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Effects of γ-Irradiation and Ageing on Surface and Catalytic Properties of nano-sized CuO/MgO System towards dehydrogenation and condensation reactions

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ABSTRACT

0.2CuO/MgO solids prepared by impregnation method was calcined at 350 and 450 ºC. The effects of γ-rays (0.2-1.6 MGy) on its structure, surface and catalytic properties were investigated by using XRD, N_2–adsorption at -196ºC and catalytic conversion of iso-propanol at 150-275 ºC using a flow technique. The results revealed that the investigated solids consisted of nano-sized MgO as a major phase beside CuO and trace amount of Cu_2O. γ-Irradiation of the solids investigated exerted measurable changes on their surface and catalytic properties. These changes are dependent on the calcination temperature and dose of irradiation. The catalysts investigated acted as active dehydrogenation solids. The five years-ageing of different solids showed a limited influence on surface and catalytic properties indicating a good catalytic stability of the prepared solids.

Keywords: nano-materials, metal oxides, γ-irradiation, catalytic activity, catalytic stability

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1. Introduction

MgO acts as a solid support in many organic reactions as alcohol coupling [1,2], aldol condensation[3,4]. Loading metal cations on MgO-based catalysts for producing new centers with different acid-base properties have been reported. Such cations as Ni $^{2+}$, Fe $^{3+}$, Cr $^{3+}$ and Cu^{2+} promoted MgO and changed the basic properties and increased the catalytic activity for many reaction as H_2O_2 decomposition and dehydrogenation of alcohols [5-7]. Modification in textural, structural, electrical, thermal, and magnetic properties of large variety of solids due to doping with small amounts of foreign ions or irradiation with ionizing one such as γ–rays have been reported. Ionizing radiation may induce changes in textural and catalytic properties of large variety of solids [8]. These changes are commonly accompanied by modification in surface, chemisorption, catalytic and thermal properties of irradiated materials. Gamma irradiation decreases the surface area of graphite because of pores blocking[9] and leads to increasing the pore size of steam activated carbon[10]. Gamma irradiation enhances the dehydroxylation (removal structural OH groups) in some synthetic aluminosilicate compound (Na Y-zeolite) thus modifying its acidity [11]. Ionizing radiation was found to be able to change catalytic activities and surface oxidative abilities of various mixed oxides[12]. Many irradiated solid oxides used as a catalysts and were investigated in different reactions such as CO oxidation with O_2, H_2O_2 decomposition and conversion of alcohols. It has been reported that γ–irradiation of CuO/Al_2O_3, CuO-ZnO/Al_2O_3 and Co_3O_4/Al_2O_3 solids increases their catalytic activity towards CO oxidation with O_2 [13-15] and decreases the catalytic activity of NiO and CuO and manganese oxides towards the same reaction [16,17]. Gamma irradiation of NiO-CdO and Co_3O_4/MgO increases their catalytic activity towards H_2O_2 decomposition [12,18] and decreases the catalytic activity of CuO/MgO and NiO oxides towards the same reaction[19,20]. Irradiating CuO-ZnO/TiO_2 and Co_3O_4/MgO with 0.4 MGy of γ–rays increases its activity towards alcohol conversion reaction using micro pulse technique [21,22] and decreases the catalytic activity for Na_2O-Mn_2O_3/Al_2O_3, Co_3O_4/Al_2O_3 and Mn_2O_3-MnO_2 systems towards the same reaction[23-25]. From all these intensive published papers it is noticed that γ–irradiation has been reported to cause both an increase and a decrease in the specific surface areas and the catalytic activities of certain catalytic systems depending on the nature of the irradiated solid, the dose of γ-rays and the nature of catalyzed reaction.

Alcohol conversion was studied using various solids such as copper oxide [26], and copper –thorium oxide[27]. The simultaneous presence of Cu^{2+}, /Cu^{1+} and /or Cu^0 in the thoria with a ratio of (Cu^0 + Cu^+)/Cu^{2+} is required for activity toward isopropyl alcohol dehydrogenation[28]. The conversion of iso-propanol over solids containing magnesia catalyst has been investigated using a pulse microcatalytic reactor [28] and flow system [6,7]. The activity depends on the reaction temperature, textural properties [28].

It is very interesting to study the influence of γ-irradiation and ageing (storing for five years) on the surface and catalytic (activity, selectivity and stability) properties of CuO/MgO system towards conversion of iso-propanol. 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 [29-31]. Methyl isobutyl ketone (MIBK) is also produced during conversion of iso-propanol, this product is a useful solvent for paints and resin-based protective coating systems [32, 33] and is a reagent for production of antibiotics [34]. This work is devoted to follow the possible changes in the physicochemical properties of CuO/MgO solid as being influenced by γ-irradiation and ageing (storing for five years) and attempt to correlate these variables with the catalytic activity of solid catalyst towards various sub reactions take place in iso-propanol conversion. The techniques employed were XRD, S_{BET} measurements and catalytic conversion of iso-propanol using the flow method.

2. Experimental

2.1. Materials

The 0.2 CuO/MgO solid (0.2 mol copper oxide to 1 mol magnesia) was prepared by impregnation method which is pore-filling method in which, fixed amount of copper nitrate $Cu(NO_3)_2.2.5(H_2O)$ dissolved in the least amount of distilled water and added to a known amounts of finely powdered magnesium carbonate solid $MgCO_3$ just for wetting and to make a paste, this paste was dried at 100 ^{o} C until constant weight then calcined in air at 350 ^{o}C and 450 ^{o}C for 4h. The CuO content in the solid sample was 28.3 wt%. The prepared calcined solid was exposed to different doses of γ -rays. The doses were 0.2, 0.4, 0.8 and 1.6 MGy. Cobalt-60 was used as the source of γ- irradiation for chemical studies through Cobalt-60 Gamma-cell 220 Atomic Energy of Canada Ltd. The γ-cell contains 2860 Curries of ^{60}Co. The dose rate for the present work was $0.27x10^{-4}$ k Gy/s.

The irradiated samples were kept in sealed tubes for 3 weeks before conducting the various measurements. The chemicals employed (copper nitrate and magnesium carbonate) were of analytical grade supplied by BDH. The aged un-irradiated and irradiated samples were stored for five years in sealed tubes before undertaking surface and catalytic measurements.

2.2. Techniques

X-ray diffractograms of fresh, aged being subjected to different doses ranged between (0.2-1.6MGy) 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 profile analysis, respectively. The patterns were run with Cukα1 with secondly monochromator, λ = 0.15405 nm at 40 kV and 40 mA . The crystallite size of the phases present was calculated using Scherer equation [35].

The surface characteristics, namely S_{BET}, V_p and r^- which characterize the specific surface areas, pore volume and pore radious of the investigated catalyst samples were determined from nitrogen adsorption isotherms measured at -196 ^oC using a quantachrome NOVA2000 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 the various solid catalyst samples were determined by using isopropyl alcohol conversion reaction at 150- 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 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 ^oC. Argon gas was used as the diluents and the isopropyl alcohol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 35 ^oC. The flow rate of the carrier gas was maintained at 15 ml/min which is corresponding to 1.23 $x10^{-2}$ mol/hour. 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 fused silica glass capillary column type PE-CW length 15 m-1.0 UM Perkin-Elmer corp.

3. Results and discussion

3.1. XRD investigation of different solids exposed to doses of γ-rays

X–Ray powder diffractograms of un- irradiated 0.2 CuO/MgO precalcined at 350 and 450 ºC and subjected to 0.2-1.6 MGy were determined. Figs.1 & 2 include the diffractograms of the un-irradiated, irradiated, fresh and aged solids for five years which calcined at 350 and 450 ºC, respectively. It is seen from Fig.1 that, the diffractograms of the fresh solid samples calcined at 350 ºC consist of a crystalline MgO as a major phase and CuO and Cu_2O phases that having small degree of crystallinity. The fact that MgO and Cu_2O show common diffraction lines at d= 2.43, 2.11 and 1.48 Å at 2Θ= 37, 43 and 62^{o} makes their distinction a difficult task. However, the brown color of the solids calcined at 350 and 450 ºC, might suggest the possible coexistence Cu_2O phase and MgO [7,35]. Besides the previous phases a very small amounts of $Mg(OH)_2$ appeared in the diffractogram. Inspection of the relative intensities of the diffraction lines , irradiation the investigated fresh solid with 0.4 MGy resulted in a limited decrease in the degree of ordering of copper oxides and also a limited increase in the degree of ordering of MgO phase. Using irradiation dose 0.8MGy increases the degree of ordering of all phases present. Fig.1 shows also the diffractogram of un-irradiated sample calcined at 350 ºC and aged for five years which consists of CuO as a major phase and MgO as a minor phase besides some diffraction lines of Cu_2O and $Mg(OH)_2$ phases. The diffractogram of irradiated sample with 0.2 MGy and aged for five years showed an increase in the degree of ordering of copper oxides phases.

Fig.2 depicts the diffractograms of the fresh, aged, and irradiated solids calcined at 450 ºC. Inspection of Fig.2 shows that: (i) increasing the calcination temperature for the fresh un-irradiated solid from 350 to 450 ºC resulted in an increase in the degree of ordering of MgO phase and a decrease in the degree of ordering of CuO phase. (ii) Increasing the calcination temperature of the fresh solid from 350 to 450 ºC followed by irradiation with 0.4 MGy did not much change the degree of ordering of all phases. (iii) Ageing the irradiated solids for five years resulted in small increase in the degree of ordering of CuO phase and small decrease in the degree of ordering of MgO phase which resulted in formation of thin layer of an amorphous Mg $(OH)_2$ coating MgO solid. This behavior is more clear in case of the solids calcined at 350 ºC.

It is clearly shown from Fig.1 that the ageing of the solids having the composition of 0.2CuO/MgO calcined at 350 ºC lead to very drastic collapse in the crystallinity of MgO phase. This phase is however the major in the freshly prepared solids. The disappearance of the well crystallized MgO phase in the aged samples might be attributed to a possible formation of an amorphous solid MgO and /or $Mg(OH)_2$.The comparison between Fig.1 and Fig.2 suggested clearly the role of calcination temperature on the stability of crystalline MgO phase. In fact, the heating of 0.2CuO/MgO at 450 ºC lead to a well stable and crystalline MgO phase that could not loose its crystallinity even by ageing for five years.

The effects of calcination temperature, γ-rays dose of fresh and aged solids on the crystalline phases present and their crystallite sizes were investigated and the results obtained are given in Table 1. Examination of Table 1 give the following: (i) the freshly prepared solids calcined at 350 ºC include MgO phase that having a crystallite size of 23.7 nm as a major phase and copper oxide with crystallite size 8.7nm as a minor phase. The crystallite size of copper oxide increases with increasing the calcination temperature while that of MgO unaffected. (ii) Ageing the solid calcined at 350 º for five years resulted in an increase in the crystallite sizes to 32.3 and 11.7 nm, respectively and the major phase becomes CuO. (iii) γ-Irradiation of most samples investigated with small doses increases slightly the crystallite sizes of all phases present then decreases it at higher doses. (iv) Ageing the un-irradiated and irradiated CuO/MgO system calcined at 350 ºC and 450 ºC for five years resulted in the formation of nano crystallites from $Mg(OH)_2$ with amount is bigger at the low calcination temperature. It has been reported that MgO phase interacts easily with atmospheric water vapor at room temperature to produce very fine crystallites from $Mg(OH)_2$[19]. This effect is more pronounced in case of the solids calcined at 350 ºC.

It had been claimed that MgO could dissolve a small portion of CuO yielding CuO-MgO solid solution [36,37]. The solubility increases by increasing both calcination temperature and the concentration of CuO present. The fact that the increase in calcination temperature of this investigated solid from 350 to 450 ºC, resulted in a measurable increase in the degree of crystallinity of CuO as separate phase might suggest that this treatment should increase the amount of CuO dissolved in MgO lattice and the other portion remained as separate phase and underwent an effective crystallization.

3.2. Specific surface areas of different investigated solids

The surface characteristics of un-irradiated and irradiated solids precalcined in air at 350 and 450 °C were determined from nitrogen adsorption isotherms conducted at -196°C. The surface characteristics, namely S_{BET}, V_p and r^- were calculated for various adsorbents and the results obtained are listed in Table 2. Inspection of Table 2 shows the following: (i) The increase of the calcination temperature of investigated fresh and un-irradiated samples from 350 to 450 °C resulted in a significant increase in the values of their S_{BET} and V_p. This increase attained 70 and 56%, respectively. (ii) Ageing of the system investigated calcined at 350 °C brought about a considerable increase in the values of its S_{BET} and Vp. This increase reached 123% and 165%. On the other hand, the ageing process of the system calcined at 450°C decreases its S_{BET} while its V_p much increased (39%). (iii) γ-Irradiation of the mixed solids calcined at 350°C to a dose of 0.4MGy increased their specific surface area (42%) which decreased upon exposure to a dose of 0.8MGy. The S_{BET} of the system calcined at 450 °C increased slightly (25%) upon exposure to a dose of 0.4MGy and irradiation at a dose of

0.8 MGy brought about a measurable decrease in its specific surface area(63%) falling to a value smaller than that measured for the un-irradiated sample.

The observed increase in the S_{BET} and pore volume of fresh CuO/MgO system due to increasing the calcination temperature from 350 to 450 °C could be attributed to a complete decomposition of $MgCO_3$ to MgO. The significant increase in the S_{BET} and pore volume of CuO/MgO due to γ-irradiation (at 0.4MGy) could be due to both splitting of particles of the treated solids[18] and a possible creation of new pores[15]. The detected increase in the specific surface area due to ageing of the solids calcined at 350 °C could be attributed to an effective decrease in the degree of crystallinity of MgO phase which became a minor phase (c.f. Fig.1). In other wards, MgO the main constituent of the system investigated suffered a significant increase in the degree of division of MgO which became a minor phase.

3.3. Catalytic activity measurements of different investigated solids towards dehydrogenation and condensation reactions in iso-propanol conversion

3.3.1. *Effect of γ- irradiation and ageing on the activity CuO/MgO system towards iso-propanl conversion*

Preliminary experiment showed that MgO resulted from calcination of $MgCO_3$ at 350 or 450 °C exhibited no measurable activity in iso-propanol conversion at temperatures ranged between 175 and 275°C. Similarly CuO obtained from the thermal decomposition of copper nitrate at 350 or 450 °C showed also small catalytic activity in alcohol conversion. However, CuO/MgO solid calcined at 350 or 450 °C exhibits high catalytic activity in alcohol conversion. This finding shows clearly an effective synergism in the co-existed CuO and MgO [36].

Fig.3 depicts the variation of catalytic activity of freshly calcined solids, expressed as total conversion of iso-propanol for the reaction carried out at temperatures between 175- 275 °C over fresh, un-irradiated and variously irradiated solids calcined at 350 and 450 °C. Fig. 4 shows the variation of catalytic activity for the reaction carried out at different temperatures over aged, un-irradiated and variously irradiated solids precalcined at 350 and 450 °C. Examination of figures (3&4) show the following: (i) Exposure the investigated fresh solids to different doses of γ–rays brought about a progressive measurable increase in the catalytic activity reaching to a maximum limit at a dose of 0.4 MGy. The increase of the dose above this limit led to a progressive decrease in the catalytic activity. (ii) The ageing process of different solids led to a significant decrease in their catalytic activity. The decrease was, however, more pronounced for the catalysts calcined at 450 °C. (iii) In Aged irradiated solids the sample irradiated with a small dose (0.2 MGy) led to a limited increase in their catalytic activity. The increase the dose above this limit led to a considerable progressive drop in their activities falling to values much below those measured for the un-irradiated solid.

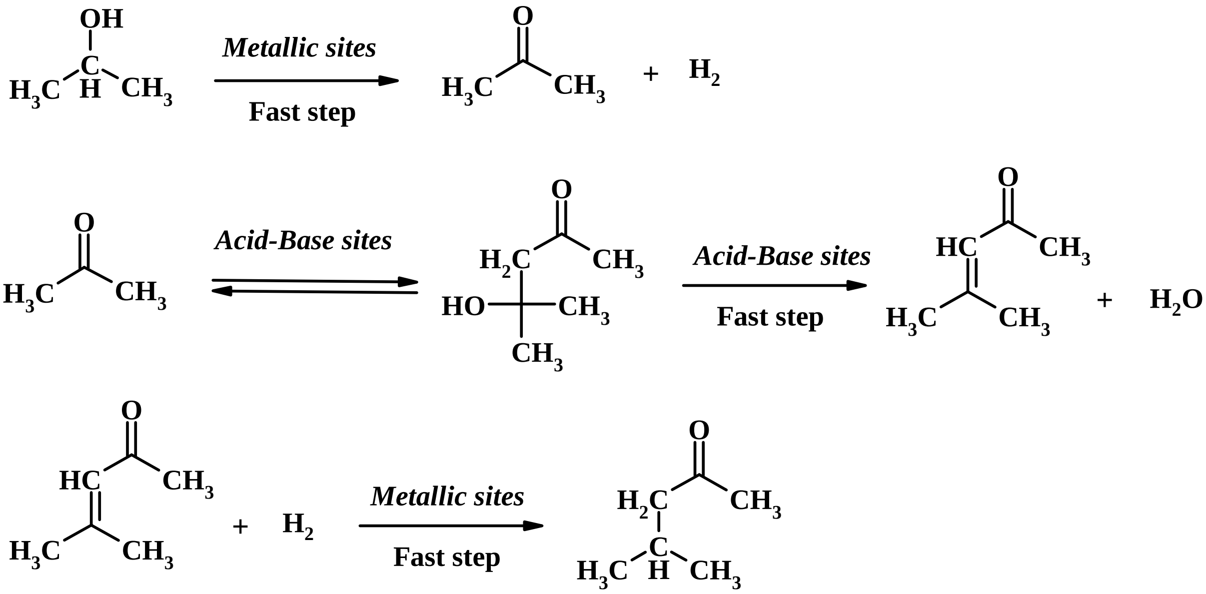
The observed measurable increase in the catalytic activity of the fresh solids due to exposure of small doses of γ–rays (0.4 MGy) might tentatively attribute to the observed increase in their S_{BET}. While the decrease in the activity to exposure to bigger doses of γ–rays (> 0.4 MGy) in fresh solids might reflect an effective decrease in the concentration of active sites involved in the dehydrogenation reaction in iso-propanol such as surface HO^- groups and chemisorbed oxygen[38] present in the top surface layers of the treated solids. It has been reported that the removal of such contaminants resulted in a significant modification in catalytic surface and electric properties of the investigated solids [14].

Ageing or storing the un-irradiated and those variously irradiated solids for five years decreases their catalytic activities towards isopropanol conversion with extent depends on the reaction and calcination temperatures. The effect of ageing is more predominant on the unirradiating solids and those calcined at lower calcination temperature. It is reported that the long storage of metal oxides showed a new equilibrium was attained between the catalysts and atmospheric oxygen during this periods. This new state is responsible for the decrease in the catalytic activity of the aged solids [38]. Generally, in fresh or aged irradiated solids, γ-rays could create charge defects in the oxides (free electrons and holes) these defects may be responsible for the observed changes in catalytic activities of irradiated samples [39,40].

3.3.2. The role of γ- rays and ageing towards the selectivity of the system investigated

CuO/MgO system is selective towards formation acetone through dehydrogenation process and condensation products such as methyl iso-butyl ketone (MIBK) from iso-propanol conversion under following up the reaction by contentious flow system was previously reported [7, 36].

MIBK is produced through consecutive reactions involved in the conversion of 2-propanol as follows :(1) dehydrogenation of 2-propanol, (ii) self-condensation of the resulting acetone to meistyle oxide(MO), and hydrogenation of MO to MIBK. MIBK is produced by using bifunctional catalyst in the novel one-step synthesis from 2-propanol at low temperature and atmospheric pressure [7,xxx].



Scheme 1. Reaction steps for MIBK synthesis from *iso*-propanol

The changes in the selectivity of different solids investigated due to exposure to different doses of γ- rays and ageing is summarized in the results cited in Table 3. Examination of Table 3 shows the following: (i) All catalysts investigated are selective to dehydrogenation of iso-propanol yielding acetone (Sa%), the selectivity towards acetone formation increases progressively as a function of reaction temperature, while MIBK selectivity (S_m%) decreases with increasing the reaction temperature. (ii) At low reaction temperatures, the exposure of freshly calcined solid at 350 °C to the smallest dose γ-rays (0.2MGy) results in a measurable increase in dehydrogenation selectivity and significant decrease in the condensation product selectivity. While at high reaction temperatures the irradiation did not much affect on the selectivity of the investigated solids (iii) The irradiation treatment of the solids calcined at 450 °C brought a considerable decrease in Sa% selectivity falling to values small than that of un-irradiated solids. (iv) S_m % as being influenced by the dose of γ- rays for the reaction carried out (175-275 °C) showed a complex behavior. (v) Ageing the irradiated solids calcined at 350 °C enhances their selectivity towards acetone formation at most reaction temperatures with comparison to the fresh irradiated solids. Opposite behavior was found for the aged catalysts and calcined at 450 °C. This behavior might be due to the high concentration of basic sites with medium strength such as O^{-2}, HO^{-} sites involved in dehydrogenation at 350 °C is bigger as compared to the solids calcined at 450°C.

The behavior of catalyst selectivity towards acetone and condensation products due to γ-irradiation, increasing the calcination temperature, and ageing the solid catalysts for five years was explained. The explanation was as follows: (i) Acetone is produced according to dehydrogenation mechanism and the active sites are copper with various oxidation states [41] and medium-strength basic active sites [Mg(M)-O] with high density responsible for the high selectivity to acetone formation[1]. The mechanism of formation of acetone and condensation products was previously discussed and published [1,42]. The concentration of the active sites contributed in formation of acetone or condensation products is big at low calcination temperature, low reaction temperature and decreases with high doses of γ-rays. The ageing factor enhances active sites formation which affect on the dehydrogenation selectivity and also condensation selectivity for the solids calcined at low calcination temperature.

The catalytic activity and selectivity of the investigated solids depend on (i) calcination temperature and (ii) reaction temperature, (iv) γ-irradiation dose, (v) ageing or storing the oxide catalyst as shown in our study.

3.3.3. *Effect of γ- irradiation and aging of CuO/MgO system towards catalytic stability*

The catalytic stability of the investigated solids were carried out through the reaction time experiments in which the run is carried out through three hours at 250 °C and constant flow rate of carrier gas 15 ml/min.. The products were analyzed through time intervals. Fig.5 and Table 4 show the effect of reaction time on catalytic activity and selectivity of investigated solids towards acetone and condensation product formation. Inspection of Fig.5 one can find that: (i) the catalytic activity in most samples increases through 15 min. from starting the reaction and at 20 min the catalytic activity decreases slightly. (ii) After 30 min. the activity tends to be stable through the reaction time 180 min. The increase in the catalytic activity through 15 min from starting the reaction may be due to the induction period in which some of active sites are created and/or redistributed. (iii) γ- irradiation the fresh solids enhances the catalyst stability through the experiment time (180 min.) (iv)Ageing the investigated solids for five years did not much affect on the catalyst stability.

From the previous results one can conclude that CuO/MgO system has a high catalytic stability towards iso-propanol conversion which is affected slightly by ageing factor. Also γ-irradiation enhances both of activity and stability of these solids especially those calcined at 450°C.

4. Conclusions

The following are the main conclusions that are drawn from the obtained results: CuO/MgO system consists of nano phases, the crystallite sizes of these phases are affected by calcination temperature, irradiation with gamma rays and also with ageing. The S_{BET} of CuO/MgO system calcined at 350 or 450 °C and being subjected to a dose of 0.2 or 0.4MGy, respectively increases their S_{BET}. The increase attained 42% and 30% for the solids calcined at 350 or 450 °C, respectively. Increasing the dose above these values brought about a decrease in its S_{BET}. Different investigated solids behave mainly as a dehydrogenation catalyst yielding acetone. Methyl iso-butyl ketone (MIBK) product was liberated in all solids involved in catalytic conversion of iso-propanol via aldol condensation mechanism. The catalytic activity and selectivity are influenced by the reaction temperature, irradiation dose, calcination temperature and ageing process. The catalytic activity and stability of the investigated solids calcined at 350 °C was found to increase by exposure to γ-rays.

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Table 1. The phases and crystallite sizes in the various investigated 0.2CuO/MgO solids calcined at 350 and 450 ^{o}C.

Sample state	Dose of γ-irradn. (MGy)	Calcn. Temp. °C	crystallite size(nm) of CuO	crystallite size(nm) of MgO
Fresh-	0	350	(8.7) m	(23.7) j
Fresh	0.4	350	(9.2) m	(25.7) j
Fresh	0.8	350	(8.2) m	(22.8) j
Fresh	0	450	(12.2) m	(22.7) j
Fresh	0.4	450	(13.6) m	(25.3) j
Aged	0	350	(11.7) j	(32.3) m
Aged	0.2	350	(12.8) j	(21.4) m
Aged	0	450	(11.2) m	(16.5) j
Aged	0.2	450	(16.4) m	(26) j

j = major phase and m = minor phase.

Table 2. The specific surface areas of different investigated 0.2CuO/MgO adsorbents calcined at 350 and 450 ^{o}C.

Sample state	**Dose of γ-irradn. (MGy)**	**Calcn. Temp.** °C	**S_{BET} (m^2/g)**	**V_p cm^3/g**	**$\bar{r}$ Å**
Fresh	0	350	53	0.108	41
Fresh	0.4	350	75	0.162	43
Fresh	0.8	350	59	0.164	56
Fresh	0	450	90	0.169	38
Fresh	0.4	450	113	0.254	45
Fresh	0.8	450	42	0.125	60
Aged	0	350	118	0.286	49
Aged	0	450	54	0.235	87

Table 3. Catalytic selectivity towards acetone (S_a%) and condensation product (S_m%) over fresh, aged, un-irradiated and variously irradiated 0.2CuO/MgO calcined at 350 °C and 450 °C, at various reaction temperatures.

Dose of γ-irradiation (MGy)	Calcination temp.	Reaction temp.	S_a% Fresh samples	S_m% Fresh samples	S_a% Aged samples	S_m% Aged samples
0	350	175	53	47	60	40
0.2			70	30	61	39
0.4			67	33	-	-
0.8			62	38	77	23
1.6			59	41	100	0
0	350	225	71	29	86	14
0.2			77	23	82	18
0.4			74	26	82	18
0.8			84	16	85	15
1.6			72	28	80	20
0	350	275	76	24	90	10
0.2			83	17	87	13
0.4			92	8	88	12
0.8			92	8	91	9
1.6			89	11	87	13
0	450	175	70	30	0	100
0.2			50	50	0	100
0.4			47	53	0	100
0.8			52	48	-	-
1.6			58	42	0	100
0	450	225	92	8	66	34
0.2			60	40	74	26
0.4			56	44	74	26
0.8			59	41	72	28
1.6			68	32	65	35
0	450	275	93	7	78	22
0.2			76	24	83	17
0.4			84	16	81	19
0.8			81	19	83	17
1.6			82	18	77	23

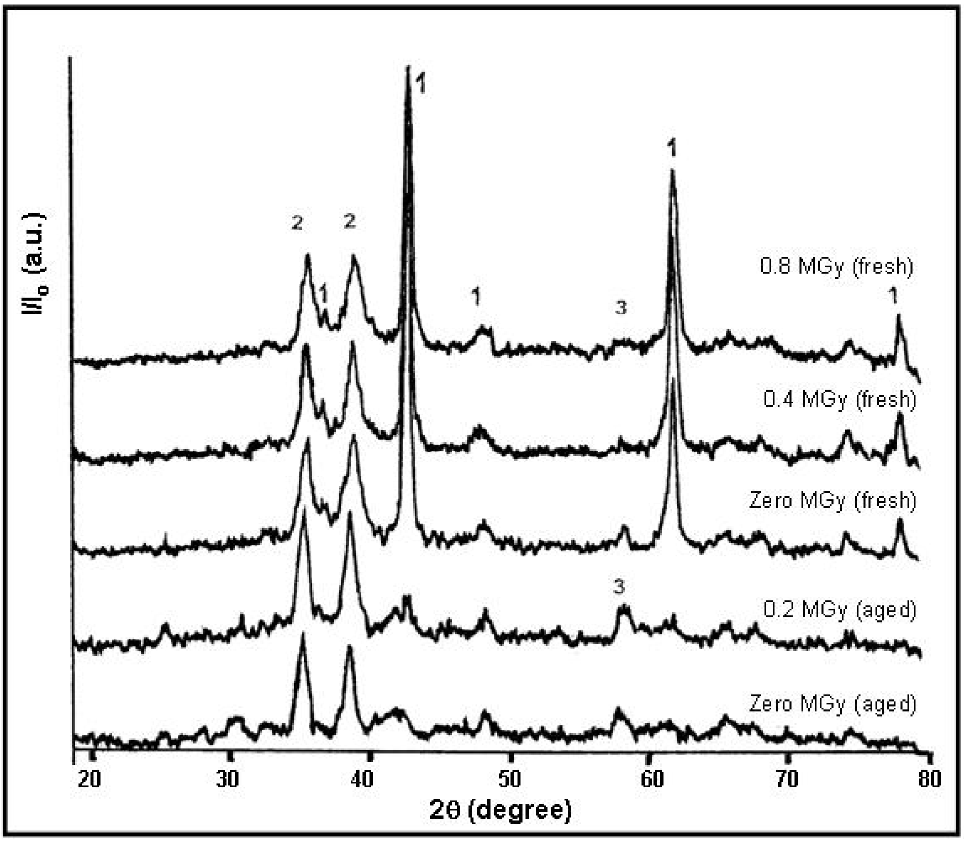

Fig. 1. XRD diffractogrames of: un-irradiated and variously irradiated, fresh and aged 0.2 CuO/MgO solids precalcined at 350 ºC. Lines (1) refer to MgO, lines (2) refer to CuO and lines (3) refer to $Mg(OH)_2$.

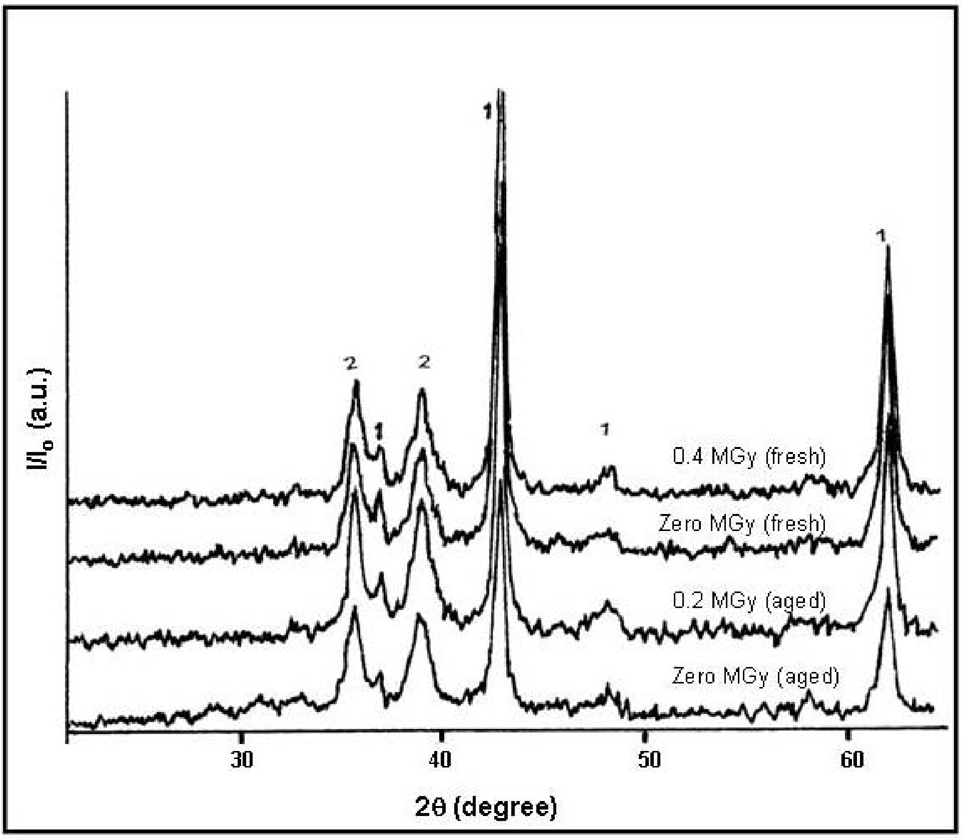

Fig. 2. XRD diffractogrames of un-irradiated and irradiated, fresh and aged 0.2CuO/MgO solid precalcined at 450 ºC. Lines (1) refer to MgO, lines (2) refer to CuO.

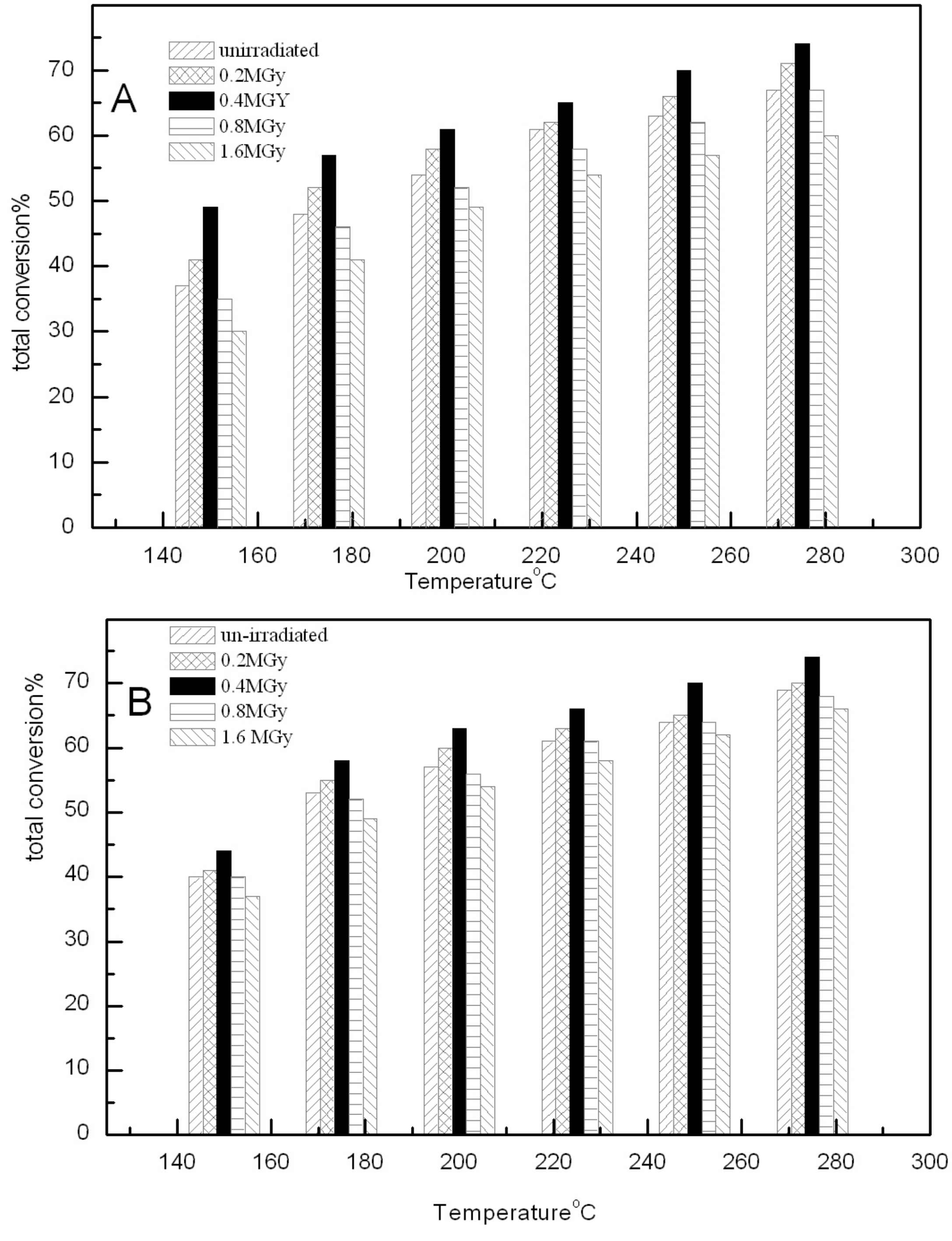

Fig. 3. Catalytic conversion of iso-propanol as a function of reaction temperature of fresh un-irradiated and variously irradiated CuO/MgO solids. The solids calcined at (A) 350 °C and (B) 450 °C.

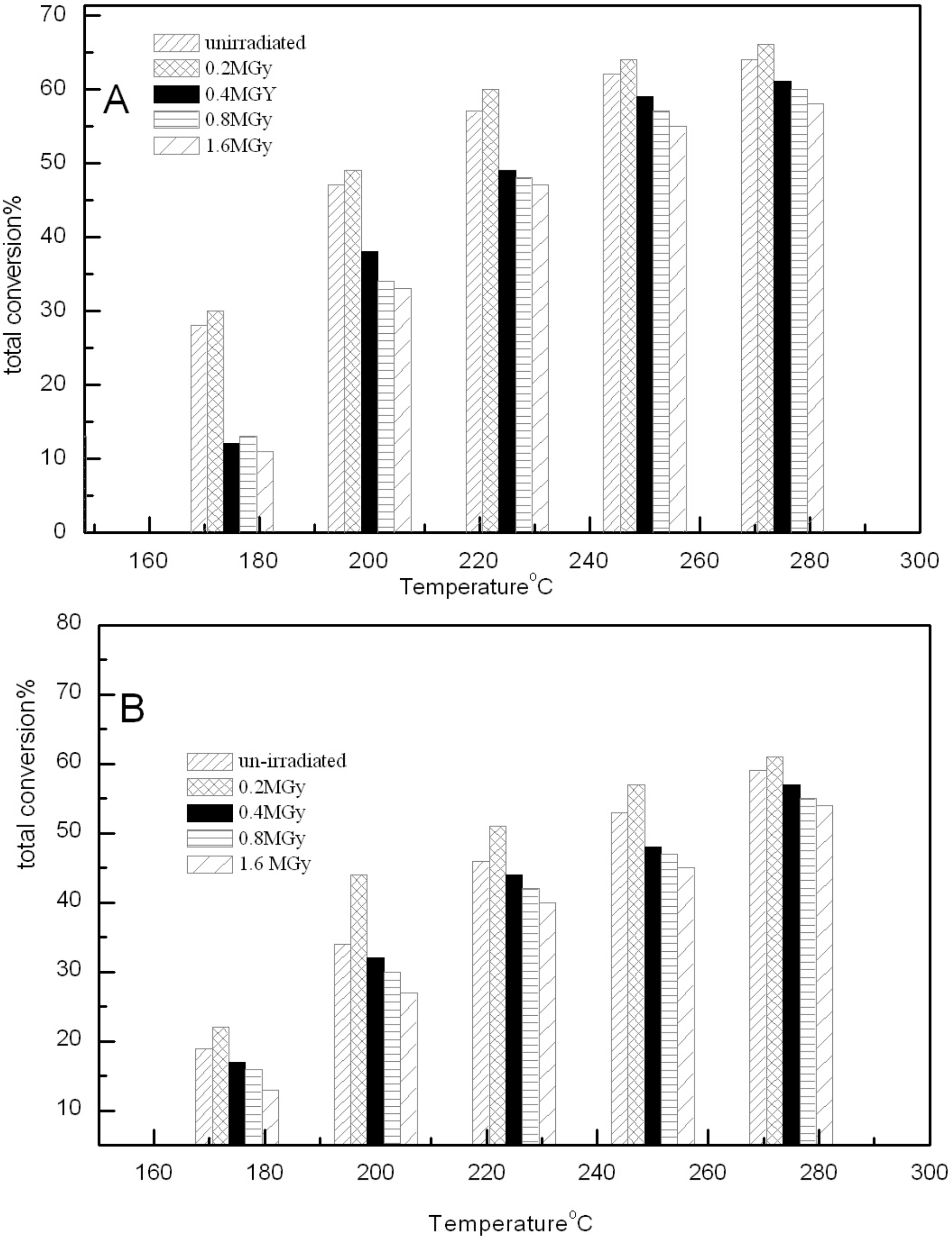

Fig. 4. Catalytic conversion of iso-propanol as a function of reaction temperature of aged un-irradiated and variously irradiated CuO/MgO solids. The solids calcined at (A) 350 °C and (B) 450 °C.

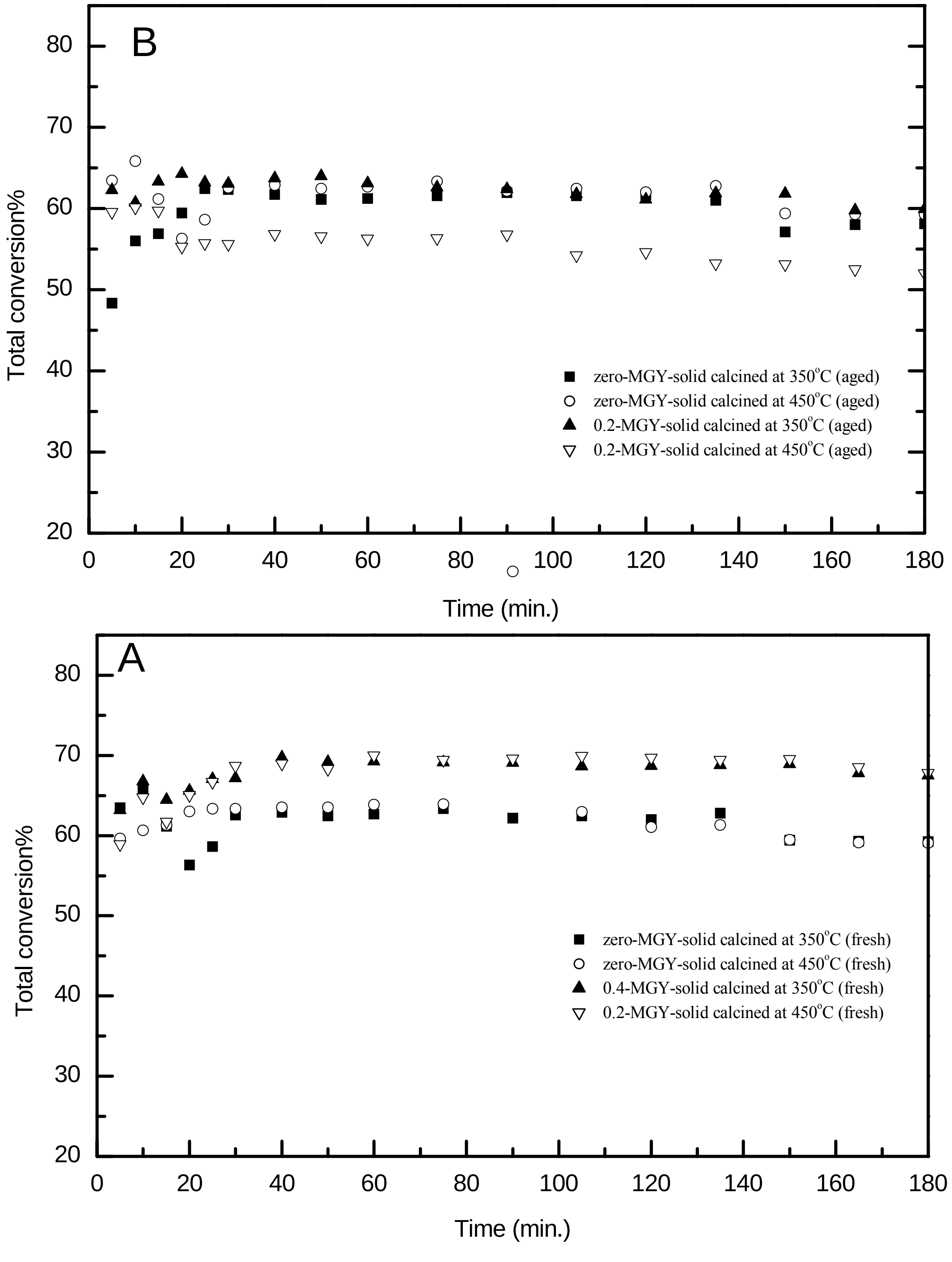

Fig. 5. Catalytic conversion of iso-propanol as a function of reaction time of un- irradiated and variously irradiated 0.2CuO/MgO solids calcined at 350 and 450 ºC. (A) Fresh solids and (B) aged solids.