# Physicochemical properties of nanosized CuO-ZnO system as being doped with by $Mg^{2+}$-species towards acetone formation from isopropanol

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*This paper is dedicated to the soul of late professor G. A. El-Shobaky*

Received : Revised

**Abstract.** Copper and zinc mixed oxides system having the formula 0.25 CuO/ZnO was prepared by coprecipitation method followed by calcination at 400 and 800 $^{o}$C. This system was doped with MgO (0.75- 3 mol %). The techniques employed were XRD, EDX, $N_2$-adsorption at -196 $^{o}$C, $H_2O_2$ decomposition at 20-40 $^{o}$C and conversion of 2-propanol at 100-275 $^{o}$C. The obtained results revealed that the crystallite sizes and surface concentrations of the phases in nanosized CuO-ZnO oxide system were influenced by calcination temperature and MgO-doping. Formation of MgO-CuO solid solution enhanced the splitting of CuO crystallites. Doping the investigated system calcined at 400°C with 1.5 mol % MgO increased its $S_{BET}$ (72%). The conversion of *iso*-propanol is improved by MgO treatment. The investigated solids behaved mainly as dehydrogenation catalysts yielding acetone.

**Keywords**: Nano materials; surface properties;, Doping, activity, selectivity.

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## Introduction

Mixed oxides catalysts have been studied for many industrial chemical reactions (Xu et al., 1991, El-Shobaky et al., 1999a). Catalysts such as CuO-ZnO-$ThO_2$, CuO-ZnO-MgO (Xu et al., 1991), CuO-ZnO-$Al_2O_3$, (El-Shobaky et al., 1999), CuO-ZnO, CuO/$ZrO_2$ (Denise and Sneeden 1986) and CuO/MgO (El-Molla 2006) have been studied for methanol synthesis from $CO_2$ and $H_2$ (Xu et al., 1991), CO oxidation (El-Shobaky et al., 1999a), conversion of alcohols( El-Molla 2006) and $H_2O_2$ decomposition (El-Molla 2006). Nanosized ZnO was used either as a support, active component, and promoter or as a structural and textural modifier (Choi et al., 2001). ZnO acted as catalyst stabilizer in CuO-ZnO/$Al_2O_3$ system in CO oxidation by $O_2$ (El-Shobaky et al., 1997) and synthesis of dimethyl ether (Li et al., 1996, Gulkova and Kraus 1994). It has been reported that the combination of ZnO and first-raw transition metal oxides gives a type of an industrial catalysts. CuO/ZnO system was widely applied in low temperature water gas shift reactions (Andreeva et al., 1992), CO oxidation by $O_2$ (El-Shobaky et al., 2009) and CO hydrogenation of higher alcohols (Calverley and Anderson 1987). Modification of the catalytic properties of solid catalysts could be achieved by preparation methods (El-Shobaky et al., 2009, El-Molla 2005, El-Molla et al., 2004, 2009). One of these methods is the well-known coprecipitation (Calverley and Anderson 1987). The change in the conditions of the coprecipitation method for preparing CuO/ZnO system affected on its physicochemical and catalytic properties towards CO oxidation (El-Shobaky et al., 2009, Calverley and Anderson 1987). Doping with certain foreign oxides is considered as an effective factor for modification the catalytic properties of solid oxide catalysts (El-Molla 2005, 2006, El-Shobaky et al., 1997). It has been reported that doping process affected the surface and acidic properties of the catalysts and modified the concentration of the catalytically active sites involved in the catalytic reactions (El-Molla et al., 2007). It has been reported that MgO-doped neodymia has a good catalytic activity towards methane coupling, which was found to increase as the MgO doping concentration increases. The synergy observed is directly linked to the dissolution of $Mg^{2+}$ ions in regions of disordered neodymia (Burrows et al., 1998). MgO-doped β–Tri calcium phosphate appears to be a good candidate for bone substitutes or bone tissue engineering applications, combining excellent biological and mechanical properties (Banerjee et al., 2010). The enhanced activity of MgO-doped-Cu/Zn/Al catalyst for the WGS reaction is probably due to the surface enrichment of MgO. Where, MgO stabilized $Cu^0$ (or $Cu^+$) species against oxidative sintering to $Cu^{2+}$ and simultaneously enhanced the activity by accelerating catalytic reduction–oxidation cycles between $Cu^0$ and $Cu^+$ (Nishida et al., 2009). Doping of $MoO_3/Al_2O_3$ system with MgO decreased the solubility of $MoO_3$ in alumina support material to an extent proportional to its amount present (El-Shobaky et al., 1999b). Addition of MgO up to10 mol% to the binary $ZnO$-$V_2O_5$ system controlled the abnormal ZnO grain growth, and modified its electrical properties (Hng and Tse, 2008). Due to both of redox and acid-base properties of CuO-ZnO system it is used in many industrial reactions such as methanol synthesis and water gas shift reactions (Andreeva et al., 1992). Catalytic decomposition of $H_2O_2$ in aqueous solution is used as a model reaction for measuring the catalytic activity of different metal oxides as a function of their redox properties at low temperatures (Fahim et al., 1981, Zaki et al., 1986). The co-existence of different valences in solid oxide catalysts form ion pairs (donor- acceptor sites) acting as active sites in the catalytic reactions (Mucka and Silber 1985). The catalytic activity of oxide catalyst was controlled by nature and concentration of sites present on its surface (Turky et al., 2001, Ferraris et al., 1991) The objective of this study was to find supporting results to evaluate the role of MgO-doping and calcination temperature on possible changes of physicochemical and catalytic properties of CuO-ZnO system using $H_2O_2$ decomposition and conversion of *iso*-propanol.

## Experimental Section

### Materials

Copper and zinc mixed oxides system having the formula 0.25CuO-ZnO was prepared by coprecipitation method from their nitrate solutions using 1M $Na_2CO_3$ solution at 70 °C and pH 8. The obtained precipitate was thoroughly washed with bi-distilled water till free from Na and nitrate ions. The obtained solid was dried at 110°C until constant weight then calcined in air at 400 and 800°C for 4 h. The MgO-doped samples were prepared by treating a known mass of uncalcined system with different amounts of magnesium nitrate dissolved in the least amounts of distilled water sufficient to make pastes. The pastes were dried at 110 $^{o}$C until constant weight then calcined in air at 400 and 800 $^{o}$C for 4h. The concentrations of MgO added were 0.75, 1.5, and 3 mol %. All the chemicals employed were of analytical grade supplied by BDH Company.

## 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° and 0.8° in 2Θ/min for phase identification and line broadening profile analysis, respectively. The patterns were run with Cukα1 with secondly monochromator,□□□= 0.145 nm at 40 kV and 40 m A. The crystallite size of the phases present was calculated using the Scherrer equation (Cullity 1978). Energy dispersive X-ray analysis (EDX) was carried out on Hitachi S-800 electron microscope with an attached kevex Delta system. The parameters were as follows: accelerating voltage 15 kV, accumulation time 100s, window width 8 $\mu$m. The surface molar composition was determined by the Asa method, Zaf-correction, Gaussian approximation.

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

The catalytic activities of pure and variously MgO-doped catalyst samples were determined by using *iso*-propanol conversion at 100- 275 $^{o}$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 $^{o}$C. Argon (carrier gas) was used as diluent and the isopropyl alcohol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 35 $^{o}$C. The quantity of *iso*-propanol introduced into the reactor by the carrier gas flow was maintained at 2.46 x$10^{-2}$ mol/hour. Before carrying out such catalytic activity measurements, each catalyst sample was activated by heating at 300 $^{o}$C in a current of argon for 1 hour then cooled to the catalytic reaction temperature. Many injections containing the reaction products and the un-reacted *iso*-propanol were carried out after 15 min from passing the reactant. 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 experiments. Detector temperature was kept at 250° C. The catalytic decomposition of $H_2O_2$ was carried out at 20–40 $^{o}$C, using 0.2 ml volume of $H_2O_2$ of known concentration (0.5mol/l). The mass of catalyst sample taken in each kinetic experiment was fixed at 50 mg in all cases. The reaction kinetics was monitored by measuring the volume of $O_2$ released at different time intervals until no further oxygen was released.

## Results and discussion

### *Energy dispersive X-ray analysis (EDX) of pure and MgO- doped solids*

EDX investigation of pure and variously MgO-doped solids calcined at 400 and 800 ºC was carried out. The CuO content present in the bulk of solids was calculated on the basis of its formula as 0.25 CuO-ZnO. The relative atomic abundance of copper, zinc, oxygen and magnesium species present in the uppermost surface layers of different investigated solids is given in Table1. It is well known that EDX technique supplies quantitative information about the effective surface atomic concentration of various solid constituents. Table1 contains also the value of atomic abundance of Cu, Zn, Mg and O present in the bulk (calculated) for various specimens. Examination of Table1 shows the following: (i) carbon species is present besides Cu, Zn and O species in all samples calcined at 400 ºC. The surface concentration of carbon content has almost the same value in all investigated samples calcined at 400 ºC. The presence of carbon species can be attributed to an incomplete decomposition of basic copper and zinc carbonates (used in preparation of the system investigated and being calcined at 400 ºC). This assumption could be evidenced from the complete disappearance of carbon species in all samples calcined at 800 ºC. (ii) The surface concentration of Cu species in all solids calcined at 400 and 800 ºC is bigger than those present in the bulk of these solids. (iii) Surface concentration of Zn species is smaller than that present in the bulk of different solids. (iv)Surface concentration of Mg species present in the solids calcined at 400 ºC is comparable to that present in the bulk. (v) The surface Cu/Zn atomic ratio in various solids is almost the same. (vi)MgO-doping modified the surface concentration of copper and zinc species depending on the dopant concentration and calcination temperature. (vii) Increasing the calcination temperature of pure and MgO- doped solids from 400 to 800 ºC brought about a limited decrease in the surface concentration of Cu and Zn species. However, the decrease is more pronounced in case of Mg–doped solids. In fact, the surface concentration of Mg species decreases in the sample doped with 1.5 % MgO with increasing the calcination temperature from 400 to 800 ºC.

According to these results, the high values of surface concentrations of Cu-species as compared to those in the bulk of different investigated solids might be due to an earlier precipitation of basic zinc carbonate prior to precipitation of basic copper carbonate. (viii) The surface concentration of Mg-dopant species is bigger than that present in the bulk of doped catalysts. This finding is quiet expected because the doped solids were prepared by wet impregnation method. This method permits an enriched presence of the Mg-cations on the top surface layers of the calcined solids, particularly solids calcined at 400 ºC.

The observed decrease in surface concentration of Cu and Mg species due to increasing the calcination temperature from 400 to 800 ºC might result from a possible migration of Cu and Mg species from the surface towards the bulk due to the concentration gradient. The migration of these cations enhances the solid-solid interaction between both of CuO-ZnO, CuO-MgO and MgO-ZnO couples. These possible interactions might hinder the aggregation of Cu and Mg species thus reducing their crystallite size. This speculation will be confirmed latter in the next section of the present work. The possible induced decrease in the crystallite sizes of various constituents is almost accompanied by an increase in their degree of dispersion.

### *XRD investigation of pure and MgO- doped solids*

X-ray diffractograms of pure and variously MgO-doped solids calcined at 400 ºC and 800 ºC were carried out. The obtained diffractograms are illustrated in figures1&2, respectively. Analysis of X-ray data permitted the determination of crystallite size of both CuO and ZnO phases. The results obtained are given in Table 2. Inspection of figures 1&2 and Table 2 shows the following: (i) The diffractograms of pure and variously MgO-doped solids calcined at 400 and 800 ºC consisted of nanosized ZnO and CuO phases.

Increasing both the dopant concentration and calcination temperature of the system investigated modified the degree of crystallinity and crystallite sizes of all phases present. (ii)The crystallite size and degree of crystallinity of the phases present in pure and doped solids increased by increasing the calcination temperature from 400 to 800 ºC. The increase, however, was more pronounced for ZnO phase. This finding might indicates an effective sintering promoted by raising the calcination temperature from 400 to 800 ºC via particle adhesion mechanism. (iii) MgO-doping of the system investigated decreased progressively the crystallite size of CuO phase to an extent proportional to the dopant concentration. The maximum decrease in the crystallite size of the CuO phase due to MgO doping measured 48 and 26% for the solids calcined at 400 and 800 ºC, respectively. The observed measurable decrease in the crystallite size of CuO phase due to MgO-doping might be tentatively attributed to some kind of splitting of CuO crystallites. It is plausible to argue that the formation of MgO-CuO solid solution enhanced the splitting of CuO crystallites.

The observed changes in structural characteristics of the investigated system due to doping with MgO and calcination temperature are expected to be followed by changes in their surface and catalytic properties.

***Specific surface areas of different investigated solids***

The different surface characteristics of pure and MgO-doped CuO-ZnO solids calcined at 400 $^{\circ}$C were determined from analysis of adsorption-desorption $N_2$ isotherms carried out at -196 $^{o}$C over various adsorbents. All the isotherms of various solids belong to type II of Brunauer's classification (Brunauer et al., 1938) having hysteresis loops closing at $P/P_o$ of about 0.4 as shown in figure 3. Surface characteristics were determined, these characteristics include specific surface area ($S_{BET}$), total pore volume ($V_p$), mean pore radius ($\bar{r}$) and pore volume distribution curves □□V/□r). These distribution curves are illustrated in figure 4. The computed $S_{BET}$, $V_p$ and $\bar{r}$ values are given in (Table 3). Examination of figure 4 reveals the following: (i) The maximum pore volume expressed in $cm^3$/Å /g of pure sample measured $2.2x10^{-4}$. The observed values of maximum pore volume for the variously doped adsorbents measured $39x10^{-4}$, $45x10^{-4}$ and $28x10^{-4}$ for the sampled doped with 0.75, 1.5 and 3 mol% MgO, respectively.(ii) The distribution curves of the pure sample shows bimodal distribution and the values of the most probable hydraulic pore radius for this particular sample is located at 33 and 39 Å. (iii) The pore volume distribution curves of the doped solids show multimodal distributions and the values of the most probable hydraulic pore radius are located at 19, 28, 33 and 40 Å for the doped samples. Inspection of the results cited in Table 3. and illustrated in figure 4.suggested clearly the role of MgO dopant in modifying the textural characteristics of CuO-ZnO system. In fact, the doping process much increased the specific surface area to an extent proportional to the amount of MgO added reaching to a maximum limit (72 %) by doping with 1.5 mol%. Increasing the dopant concentration above this limit decreased its $S_{BET}$ reaching to a value near from that measured for the un-doped sample. Furthermore, the doping process induced a considerable increase in the pore volume expressed in $cm^3$/g. The maximum increase was 50-fold reached by doping with 1.5 mol% MgO. The significant increase in the values of $S_{BET}$ and $V_P$ of the system investigated due to MgO-doping might be attributed to creation of a big deal of pores created from libration of nitrogen oxides gases in the course of the thermal decomposition of $Mg(NO_3)_2$

dopant. It can also be seen from Table 3. that the doping process was accompanied by a progressive increase in the $\bar{r}$-values. However, pure and variously doped adsorbents calcined at 400 $^{o}$C are mesoporous solids. The observed changes in surface characteristics of the investigated system due to doping with MgO are expected to modify its catalytic properties.

**Catalytic activity measurements of different investigated solids**

***Catalytic decomposition of $H_2O_2$ over pure and variously doped solids***

The catalytic decomposition of $H_2O_2$ was carried out at 20-40 $^{o}$C over different solids. First-order kinetics was observed in all cases. Figure 5 depicts a representative figure showing first-order plots for the catalyzed reaction conducted at 40 $^{o}$C over pure and variously MgO-doped solids precalcined at 400 $^{o}$C which allowed a ready determination of the reaction rate constant (k). The calculated values of reaction rate constant for the reaction carried out at 30 and 40 $^{o}$C in presence of the catalysts calcined at 400 $^{o}$C are cited in Table 4. Inspection of figure 5 and Table 4 reveals the following: (i) k increases progressively by increasing the amount of dopant for the solids precalcined at 400 $^{o}$C. The maximum increase in the values of $k_{40}{}^{o}{}_{C}$ due to doping with 3 mol% MgO attained 192 % for the solids precalcined at 400 $^{o}$C. These results clearly indicate that the doping process increased the concentration of catalytically active sites involved in the catalytic reaction to an extent proportional to the amount of the dopant added. It is shown in section (3.3) that doping the investigated system with 1.5 mol% MgO increased its specific surface area to a maximum limit (72%) above which the specific surface area decreased. It has been reported that MgO-doping of copper oxide solid resulted in an increase in its specific surface area without greatly affecting its pore size (Turky, et. al (2001). Also, doping of CuO with MgO resulted in a measurable increase in its catalytic activity towards $H_2O_2$ decomposition (Turky, et. al (2001). So, in order to account for the observed decrease in the $S_{BET}$ value due to doping with MgO with concentration bigger than 1.5 mol%, the reaction rate constant per unit surface area for the reaction carried out at 40 $^{o}$C over pure and variously doped solids calcined at 400 $^{o}$C was calculated. The computed $\bar{k}_{40}{}^{o}{}_{C}$ values were $5.37 \times 10^{-3}$, $4.84 \times 10^{-3}$, $6.52 \times 10^{-3}$ and $15.47 \times 10^{-3}$ $min^{-1}.m^{-2}$ for pure and solids doped with 0.75, 1.5 and 3 mol%, respectively. The maximum increase in the $\bar{k}_{40\,^{o}C}$ value attained about 2.9-fold for the heavily doped samples precalcined at 400 $^{o}$C. The decrease in the catalytic activity due to increasing the calcination temperature may be due to the decrease in the surface concentration of Cu species (catalytically active constituent in $H_2O_2$ decomposition), and also due to an effective increase in the crystallite size and degree of ordering of phases present via grain growth (El-Molla, et al., 2011a). Decomposition of hydrogen peroxide over the investigated system takes place on the following ion pairs $Zn^{2+}$–$Cu^{2+}$, $Mg^{2+}$– $Cu^{2+}$ion pairs.  Beside these ions $Cu^{+}$ or $Cu^{0}$ could be present and affect on catalytic decomposition of $H_2O_2$. It has been reported that CuO/MgO system calcined at 400 $^{o}$C contains $Cu^{+}$ species (El-Molla, 2006) and MgO stabilized $Cu^{0}$ (or $Cu^{+}$) and simultaneously enhanced the activity by accelerating catalytic reduction–oxidation cycles between $Cu^{0}$ and $Cu^{+}$ (Nishida et. al., 2009). So, the observed increase in the catalytic activity due to MgO-doping is understood.

### ***Catalytic conversion of iso-propanol in presence of different investigated solids***

he catalytic conversion of 2-propanol was carried out over pure and variously doped solids calcined at 400 and 800 ºC. The change in the percentage conversion as a function of reaction temperature varied between 100 and 275 ºC was investigated.  Figure 6 depicts this relationship between % conversion and reaction temperature for the reaction carried out over various solids calcined at 400 ºC. Tables 5,6 show the catalytic activity, expressed as, total conversion of *iso*-propanol and catalytic selectivities towards the reaction products as a function of the reaction temperature over various catalysts calcined at 400 and 800 ºC, respectively. Examination of figure 6 and Tables 5,6 shows the following: (i) The % conversion increases progressively as a function of reaction temperature reaching a maximum limit at 175 ºC  then suffers a limited small increase. The observed significant increase in the catalytic activity, in *iso*-propanol conversion, of the investigated system due to MgO doping could be attributed to an effective increase in the degree of dispersion of CuO phase (*c.f.* Table 2). This increase in the catalytic activity could be also attributed to the significant increase in the $S_{BET}$ of the doped solids (*c.f.* Table 3). Furthermore, it has been reported by two of the authors ( El-Molla et al.,2013, 2011b) that the coexistence of CuO and MgO in a system calcined at 350 or 450 °C exhibited high catalytic activity in alcohol conversion as compared to those measured for the individual oxides suggesting an effective synergism between CuO and MgO. It has been reported that MgO could stabilize $Cu^0$ (or $Cu^+$) species against oxidative sintering to $Cu^{2+}$ and simultaneously enhanced the activity by accelerating catalytic reduction–oxidation cycles between $Cu^0$ and $Cu^+$ (El-Molla 2006, Nishida et al., 2009), this role may be another factor. (ii)All the investigated solids have selectivities towards acetone (Sa%) and methyl iso-butyl ketone "MIBK " (Sm%) formation. Acetone was produced through dehydrogenation process (El-Molla 2006, 2013).

MIBK is produced through consecutive reactions involved in the conversion of *iso*-propanol as follows: (1) dehydrogenation of *iso*-propanol, (2) self-condensation of the resulting acetone to meistyle oxide (MO), and hydrogenation of MO to MIBK. MIBK was produced by using bifunctional catalyst in the novel one-step synthesis from *iso*-propanol at low temperature and atmospheric pressure (El-Molla, 2006, 2013). The selectivity towards acetone formation (dehydrogenation) "Sa" increases with increasing the reaction temperature while the selectivity towards MIBK ($S_m$) decreases with increasing the reaction temperature. MgO-doping increases the selectivities towards acetone formation and decreases the selectivities towards MIBK formation.

(iii) Increasing the calcination temperature of the various investigated catalysts from 400 to 800 ºC decreased the catalytic activity of pure and variously MgO-doped solids. This decrease could be attributed to the effective increase in the crystallite size and degree of crystallinity of the active phase (El-Molla et al., 2011a) and also due to a decrease in the surface concentration of Cu-species as shown in Table 1. (iv) By increasing the calcination temperature from 400 to 800 ºC resulted in the formation of small quantities of propene with subsequent disappearance the condensation product for the reaction carried out over all MgO-doped samples. The selectivities towards propene formation (Sp %) increased with increasing the reaction temperature. Increasing MgO concentration from 0.75 to 3 mol% didn’t much affect the Sp%. Several authors claimed that, acetone production as shown in (Scheme 1) depends on the presence of basic centers (El-Molla et al., 2011b).

Several studies showed that, alcohol interacts with solid catalyst with subsequent formation of alkoxide (Haffad et. al, 2001) through adsorption on $M^{+n}$ —— $O^{II}$ sites or by interaction of alcohol with residual surface OH─ groups (Zaki and Sheppard 1983). The behavior of catalyst selectivity towards acetone and condensation products due to MgO-doping which increased by increasing the calcination temperature, could be explained as follows: (i) Acetone is produced according to dehydrogenation mechanism and the active sites are copper oxide species and medium-strength basic active sites [Mg(M)-O] with high density in MgO-doped samples ( Diez et al., 2000, Torres et al., 2007). The concentration of the active sites contributed in formation of acetone or condensation products is big at low calcination temperature, low reaction temperature and in presence of MgO dopant. It has been reported that the formation of propene depends on the concentration of acid centers. The formation of propene may take place via synchronous elimination of β-hydrogen in iso-propanol and hydroxyl groups on the catalyst surface (Noller et al., 1988).

So, by increasing the selectivity towards propene formation as a result of MgO doping is owing to increasing surface hydroxyl groups. So, the catalytic activity and selectivity of the investigated solids depend on each of calcination temperature, reaction temperature, and MgO-doping.

## Conclusions

In summary, CuO-ZnO system prepared by coprecipitation and calcined at 400 and 800 °C consisted of nanosized CuO and ZnO phases. The crystallite sizes of these phases were much influenced by calcination temperature and MgO-doping. MgO-doping decreased the crystallite size of CuO phase to an extent proportional to its amount present. MgO-doping of the investigated system increased its $S_{BET}$ reaching a maximum limit (72%) in presence of 1.5 mol%. The surface concentration of copper and zinc species in different solids measured by EDX investigation was modified by calcination temperature and MgO-doping. MgO doping much increased the catalytic activity in $H_2O_2$ decomposition to an extent proportional to the amount of dopant added. Pure and doped solids acted as active dehydrogenation catalysts yielding acetone and MIBK. The catalytic activity and selectivity in manner depending on the concentration of the dopant added.

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