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Dehydrogenation and Condensation in Catalytic Conversion of *iso*-Propanol over CuO/MgO System Doped with Li₂O and ZrO₂

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Abstract

The effects of Li₂O and ZrO₂-doping on the surface and catalytic properties of CuO/MgO system have been investigated. The dopant concentration was changed between 0.6 and 3.6 mol % Li₂O and that of ZrO₂ between 2.4-7.7mol %. Pure and variously doped solids were calcined at 673 and 773 K. The techniques employed for characterization of different solids were XRD, nitrogen adsorption at 77 K and catalytic conversion of *iso*-propanol at different reaction temperatures ranged between 423 and 573 K. The results revealed that the addition increasing amounts of dopant (Li₂O and ZrO₂) to CuO/MgO solid led to an increase in the degree of dispersion of CuO phase and a decrease in the specific surface areas of the investigated solids. Li₂O and ZrO₂-doping increases the catalytic conversion of *iso*-propanol, which proceeds mainly via dehydrogenation to give acetone and aldol condensation of the produced acetone to give methyl isobutyl ketone (MIBK). Doping with 1.2 mol % Li₂O for the solids calcined at 673 K increases both of total conversion and selectivity to MIBK at reaction temperature 473 K with 24 % and 25 %, respectively. Doping with 7.7 mol % ZrO₂ for the investigated solids calcined at 673 K increases both of total conversion and selectivity to MIBK at reaction temperature 473 K with 32 % and 99 %, respectively.

Keywords: CuO/MgO catalyst, ZrO₂ –and Li₂O-doping, *iso*-propanol conversion, MIBK

1. Introduction

MgO as an alkaline earth metal oxide acts as a solid base catalyst and as a support in a variety of organic reactions such as alcohol coupling [1-3], Knoevenagel condensation [4], aldol condensation [5,6]. Deposition metal cations on MgO-based catalysts for producing new centers with different acid-base properties have been reported. Such cations as Ni²⁺, Fe³⁺, Cu²⁺ and Cr³⁺ promoted MgO and increased the basic properties and the catalytic activity for 2-propanol dehydrogenation [7,8]. The acid-base properties of MgO induced by promotion with alkaline cations depend on both the amount and the kind of the cation added [1,6]. Lithium exhibits some affinity for MgO lattice, probably due to its similar ionic radius with Mg²⁺, small amounts of Li⁺ can be incorporated into MgO lattice by creating electron holes [9]. Conversion of *iso*-propanol on metal oxide surface has been employed frequently as a probe of surface acid-base properties [10-13]. The well-known two directions for conversion of *iso*-propanol are dehydration to give propene, which is assumed to proceed at acidic sites and dehydrogenation to give acetone is catalyzed in a concerted fashion by both acidic and basic sites [10,14]. There is an important product is produced indirectly during the conversion of *iso*-propanol, this compound is MIBK (methyl isobutyl ketone)[15].

MIBK is produced through consecutive reactions involved in the conversion of 2-propanol as follow: (i) dehydrogenation of 2-propanol, (ii) self-condensation of the resulting

acetone to meistyle oxide (MO) and (iii) hydrogenation of MO to MIBK [15]. MIBK is produced by using bifunctional catalyst such as $\text{CuM}_I\text{M}_{II}\text{O}_x$ mixed oxides where, M_I and M_{II} are metal cations such as Mg^{2+} , Al^{3+} or Ce^{3+} in the novel one-step synthesis from 2-propanol at low temperature and atmospheric pressure [15]. The importance of MIBK evolved from its use as a useful solvent for paints and resin-based protective coating systems [16,17], an important reagent in dewaxing mineral oils [17], extracting agent for the production of antibiotics and commercial lubricating oils and an intermediate for production of various plastics and resins such as polystyrol, acryl-and alkyl-phenol resins, nitrocellulose and epoxy resins [18].

This work was devoted to follow the possible changes in the physicochemical properties of CuO/MgO as being influenced by doping with small amounts of lithium and zirconium oxides and attempt to correlate the oxide-oxide or the oxide-support interactions with catalytic activity towards various sub-reactions take place in *iso*-propanol conversion (dehydrogenation to produce acetone and self condensation of acetone followed by hydrogenation to produce MIBK).

The dopant amounts were 0.6–3.6 mol % lithium ions, and 2.4–7.7 mol % Zr^{4+} ions, the CuO loading was fixed at 16.7 mol %. The techniques employed were XRD, nitrogen adsorption at 77 K and the catalytic conversion of *iso*-propanol at 423–573 K using the flow system.

2. Experimental

2.1. Materials

CuO/MgO sample was prepared by impregnating a known amount of finely powdered $\text{Mg}(\text{OH})_2$ solid with an aqueous solution containing a known amount of copper nitrate dissolved in the least amount of distilled water necessary to make pastes. The resulting paste were dried at 373 K to constant weight and then subjected to heat treatment at 673 and 773 K for 4 hours. The nominal composition of the prepared precalcined product was 0.2 CuO/MgO, which contained 16.7 mol % CuO.

Lithium–or zirconium-doped CuO/MgO samples were prepared by treating a known weight of finely powdered $\text{Mg}(\text{OH})_2$ with different proportions of lithium nitrate or zirconyl nitrate dissolved in the least amount of distilled water necessary to make pastes. The resulting pastes were dried at 373 K followed by heating at 773 K for 4 hours. The amounts of lithium were 0.6, 1.2 and 3.6 mol % lithium ions. The amounts of zirconium were 2.4, 4 and 7.7 mol % zirconium ions. The obtained lithium-and zirconium-treated samples were impregnated with fixed amounts of copper nitrate dissolved in the minimum amount of distilled water followed by drying at 373 K and calcinations at 673 and 773 K for 4 hours. All the chemicals employed were of analytical grade supplied by BDH Ltd.

2.2. Techniques

Phase analysis, lattice parameter and particle size of the pure and variously doped specimens preheated in air at 673 and 773 K were performed by X-ray powder diffraction employing a BRUKER Axs D8 Advance, Germany. Patterns were run using Ni-filtered copper radiation ($\lambda = 1.5404 \text{ \AA}$) at 40 kV and 40 mA at a scanning rate of 0.02 degree/min. Particle size was evaluated by means of Scherrer's equation; through TOPAZ2.Inc program. The specific surface areas of the pure and variously doped catalyst samples were determined from nitrogen adsorption isotherms measured at 77 K using a quantachrome NOVA2000 automated gas sorption apparatus model 7.11. All samples were degassed at 473 K for 2 hours under a reduced pressure of 10^{-5} Torr before undertaking such measurements.

The catalytic activities of the various solid catalyst samples were determined by using *iso*-propanol conversion reaction at different temperatures varying between 423 and 573 K, the catalytic reaction being conducted in a flow reactor under atmospheric pressure. Thus, a 100 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 K. Nitrogen gas was used as the diluent and the *iso*-propanol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 308 K. The flow rate of the carrier gas (nitrogen) was maintained at 25 ml/min. Before carrying out such catalytic activity measurements each catalyst sample was activated by heating at 623 K in a current of nitrogen for 2 hours then cooled to the catalytic reaction temperature. 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 fused silica glass capillary column type PE-CW length 15 m-1.0 μ m Perkin-Elmer corp.

3. Results and Discussion

3.1. XRD Investigation of pure and doped solids

The X-Ray diffractograms of pure and variously doped CuO/MgO solid samples precalcined at 673 (not shown) and 773 K were determined. Figure (1) depicts the diffractograms of pure and variously Li₂O-doped CuO/MgO solid samples precalcined at 773 K. Inspection of the figure 1 revealed that: (i) The diffractogram of pure sample consists of all diffraction lines of well crystallized MgO phase as a major phase beside the diffraction lines of poorly crystalline CuO as a minor phase. The fact that MgO and Cu₂O show common diffraction lines at $d = 2.43, 2.11, 1.48 \text{ \AA}$ (as shown in table 1) makes their distinction a difficult task. However, the brown coloration of the solids subjected to heat treatment at 673 and 773 K might suggest the possible formation of Cu₂O phase together with CuO and MgO phases. This speculation may find an additional evidence from the significant increase in the relative intensity of diffraction peak at $d = 2.43 \text{ \AA}$ which correspond to 10 % in case MgO increased to 23 % due to a possible superposition with the main line of Cu₂O found at the same d -value. The possible presence of zero-, mono- and divalent copper ions in CuO lattice especially when it is loaded on MgO support material has been reported [19-21]. So, the possible presence of Cu₂O in our case is confirmed from both work done previously and brown coloration acquired by pure and Li₂O, ZrO₂-doped CuO/MgO solids heated at 673 and 773 K. (ii) The addition increasing amounts of Li₂O (0.6-1.2 mol %) led to a disappearance all diffraction lines of CuO phase and increasing the degree of ordering of MgO phase.

Table 1. The phases present, their d -values, experimental and standard their relative intensities as derived from XRD-measurements of CuO/MgO solid precalcined at 673 K.

Phase	d -value \AA	I/I ₀ %	Found I/I ₀
MgO	2.106	100	100
	1.48	72	52.0
	1.21	26	13.1
	2.43	10	21.0
CuO	2.31	100	8.8
	2.52	92	18.5
Cu ₂ O	2.42	100	–
	2.12	86	–

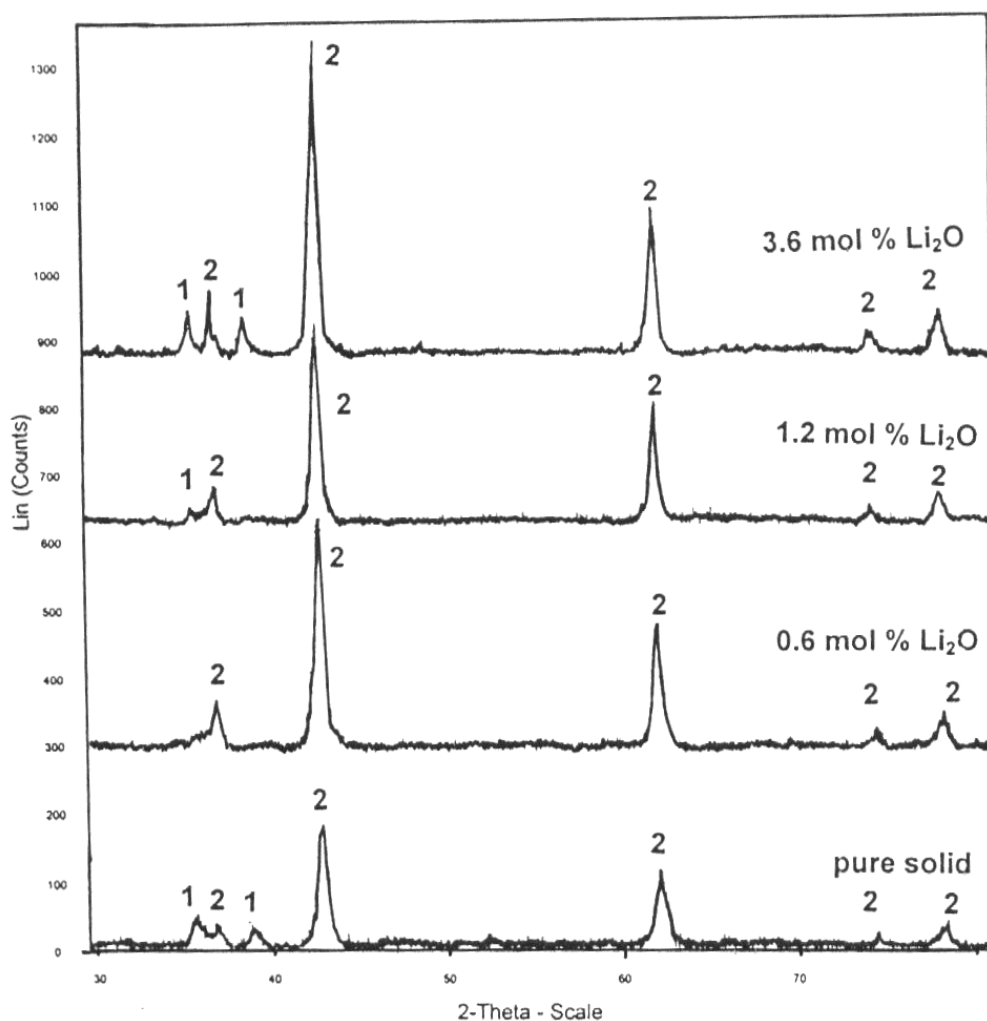


Figure 1. XRD of pure and treated 0.2 CuO/MgO solids with various amounts of Li₂O, precalcined at 500 °C. Lines (1) refer to CuO and (2) refer to MgO phases.

The disappearance of free CuO might reflect an effected dissolution of CuO in MgO lattice [22] or may be the interaction between lithium and copper oxide forms lithium copperate, the small amount of lithium copperate is hardly to detect by XRD-technique [23]. So, it seems that Li₂O-doping increased the mobility of copper and magnesium ions in CuO and MgO solids facilitating the formation of CuO-MgO solid solution. Upon increasing in Li₂O amount above 1.2 mol% opposite effect of Li₂O-doping was manifested i.e. more ordering of CuO-crystallites present as a separate phase. (iii) Increasing the precalcination from 673 to 773 K, as shown in table (2), resulted in an increase in the crystallite size of MgO and copper oxides. (iv) The existence of Cu₂O together with CuO in pure CuO/MgO calcined at 673 and 773 K has been confirmed via determination the lattice parameter (a) of MgO as a result of treating with CuO, where a-parameter corresponds to the cation-cation distance within the cubic symmetry structure and calculated from the following relation $a = d(h^2 + k^2 + l^2)^{1/2}$, where d corresponds to the inter planer spacing of the main diffraction peak of MgO having hkl (200) [jcpds (4-829)]. The computed a-value for MgO phase was found to increase from

4.213 Å (standard value) to 4.219 and 4.227 Å in the pure CuO/MgO solid calcined at 673 and 773 K, respectively. This increase might be attributed to a possible incorporation of Cu^{1+} in MgO lattice. In fact, the ionic radii of Mg^{2+} and Cu^{1+} are 0.66 and 0.96 Å, respectively [24].

Figure (2) depicts the diffractograms of pure and variously ZrO_2 -doped CuO/MgO solid samples precalcined at 773 K. Inspection of figure (2) revealed the following: (i) The addition of increasing amounts (2.4-7.7 mol %) zirconium oxide to CuO/MgO solid samples precalcined at 673 (not shown) or 773 K resulted in disappearance of all diffraction lines of CuO phase. This treatment resulted also in a measurable decrease in the crystallite size of MgO phase as shown in table (2) and a decrease in the degree of ordering of this phase as evidenced from a significant decrease in the peak area of the of the main diffraction line of MgO phase. These results clarify the role of ZrO_2 -treatment in increasing effectively the degree of dispersion of CuO phase. (ii) The rise in precalcination temperature from 673 to 773 K resulted in an increase in the degree of crystallinity of CuO phase and also its particle size.

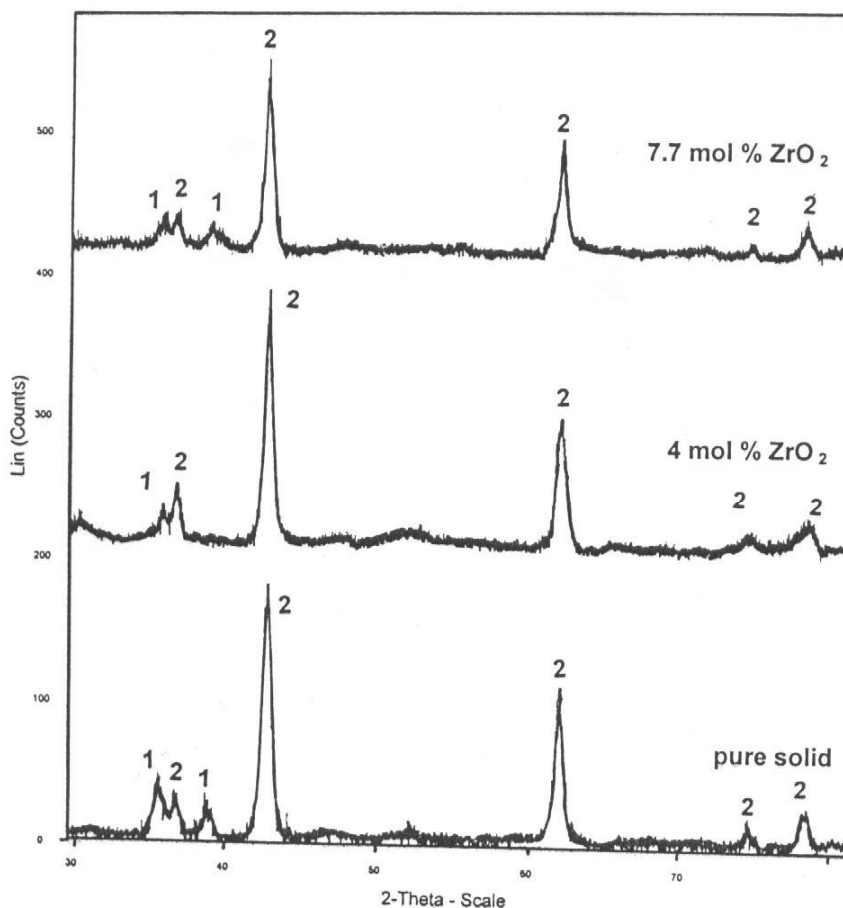


Figure 2. XRD of pure and treated 0.2 CuO/MgO solids with various amounts of ZrO_2 , precalcined at 500 °C. Lines (1) refer to CuO and (2) refer to MgO phases.

These findings suggest that ZrO_2 has a capability to increase the degree of dispersion of CuO phase also at higher calcinations temperature. (iii) Addition of 7.7 mol % ZrO_2 to the system investigated followed by calcinations at 773 K enhanced crystallization of CuO phase. Treatment CuO/MgO solid with 7.7 mol % of ZrO_2 led to enlargement of lattice parameter of

MgO, as shown in table (2), from 4.213 to 4.227 and 4.228 Å when the solids calcined at 673 and 773 K, respectively.

Table 2. S_{BET} , crystal sizes of different phases and lattice parameter constant of MgO measured for pure and variously-doped CuO/MgO solid precalcined at 673 and 773 K.

Dopant concn. mol %	Calc. Temp. K	S_{BET} m^2/g	Crystal Size (nm) of the present phases			a-const [MgO]* Å
			MgO	CuO	Cu ₂ O	
0	673	53	29.9	18.3	43.1	4.219
7.7 mol % ZrO ₂	673	27	27.4	–	23.4	4.227
0	773	47	29.3	26.5	30.1	4.227
4.0 mol % ZrO ₂	773	38	33.0	–	37.2	4.222
7.7 mol % ZrO ₂	773	22	35.7	21.1	25.6	4.228
0.6 mol % Li ₂ O	773	40	31.1	–	27.0	4.223
1.2 mol % Li ₂ O	773	36	36.8	–	36.6	4.218
3.6 mol % Li ₂ O	773	20	35.1	35.2	44.6	4.220

*The standard a-value of MgO is 4.213 Å

3.2. Specific Surface areas of pure and variously doped solids

The specific surface areas (S_{BET}) were determined for pure and doped solids precalcined at 673 and 773 K from nitrogen adsorption isotherms conducted at 77 K. The computed values of S_{BET} for different investigated solids are given in table (2). This table shows that Li₂O and ZrO₂-doping of the system investigated followed by heat treatment at 673 and 773 K affected a progressive decrease in its BET-surface area to an extent proportional to the amount of dopant added. It has been shown in XRD section that Li₂O-treatment of CuO/MgO system calcined at 673 and 773 K affected a significant increase in degree of ordering and particle size of both MgO and CuO phases, these effects led to a decrease in the BET-surface area of the treated system and that was found experimentally. While in XRD-study of ZrO₂-doping of the system investigated affected a significant decrease in the particle size and degree of ordering of both CuO and MgO-crystallites. These effects might be normally accompanied by an increase in the S_{BET} values of the treated system. This conclusion was not verified in our case simply because a significant decrease in the BET-surface areas of the treated solids was observed, so, one can speculate that small sized CuO crystallites due to ZrO₂-treatment may be located in some pores of MgO support material leading to an effective decrease in the specific surface area of the investigated system.

The observed changes in the surface characteristics of the investigated system due to doping with Li₂O and ZrO₂ could be followed by possible changes in its catalytic activity.

3.3. Catalytic conversion of iso-propanol over pure and doped solids

The catalytic conversion of *iso*-propanol was undertaken over pure and variously doped CuO/MgO samples precalcined at 673 and 773 K. Preliminary experiments showed that MgO support material preheated at 673 and 773 K showed extremely small catalytic activity towards *iso*-propanol conversion even at temperatures as high as 673 K. On the other hand pure and variously doped CuO/MgO samples precalcined at 673 and 773 K showed significant catalytic activity in *iso*-propanol conversion. This reaction proceeds via dehydration to yield propene with negligible amounts and dehydrogenation to give acetone as the major product, another side reaction takes place which is the self condensation of the produced acetone followed by hydrogenation to give methyl isobutyl ketone (MIBK)[15]. The total conversion of *iso*-propanol and the catalyst selectivity towards various products were much affected by doping CuO/MgO with Lithia and zirconia.

Table 3. Total conversion of *iso*-propanol, selectivity to propene, acetone and MIBK at reaction temperature 473 K using pure and variously doped-CuO/MgO solids precalcined at 673 and 773 K.

Solid (CuO/MgO) + dopant	Calcn. Temp. K	Total Conversion %	S% to propene	S% to acetone	S% to MIBK
Pure Solid	673	71	0.5	90	9.5
0.6 mol % Li ₂ O	673	83	0.2	89	10.8
1.2 mol % Li ₂ O	673	88	0.1	88	11.9
3.6 mol % Li ₂ O	673	85	0.1	96	3.9
2.6 mol % ZrO ₂	673	77	0.1	89	10.9
4.0 mol % ZrO ₂	673	92	0.1	84	15.9
7.7 mol % ZrO ₂	673	94	0.1	81	18.9
Pure Solid	773	84	0.3	91	8.7
0.6 mol% Li ₂ O	773	86	0.1	93	6.9
1.2 mol% Li ₂ O	773	94	0.1	93	6.9
3.6 mol% Li ₂ O	773	85	0.1	97	2.9
2.6 mol% ZrO ₂	773	90	0.1	90	9.9
4.0 mol% ZrO ₂	773	92	0.1	86	13.9
7.7 mol% ZrO ₂	773	93	0.1	85	14.9

Table (3) includes the values of total conversion of *iso*-propanol and the catalytic selectivity towards various products at reaction temperature 473 K using the pure and doped solids. Figures (3 & 4) depict the variation in the total conversion of *iso*-propanol using CuO/MgO solid, which influenced by doping with Lithia and zirconia, respectively. Inspection of table (3) and Figs. (3,4) reveal the following:

(i) All the solids investigated acted as dehydrogenation catalysts and the selectivity towards acetone formation changes slightly with the increase in the reaction temperature from 423-573 K (data not shown) and the selectivity towards aldol condensation product (MIBK) was limited.

(ii) Doping CuO/MgO system with 0.6-1.2 mol% Li₂O followed by calcinations at 673 and 773 K enhanced the total conversion and the selectivity to MIBK especially for the solids calcined at 673 K, while the selectivity to acetone formation suffered a slight changes. The maximum increase in the total conversion and selectivity to MIBK was 24 and 25 %, respectively for the reaction conducted at 473 K when the amount of dopant increased to 1.2 mol % and the solid calcined at 673 K. Further increase in Li₂O-content to 3.6 mol % led to a limited decrease in the total conversion of *iso*-propanol, which remained bigger than that measured for un-doped samples.

(iii) ZrO₂-doping of the investigated system enhances the total conversion and the selectivity to MIBK. The maximum increase in the total conversion of *iso*-propanol conducted at 473 K when the amount of dopant increased to 7.7 % ZrO₂ was 32 % and 11 % for the calcined solids at 673 and 773 K, respectively.

(iv) The maximum increase in the selectivity to MIBK due to doping with 7.7 % ZrO₂ was 99 and 71 % for the calcined solids at 673 and 773 K, respectively.

(v) There is a slight decrease in the selectivity to acetone formation by doping with Lithia or zirconia. The rise in precalcination temperature from 673 to 773 K resulted in a measurable decrease in the selectivity to MIBK formation.

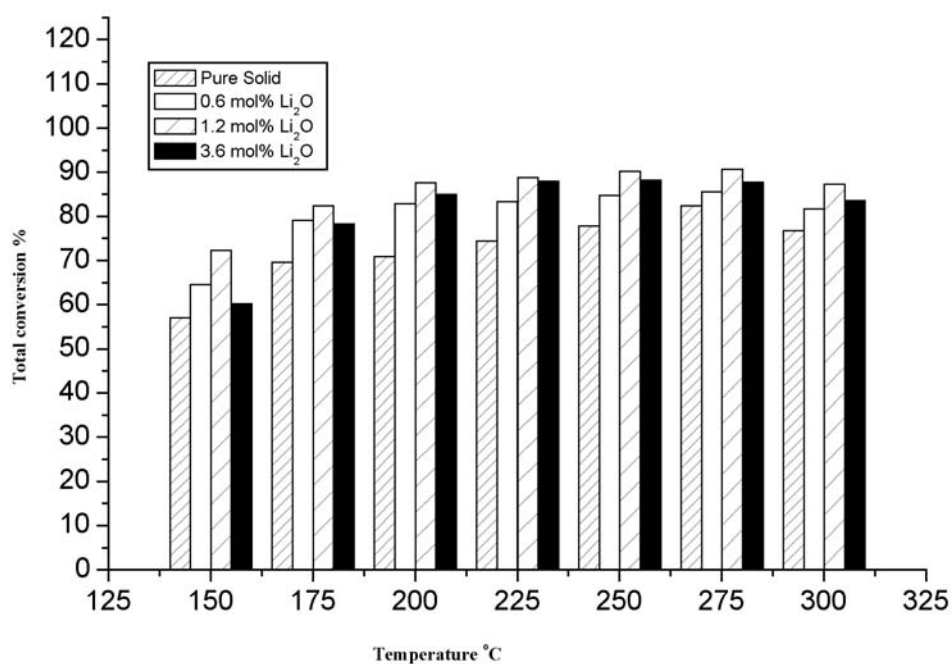


Figure 3. Total conversion of iso-propanol as a function of reaction temperature using pure and variously Li₂O-doped CuO/MgO solids calcined at 400° C.

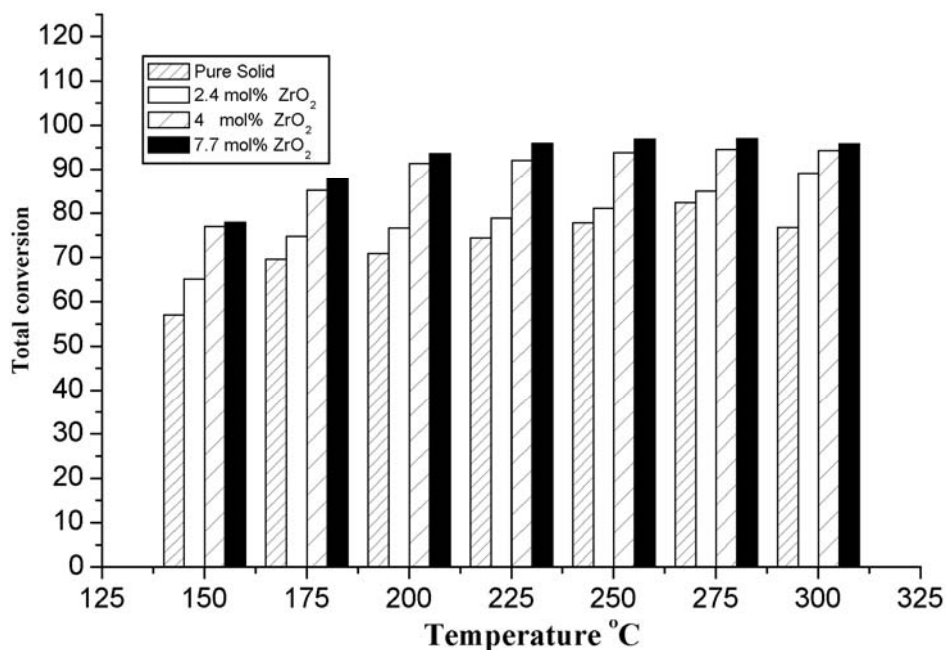


Figure 4. Total conversion of iso-propanol as function of reaction temperature using pure and variously ZrO₂-doped CuO/MgO solids calcined at 400° C.

These results can be discussed in the light of the following: (i) pure and doped CuO/MgO system showed high catalytic activity in the dehydrogenation of *iso*-propanol this may be attributed to the possible presence of zero, mono and divalent copper ions in CuO lattice supported on MgO [19-21], the presence of Cu⁰ and Cu¹⁺ centers are responsible for the activity in dehydrogenation of *iso*-propanol [19,20]. (ii) Li₂O-doped CuO/MgO solid with (0.6-1.2 mol %) enhances the catalytic activity (total conversion), this may be attributed to the dissolution of some Li⁺ ions in CuO lattice to give copper with various oxidation states [25,26] which led to presence pairs of medium-strength basic active sites [Mg(M⁺)-O] with high density responsible for the high selectivity to acetone formation[1]. (iii) The doping with increasing amounts of ZrO₂ (2.4-7.7 mol %) enhances the catalytic activity and the selectivity to MIBK. This can be explained in the light of the nature of catalytic material used in MIBK synthesis from *iso*-propanol in one-step. This material contains in intimate contact the metallic and acid-base sites required for consecutive reactions leading to MIBK formation and the best results are obtained on copper-mixed oxide bifunctional catalysts in which Cu⁰ atoms are finely dispersed in a matrix of moderately basic properties [15]. So, the rate determining step in aldol condensation to produce MIBK requires an appropriate balance of medium-strength bronsted-weak lewis acid sites which takes place by introducing ZrO₂ in the matrix of CuO/MgO solid. (iv) The decrease in MIBK selectivity with increasing the reaction temperature greater than 473 K may be attributed to coke deposition, since multiple condensations between MIBK and acetone gives high molecular weights-compounds that could be acted as a coke precursors [17]. In fact, the color of all investigated solids after the reaction changed to black, which supports the previous explanation. The decrease in MIBK selectivity due to increase the calcinations temperature from 673 to 773 K could be explained by a loss of basic sites responsible for acetone aldol condensation, these sites can be based on surface-OH groups [17, 27-29].

4. Conclusions

The main conclusions that may be drawn from the results obtained are as follows:

1. Addition of increasing amounts of Li₂O (0.6-1.2 mol %) to CuO/MgO solid calcined at 773 K led to disappearance all diffraction lines for CuO phase and did not much affect on the degree of ordering of MgO phase. Further increasing in Li₂O-amount to 3.6 mol % resulted in increasing in the degree of ordering and the crystallite size of CuO and MgO phases.
2. Addition of increasing amounts of ZrO₂ (2.4-7.7 mol%) to CuO/MgO solid samples precalcined at 773 K resulted in disappearance all diffraction line of CuO phase and resulted also in a measurable decrease in the crystallite size of MgO.
3. Treatment of CuO/MgO system by small amounts of Li₂O or ZrO₂ followed by calcination at 673 or 773 K was accompanied by a decrease in its specific surface.
4. The catalytic conversion of *iso*-propanol using the investigated solids proceeds mainly via dehydrogenation to give acetone as the major product, another side reaction takes place, which is the self-condensation of the produced acetone followed by hydrogenation to give methyl isobutyl ketone (MIBK).
5. The catalytic activity of the investigated system increased by increasing the Li₂O-content till 1.2 mol%. The maximum increase in the total conversion and selectivity to MIBK for the reaction conducted at 473 K and the solid calcined at 673 K was 24 and 25 %, respectively. Further increase in Li₂O-content to 3.6 mol % led to a limited

decrease in the total conversion of *iso*-propanol, which remained bigger than that measured for un-doped samples.

6. ZrO₂-doping of CuO/MgO system enhances the total conversion of *iso*-propanol and the selectivity to MIBK. The maximum increase in the total conversion of *iso*-propanol conducted at 473 K using 7.7 mol % ZrO₂ as a dopant was 32 % and 11 % for the solids calcined at 673 and 773 K, respectively. The maximum increase in the selectivity to MIBK at reaction temperature 473 K due to doping with 7.7 mol % ZrO₂ was 99 and 71 % for the solids calcined at 673 and 773 K, respectively.
7. The high selectivity to acetone formation and the increase in MIBK selectivity due to doping of CuO/MgO solid with ZrO₂ may be attributed to presence of the pairs of medium-strength basic active sites [Mg(M⁺)-O] with high density.
8. The decrease in MIBK selectivity with increasing the reaction temperature greater than 498 K may be due to coke formation.

5. References

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