due to ZnO-doping is expected to be accompanied by a corresponding improvement in their catalytic activity.

### Catalytic activity and selectivity of the pure and ZnO-doped CuMgO systems towards methanol dehydrogenation reactions

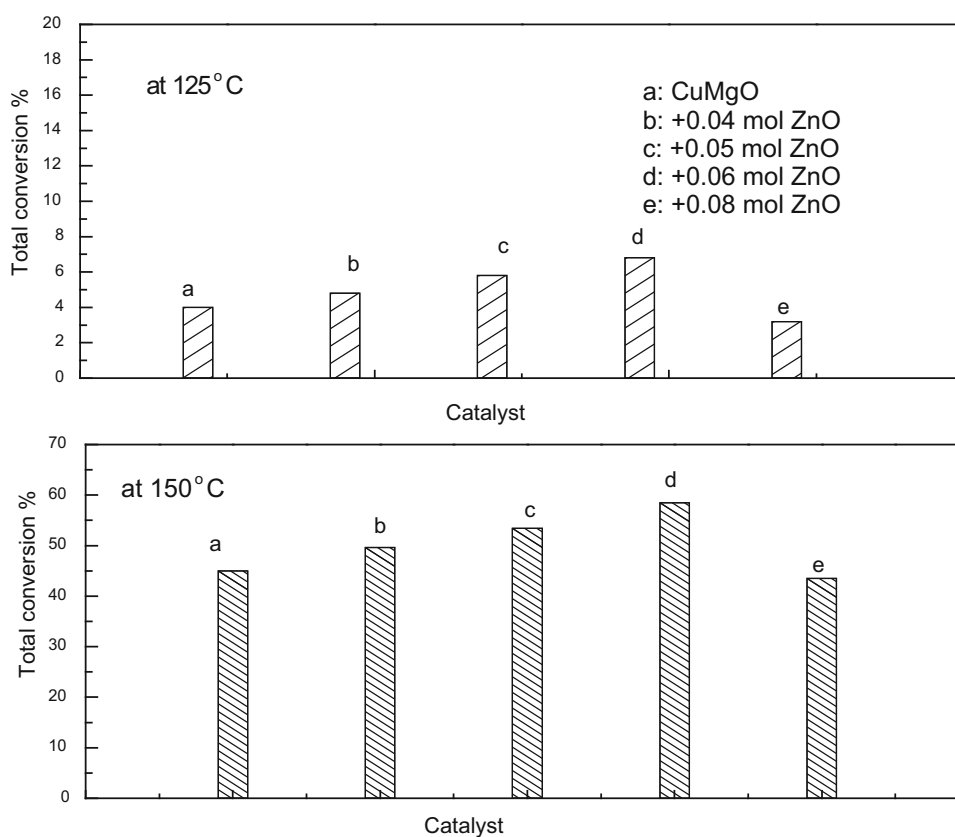
Doping with small amounts of ZnO affected both structural and surface properties of the investigated CuMgO system. The changes in structure and/or the surface can reflect the catalytic properties of these solid catalysts. The effect of ZnO-doping (0.04–0.08 mol) corresponding to (4.83–9.21 wt%) of CuMgO followed by calcinations at 350–650 °C on the catalytic activity and selectivity was investigated at different reaction temperatures (125–275 °C) as shown in Figs. 3 and 4 and Tables 3 and 4. The reaction proceeded via dehydrogenation to give both methyl formate and formaldehyde [28]. Examination of Figs. 3 and 4 and Tables 3 and 4 shows the following: (1) the catalytic activity of investigated solids (expressed as conversion of methanol) increases with increasing reaction temperature in the range of 125–175 °C. Further increase in the reaction temperature is followed by a small decrease in the catalytic activity (above this temperature the activity tends to be stable).



**Fig. 3** Total conversion of methanol as a function of reaction temperature over (a) CuMgO (b) 0.06 mol ZnO-doped CuMgO sample at different calcination temperatures

(2) Doping CuMgO solid with ZnO from 0.04 to 0.06 mol in the range of 125–175 °C led to increasing the conversion and selectivity of both formaldehyde and methyl formate. But increasing reaction temperature above 175 °C led to small increase in the conversion of methanol. (3) Further increase in ZnO content to (0.08 mol) decreases the conversion of methanol. (4) The catalytic activity and selectivity of pure and ZnO-doped solids increased with increasing the calcination temperature from 350 to 550 °C, but above this temperature the catalytic activity and selectivity decrease. (5) The investigated solids are selective to formaldehyde ( $S_F$  %) at low temperature, this selectivity decreases with increasing reaction temperature from 125 to 275 °C. The selectivity towards methyl formate ( $S_m$  %) was more pronounced at high reaction temperature.

**Fig. 4** Total conversion of methanol at reaction temperature 125 and 150 °C over pure CuMgO and those variously ZnO-doped samples calcined at 550 °C



**Table 3** Effect of ZnO-doping on the selectivity of CuMgO solids calcined at 550 °C towards methanol dehydrogenation (with reference to formaldehyde ( $S_f$  %) and methyl formate ( $S_m$  %))

The solids	Selectivities (%)	150 °C	175 °C	200 °C	225 °C	250 °C	275 °C
0.3CuMgO	$S_m$	17	43	46	48	53	59
	$S_f$	83	57	54	52	47	41
0.04ZnO/0.3CuMgO	$S_m$	17	47	50	52	55	57
	$S_f$	83	53	50	48	45	43
0.05ZnO/0.3CuMgO	$S_m$	18	47	50	53	55	57
	$S_f$	82	53	50	47	45	43
0.06ZnO/0.3CuMgO	$S_m$	23	42	48	50	52	52
	$S_f$	77	58	52	50	48	48
0.08ZnO/0.3CuMgO	$S_m$	16	42	45	50	51	58
	$S_f$	84	58	55	51	49	42

The results mentioned above can be explained in the light of: (1) the investigated CuMgO system is dehydrogenation catalyst. The prepared catalysts are selective to formaldehyde formation due to the presence of dehydrogenation sites (copper species) [15, 29–31]. (2) The observed increase in the catalytic activity and selectivity of solid samples doped with ZnO (0.06 mol) 7.07 wt% may be attributed to an affective increase in the concentration of active sites involved in the catalytic reaction via decreasing the crystallite size of CuO and MgO phase (as shown in “XRD” section), beside increasing the  $S_{BET}$  as shown in Table 2 and the presence of ZnO as dehydrogenation catalyst.

(3) Decreasing the catalytic activity and selectivity of doped solids above 0.06 mol% ZnO may be due to decreasing the ability of ZnO to hinder the grain growth of CuO and small amount of ZnO dissolves in MgO matrix. These effects yielded big crystallites of CuO (as shown in “XRD” section). (4) The observed increase in the catalytic activity by increasing the calcination temperature from 350 to 550 °C can be explained in the light of possible completeness of thermal decomposition of  $Mg(OH)_2$  and also formation of new active sites responsible for increasing the catalytic activity, beside increasing the  $S_{BET}$  as shown in Table 2. (5) Beside the possible dissolution of ZnO in both CuO and MgO

**Table 4** Effect of calcination temperature of pure 0.3CuMgO and ZnO-doped solids on their selectivities in the course of methanol dehydrogenation with respect to formaldehyde ( $S_f$  %) and methyl formate ( $S_m$  %)

The Solids	Calcination temperature (°C)	Selectivities (%)	125 °C	150 °C	175 °C	200 °C	225 °C	250 °C	275 °C
0.3CuMgO	350	$S_m$	100	12	42	50	54	56	58
		$S_f$	0	88	58	50	46	45	42
0.06ZnO/0.3CuMgO	350	$S_m$	74	14	38	48	52	55	57
		$S_f$	26	86	62	52	48	45	43
0.3CuMgO	650	$S_m$	100	9	41	49	54	57	58
		$S_f$	0	92	59	51	46	44	42
0.06ZnO/0.3CuMgO	650	$S_m$	65	11	41	45	52	56	58
		$S_f$	35	90	59	55	48	44	42

lattice yielding various solid solutions [32], the obtained decrease in the catalytic activity as a result of increasing the calcination temperature above 550 °C may be attributed to an effective increase in the crystallite size of copper oxides in pure and doped solids (as shown in “XRD” section), which was evidenced also, by decreasing the  $S_{BET}$  as shown in Table 2. The portion of CuO and/or ZnO involved in solid solution should have very small catalytic activity.

## Conclusions

In conclusion, the physicochemical and catalytic properties of CuMgO system are affected by ZnO-doping and calcination temperature. The results revealed that:

1. The crystallite size and ordering of CuO phase decrease to (4 nm) by ZnO-doping (<0.08 mol) for samples calcined at 350–550 °C. Opposite trends was observed by increasing ZnO amount to 0.08 mol (i.e. 9.21 wt%).
2. The BET surface area and catalytic activity of CuMgO catalyst increase by increasing the calcination temperature from 350 to 550 °C and/or by increasing the amounts of ZnO up to certain extent reaching to a maximum at 7.07 wt% ZnO.
3. In the pure and doped samples, increasing the calcination temperature to 650 °C led to increasing the crystallite size of CuO, decreasing the catalytic activity and selectivity.
4. The prepared catalysts were selective towards formaldehyde and methyl formate formation.

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