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

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ABSTRAT

The effect of ZnO-doping on the physicochemical and catalytic properties of CuO/MgO catalyst calcined at 350-650°C was investigated. The catalysts were characterized by XRD, S_{BET} techniques and the methanol conversion as the catalytic probe reaction. The results revealed that the crystallite size of CuO phase decreases by ZnO-doping. The BET surface area of samples increases by ZnO-doping.and catalytic activity of CuMgO catalyst increases by increasing the amounts of ZnO up to certain extent reaching to a maximum at 7.07 wt % ZnO above this concentration the activity decreases. The catalytic conversion of methanol and selectivity towards formaldehyde and methyl formate of pure powder catalyst increases by ZnO-doping.

Keywords: ZnO-doping; CuO/MgO system; methanol conversion; selectivity;

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1. Introduction

Doping of single or multicomponents metal or metal oxide system with certain foreign oxides brought about significant modifications in their thermal stability, electrical , optical , magnetic , surface and catalytic properties [1]. The addition of small amounts of certain foreign cations such as Li^+, Zr^{4+} and K^+ to CuO/MgO has influenced the mutual solid- solid interaction between constituents

[2,3]. This influence may be accompanied by significant changes in the catalytic and physicochemical properties of the doped catalysts [1]. Doping CuO/MgO system with K_2O decreased the degree of ordering of CuO and MgO phases [3]. Li_2O-doping of CuO/MgO solid enhanced its catalytic activity towards conversion of iso-propanol [2, 4]. ZnO is well-known dopant for many catalytic systems such as NiO and Co_3O_4, in which ZnO brought about measurable changes in their specific surface areas and the crystallite sizes of their phases [5]. Doping Ni- Al_2O_3 system with ZnO affected on the range of reduction temperature of NiO due to formation of $ZnAl_2O_4$ spinel-liked structure [6]. It was reported that the reactivity of Fe_2O_3 to interact with MO (M = Mg, Ni, Co and Mn) yielding the corresponding MFe_2O_4 had been found to be much stimulated by doping with ZnO [7, 8]. Zn^{2+} had a high chemical activity to diffuse into Co_3O_4 and Fe_2O_3 solids at about 600 °C [9]. Doping CuO / TiO_2 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 [10]. Methanol has been considered as an important raw material in the synthesis of various chemicals . Dehydrogenation of methanol is expected as a promising process to transfer methanol into formaldehyde and methyl formate [11]. Formaldehyde is an industrial chemical that is widely used to manufacture numerous household products [12]. Formaldehyde and methyl formate are produced in large quantity by the coal chemical industry and natural gas chemical industry [13], both of them are important organic chemical materials are usually used as the raw material of medicines [14]. Methanol is also considered as a candidate for the chemical carrier to transport hydrogen [15]. 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_3O species decomposed near 370 K to form formaldehyde and methyl formate [16]. 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, TiO2 and other oxides [17-21]. This work is interesting in preparation and characterization CuO/MgO system and investigation the influence of ZnO doping and calcination temperature on the catalytic activity and selectivity towards formaldehyde and methyl formate as products of methanol conversion.

2. Experimental

2. 1. Materials

A known mass of magnesium hydroxide (previously prepared [22] was impregnated with a solutions containing a known amount of copper nitrate dissolved in the least amount of distilled water and a solution containing different proportions of $Zn(NO_3)_2.6H_2O$. The obtained pastes were dried at 110 ^oC and then calcined at 350-650 ^oC for 4 hours. The amount of zinc oxide expressed in mol % were 0.04 , 0.05 , 0.06 and 0.08. The chemical composition of various prepared ZnO-doped 0.3CuO/MgO solids are listed in Table (3). The CuO content in all solid samples was fixed at 23 mol %. The Undoped sample was nominated as CuMgO.

2.2 Techniques

X-ray diffractograms of various prepared solids were determined using a Bruker diffractometer (Bruker D8 Advance target). 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 Scherer equation [23].

The specific surface areas of the solid catalyst samples were determined from nitrogen adsorption desorption isotherms measured at -196 ^oC using a Quanta chrome NOVA 2000 automated gas-sorption apparatus model 7.11. All samples were degassed at 200 ^oC for 2 hours under a reduced pressure of 10^{-5} Torr before undertaking such measurements.

The catalytic activities of pure and variously ZnO doped-CuO/MgO solid catalyst samples were determined by using methyl alcohol conversion at reaction temperatures 75- 275 ^oC, 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 1cm internal diameter packed with quartz fragments 2-3 mm length. The temperature of the catalyst bed was regulated and controlled to within ±1 ^oC. 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 ^oC. 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 ^oC in a current of argon for 1 hour then cooled to the catalytic reaction temperature. The injection time of the sample products and the un-reacted isopropyl alcohol was fixed after 15 min, and many injections were carried out to give constant conversion. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. The column used was stainless steel chromatographic columns, 4m 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.

3. Results and Discussion

3.1. XRD investigation of pure ZnO-doped 0.3 CuO/MgO solids calcined at different calcination temperatures

X-ray diffractograms of pure and variously ZnO-doped solids precalcined at 350-650 °C were determined and illustrated in Figs. 1&2. The computed values of crystallite sizes of different phases were calculated using sheerer equation [23] are given in Table (1). Inspection of Figs. 1&2 and Table (1): (i) All investigated solids precalcined at 350, 550 °C consisted of MgO phase as a major phase, CuO as a minor phase together with Cu_2O phase in nano crystalline nature. The presence of Cu_2O phase was evidenced from the brown color of the calcined solids beside presence of diffraction line at d =2.44 Å (at I /I >10 %). (ii) Doping 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 9.21 wt % ZnO resulted in an increase in the degree of ordering of CuO phase while opposite result was found in case of MgO phase. (iii) Treatment $CuMgO_{III}$ system with ZnO and calcined at 350 and 550 °C resulted in formation of nano crystalline ZnO phase, its crystallite size increases with increasing ZnO content. (iv) The rise in calcination temperature of pure and ZnO-doped solids from 350 to 650 °C decreases the degree of ordering of CuO and MgO and ZnO phases. (v) Increasing the calcinations temperature of CuMgO from 350 to 650 °C didn’t much affect the crystallite sizes of MgO and increases that of CuO phase while in the doped sample increasing the calcination temperature from 350 to 650 °C increases the crystallite size of CuO (4.7 to 25 nm).

These obtained results can be explained in the role of ZnO–doping in increasing the degree of dispersion of active phase [24, 25] 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 [24]. The re-increase of degree of crystallinity of CuO phase in the highly doped sample (0.08 mol) could be due to presence of maximum limit for ZnO to hinder the grain growth of CuO. Increasing ZnO content dissolves MgO and forms some sort of 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). Increasing the calcination temperature to 650 ºC dissolved ZnO in both of MgO and CuO crystallites. It has been reported that ZnO dissolves in lattice of MgO and CuO solid forming solid solutions [26, 27] .

3.2. Specific surface areas of pure and ZnO- CuO / MgO 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 °C. The dopant concentrations were 0.06 and 0.08 mol ZnO per mol MgO corresponding to 7.07 and 9.21wt%, respectively. The surface characteristics, namely S_{BET}, V_p and r^- calculated for various adsorbents are listed in Table (2). Inspection of the results in Table (2) shows that (i) Addition of increasing amounts of ZnO resulted in a progressive increase in the specific surface areas of the treated solids. The maximum increase in the S_{BET} due to treatment with 0.06 and 0.08 mol ZnO attained about 33 and 52% for the solids calcined at 550 °C. Similar results have been reported [28]. The observed increase in the specific surface areas of ZnO-doped solids may be attributed to formation of new pores due to liberation of gaseous nitrogen oxides in the course of the heat treatment of zinc nitrate added. (ii) Increasing the calcination temperature from 550 to 650 °C decreases the specific surface areas of the treated solids. The decrease in the S_{BET} due to increasing calcination temperature from 550 to 650 °C attained 24 and 21% for pure and doped solid with 0.06 mol ZnO, respectively. The decrease in specific surface areas of the treated solids as a result of increasing calcination is due to collapse of the pore structure and/or the particle adhesion process (grain growth). In fact, the BET-surface area of 0.3 CuO/MgO treated with 0.06 mol ZnO/mol MgO conducted at 650 °C measured 22 m^2/g while the ZnO-free sample calcined at the same temperature measured 16 m^2/g. These findings might suggest that ZnO acted as convenient stabilizer against thermal sintering process of the treated solids. The improvement in the surface area due to ZnO-doping is expected to be accompanied by a corresponding improvement in their catalytic activity.

3.4. Catalytic activity and selectivity measurements of different investigated solids

Doping with small amounts of ZnO affected on both structural and surface properties of the investigated CuMgO system. The changes in structure and/or the surface can reflect on the catalytic properties of this solid catalyst. The effect of ZnO–doping (0.04 – 0.08) mole corresponding to (4.83 – 9.21 wt%) of CuMgO followed by calcinations at 350–650 ºC on the catalytic activity and selectivity was investigated at different reaction temperatures (125 – 275 ºC) as shown in figures (3,4) and Table(3). The reaction proceeds via dehydrogenation to give both of methyl formate and formaldehyde [29]. Examination of Figs.(3,4) and Table(3) show the following: (i) The catalytic activity of investigated solid towards methanol conversion(expressed as total conversion of methanol) increases with increasing reaction temperature from 125-175 ºC. 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). (ii) Doping CuMgO solid with increasing amounts of ZnO from 0.04 to 0.06 mol increases the total conversion and selectivity to both of formaldehyde and methyl formate. Further increase in ZnO content to (0.08 mol) decreases the total conversion and selectivity. (iii) The catalytic activity and selectivity of pure and ZnO-doped solids increases with increasing the calcination temperature from 350 to 550 º C, above this temperature the catalytic activity and selectivity decreases. (iv) The investigated solids are selective to formaldehyde (S_F%) at low temperature, this selectivity decreases with increasing reaction temperature from 125 to 275 ºC. The selectivity towards methyl formate (Sm %) was more pronounced at high reaction temperature.

The previous results can be explained in the light of: (i) The investigated CuMgO system is dehydrogenation catalyst and is selective to formaldehyde formation due to presence dehydrogenation sites (copper species) [2,30-32].(ii) The observed increase in the catalytic activity and selectivity towards formaldehyde and methyl formate due to doping with increasing amounts of ZnO to (0.06 mol) 7.07

wt % is due to the 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 presence ZnO as dehydrogenation catalyst (ii) Above 7.07 wt % ZnO , the ability of ZnO to hinder the grain growth of CuO decreases and small amount of ZnO dissolves in MgO matrix . These effects yielded big crystallites of CuO (as shown in XRD section). (iii) The observed increase in the catalytic activity due to increasing the calcination temperature from 350 to 550 ºC can be explained in the light of possible completeness of thermal decomposition of $Mg(OH)_2$ and also formation a new active sites responsible for increasing the catalytic activity. (iv) The obtained decrease in the catalytic activity as a result of increasing the calcination temperature above 550 ºC is attributed to an effective increase in the crystallite size of copper oxides in pure and doped solids (as shown in XRD section). Beside the possible dissolution of ZnO in both CuO and MgO lattice yielding various solid solutions [26]. The portion of CuO and / or ZnO involved in solid solution should have very small catalytic activity.

The postulated mechanism of catalytic dehydrogenation of methanol to produce water–free formaldehyde as shown in the following reaction

$CH_3OH \rightarrow CH_2O + H_2$ was as follows :

$CH_3OH_{\,g} \leftrightarrow CH_3OH_{\,S}$ - ---------1 s-catalyst surface
$CH_3OH_{\,S} \leftrightarrow H^{\cdot}_{\,S} + CH_3O^{\cdot}_{\,S}$ ----------2
$CH_3OH_{\,S} \leftrightarrow H^{\cdot}_{\,S} + {}^{\cdot}CH_2OH_{\,S}$ ----------3
$CH_3O^{\cdot}_{\,S} \rightarrow CH_2O_{\,g} + 1/2H_{2\,g}$ ----------4
${}^{\cdot}CH_2OH_{\,S} \rightarrow CO_{\,g} + 3/2H_{2\,g}$ ----------5
$H^{\cdot}_{\,S} + H^{\cdot}_{\,S} \rightarrow H_{2\,g}$ ----------6

The high selectivity towards formaldehyde formation shows reaction step (4) is faster than (5) [29]. The other dehydrogenation reaction is formation methyl formate which is an endothermic reaction, this reaction takes place in presence of copper containing catalysts [33] as follows:

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2$$

The mechanism of this reaction was studied by others [33-35], one of them is Tishchenko reaction [36-38]. This reaction is a dimerization of the aldehyde forming an ester, and catalyzed by solid base catalysts such as MgO, CaO and SrO [36,38] under mild conditions. Tishchenko reaction over a metal oxide catalyst is initiated by basic sites and driven by acidic sites. The basic sites are believed to be the oxygen atoms at coordinatively unsaturated sites and the acidic sites are metal cations or oxygen vacancies adjacent to basic sites [37]. This explanation is supported by two factors : (i) The catalyst used in this study contains dehydrogenation catalysts (CuO and / or ZnO)and the basic surface (support) is MgO. (ii) The selectivity of methyl formate increases with a decrease in the selectivity of formaldehyde formation as a function of reaction temperature. These items shed some lights on the importance of the investigated system CuMgO and ZnO-CuMgO towards the dehydrogenation of methyl alcohol.

4. Conclusions

In conclusion, the physicochemical and catalytic properties of CuMgO system are affected by ZnO-doping and calcination temperature. The crystallite size of CuO phase decreases by ZnO-doping. The surface area of CuMgO catalyst increases by increasing the amounts of ZnO, and catalytic activity of CuMgO catalyst increases by increasing the amounts of ZnO up to certain extent reaching to a maximum at 7.07 wt % ZnO which above the activity decreases. The catalytic activity and selectivity towards formaldehyde and methyl formate of pure powder catalyst increase by ZnO-doping.

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Table 1. Intensity count , crystallite sizes of various phases present in pure and ZnO-doped 0.3 Cu MgO $_{III}$ solids calcined at 350 , 550 and 650 °C.

Solid	**Calcinat. Temp.**	**Intensity count(a.u.)**			**Crystallite size (nm)**			I /Io
		MgO	CuO	ZnO	MgO	CuO	ZnO	**Cu_2O**
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**

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

Moles of ZnO	**Calcn. Temp.** °C	**S_{BET} (m^2/g)**	**V_p cm^3/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

Table 3. Effect of ZnO- doping on the selectivity of CuMgOIII solid towards methanol conversion at calcination temperature 550°C

The Solids	Selectivities	125 ºC	150 ºC	175 ºC	200 ºC	225 ºC	250 ºC	275 ºC
0.3CuMgOIII	S_m %	100	17.1	42.7	45.9	48	53.2	58.6
	S_f %	0.00	82.9	57.3	54.1	52	46.8	41.4
0.04ZnO/0.3CuMgOIII	S_m %	42.1	16.9	47.1	49.9	52.2	55.2	56.8
	S_f %	57.9	83.1	52.9	50.1	47.8	44.8	43.2
0.05ZnO/0.3CuMgOIII	S_m %	58.2	18.3	46.8	49.8	53.1	54.7	57.1
	S_f %	41.8	81.7	53.2	50.2	46.9	45.3	42.9
0.06ZnO/0.3CuMgOIII	S_m %	49.6	22.9	42.3	48.1	49.6	52	51.6
	S_f %	50.4	77.1	57.7	51.9	50.4	48	48.4
0.08ZnO/0.3CuMgOIII	S_m %	100	16.1	42.2	45	49.5	50.8	58.2
	S_f %	0.00	83.9	57.8	55	50.5	49.2	41.8

Table 4. Effect of calcination temperature of pure and ZnO-doped solid on the products' selectivities .

The Solids	Calcination Temperature	Selectivities	125 ºC	150 ºC	175 ºC	200 ºC	225 ºC	250 ºC	275 ºC
0.3CuMgOIII	350 ºC	S_m %	100	12.4	41.6	49.8	53.9	55.5	57.8
		S_f %	0.00	87.6	58.4	50.2	46.1	44.5	42.2
0.06ZnO/0.3CuMgOIII	350 ºC	S_m %	73.7	14.3	38.4	47.9	52.4	55.3	57.4
		S_f %	26.3	85.7	61.6	52.1	47.6	44.7	42.6
0.3CuMgOIII	650 ºC	S_m %	100	8.5	41.2	48.8	53.7	56.5	58.1
		S_f %	0.00	91.5	58.8	51.2	46.3	43.5	41.9
0.06ZnO/0.3CuMgOIII	650 ºC	S_m %	64.9	10.5	40.9	45.2	51.7	56	58.3
		S_f %	35.1	89.5	59.1	54.8	48.3	44	41.7

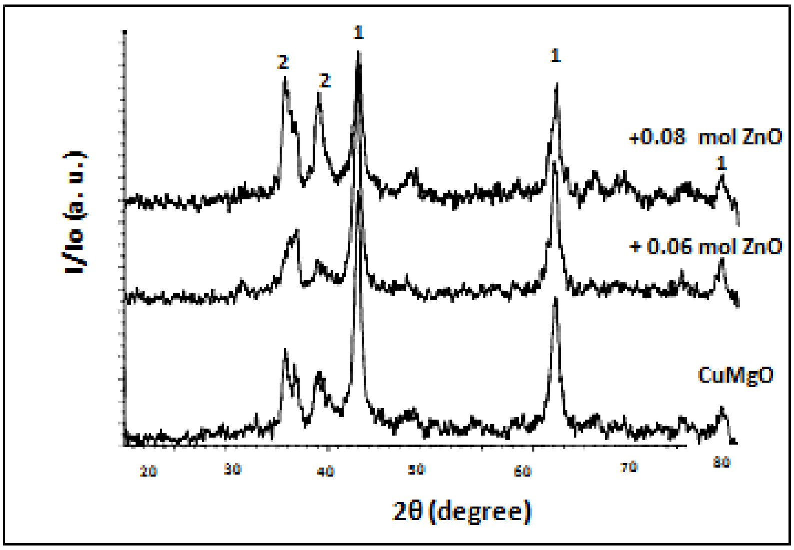

Fig. 1 XRD diffractograms of pure and ZnO doped CuMgO solids precalcined at 550 ºC. Lines (1) refer to MgO, lines (2) refer to CuO phases.

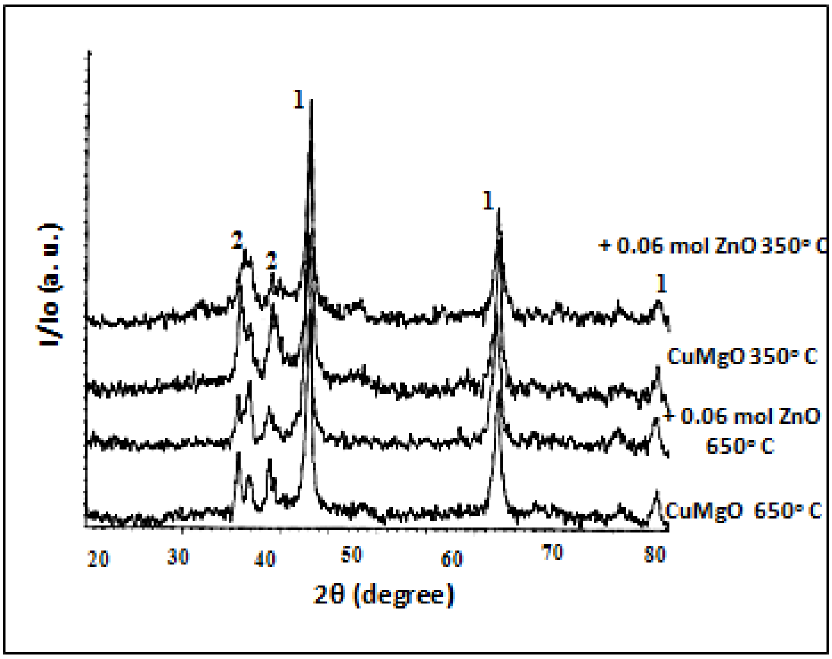

Fig. 2 XRD diffractograms of pure and ZnO-doped CuMgO solids precalcined at 350 and 650 ºC. Lines (1) refer to MgO, lines (2) refer to CuO phases.

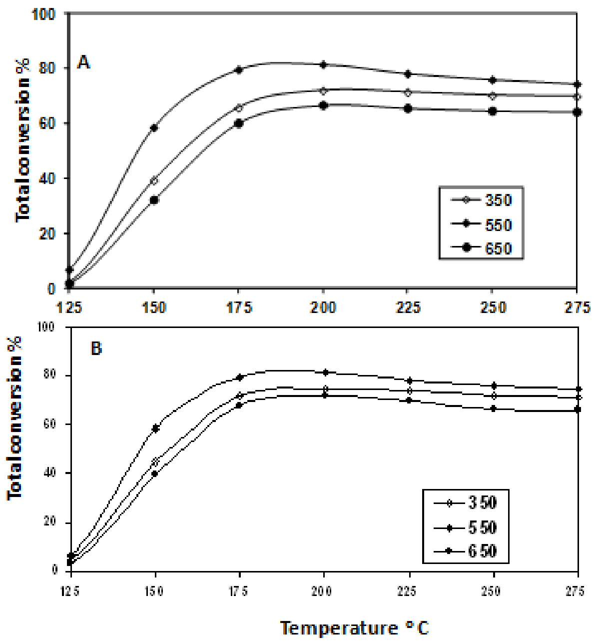

Fig. 3. Total conversion of methanol as a function of reaction temperature over (A) CuMgO (B) 0.06 mol ZnO-doped sample at different calcination temperatures.

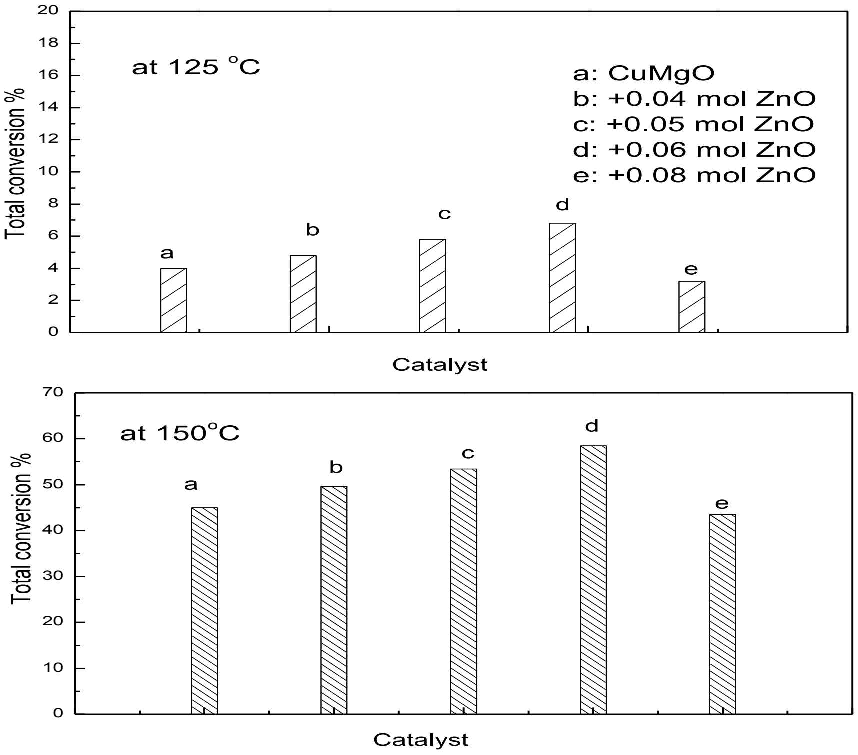

Fig. 4. Total conversion of methanol at 125 and 150 °C over pure CuMgO and those variously ZnO-doped samples calcined at 550 °C.