Surface and Catalytic Properties of Nanocrystalline Pure and Li$_2$O - Doped CoO/Mn$_2$O$_3$ System

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Abstract: The effects of calcination temperature (350 - 700°C) and Li$_2$O - doping (0.75 - 4.5 mol%) on solid - solid inter-action, surface and catalytic properties of CoO/Mn$_2$O$_3$ were investigated using XRD, N$_2$ adsorption at -196ºC and isopro-panol conversion carried out at 180 - 280°C using a flow method. The results obtained revealed that solid - solid interac-tion between pure and doped - solids took place at temperatures starting from 350°C to yield cobalt manganese oxide (Co, Mn) (Co,Mn)$_2$O$_4$ phase. The degree of crystallinity and crystallite size of the produced phase increased progressively as a function of calcination temperature but still remained as nanocrystalline phase 15 - 33 nm. Li$_2$O - doping of the system in-vestigated decreased the crystallite size of the produced phase. The doping process decreased the specific surface area of the system investigated, the decrease attained 33% and 32% in presence of 4.5 mol% Li$_2$O in solids calcined at 500 and 700ºC, respectively. Li$_2$O - doping exerted an effective increase in total pore volume, the increase reached 57% and 27% by doping with 4.5 mol% Li$_2$O followed by calcination at 500 and 700, respectively. Pure system showed a broad pore volume distribution while the doped solids exhibited multimodal pore volume distribution curves. Pure and variously doped solids acted as dehydrogenation catalysts yielding only acetone. The activity increased by increasing the calcina-tions temperature from 350°C to 400°C, then decreased upon increasing the calcinations temperature above this limit. The doping process carried out at 500°C and 700°C much increased the catalytic activity. The maximum increase in the cata-lytic activity, measured at 280°C, in presence of 4.5 mol% Li$_2$O attained 45 and 94% for the solids calcined at 500°C and 700°C, respectively. The increase in calcination temperature within 350°C and 700°C and doping with different amounts of Li$_2$O did not change the mechanism of the catalyzed reaction.

Keywords: Catalytic conversion of isopropanol, XRD technique, Li$_2$O - doping, Nanocrystalline materials.

1. INTRODUCTION

Mixed oxides containing transition metal oxides are used to design the catalytic materials to replace noble metal cata-lysts. In a previous study, Lahousse *et al.* have compared the activity of γ-MnO$_2$ and Pt/TiO$_2$ catalysts [1]. They concluded that metal oxides are not necessarily less active than noble metals. Mixed oxide solids are active for oxidation-reduction reactions and combustion processes. For example, cobalt - zinc manganites and Co-containing mixed oxides prepared from hydrocalcite like precursors were active catalysts in the reduction of nitrous oxide [2-4]. Also, Co-Mn mixed oxides were active catalysts for oxidation of ethanol [5] and conver-sion of synthesis gas to light olefins [6]. However, Ag-Mn, Ag-Co and Ag-Ce composite oxides supported on Al$_2$O$_3$ have been reported to act as catalysts used in oxidation of volatile organic compounds [7].

Manganese oxides are reported to be among the most efficient transition-metal compounds in catalytic combustion [8-11] and are considered as environment- friendly materials. In recent studies, MnO$_2$ and Mn$_3$O$_4$ were found to be active and stable catalysts for the combustion of organic com-pounds [1, 12]. Mixing manganese with transition-metal oxides

oxides in many catalytic reactions might modify the catalytic activity of separate components [13, 14]. In a previous study, Mn-Cu mixed oxides were catalytically active towards etha-nol oxidation than pure Mn$_2$O$_3$ and pure CuO [14]. Both copper and manganese mixed oxide catalysts were found to be active catalysts in many industrial oxidation processes, such as CO oxidation, combustion of toluene, methanol, eth-ylene, ammonia, NO$_2$ and other combustion reactions [15-17]. However, Mn-Zr mixed oxide samples are active to-wards oxidation of isopropanol, giving rise to acetone with high selectivity at partial conversion [18].

The catalytic activity of transition metal oxides could be modified by a variety of methods as loading on suitable sup-port material [19-22], subjecting to ionization radiations [23] and doping with certain foreign oxides [19, 23-26]. The in-teraction of manganese with the support as well as with other components constituting the catalyst has a significant influ-ence on the structure definition [27]. Increasing dispersion of MnO$_x$ on the support surface led to a significant increase in the catalytic activity [28]. The most often applied supports for transition metal oxide catalysts are the oxides as Al$_2$O$_3$ [21]. However, it has been reported that magnesium fluoride performance as a support for Cu-Mn and Cu-Co mixed ox-ides is better than that of Al$_2$O$_3$ towards CO oxidation by O$_2$ [21]. Doping with certain foreign oxides may also modify the structure and catalytic activity of the catalysts. Cobalt and manganese oxides were used as a dopant (0.25-4 mol %)

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for ferric oxide [23]. It was found that doping pure Fe_2O_3 with Co_3O_4 or Mn_2O_3 followed by calcination at 350-550°C led to a progressive increase in the catalytic activity towards H_2O_2 decomposition. This increase was attributed to the role of dopants in increasing the concentration of catalytically active constituents and/or the formation of new active sites due to the change in the oxidation state [23]. The effect of doping on the solid-solid interactions between pure and Li_2O-doped oxide catalysts had been investigated by El-Shobaky *et al.* [24-26, 28, 29]. These authors claimed that doping with Li_2O much enhanced the solid-solid interaction between CdO/Fe_2O_3, CoO/MgO, CuO/Fe_2O_3, MgO/Fe_2O_3 and Fe_2O_3/Mn_2O_3 mixed oxides prepared by impregnation method to an extent proportional to the amount of Li_2O added.

The present work reports the results of a study on the effect of Li_2O-doping and calcination temperature of CoO/Mn_2O_3 on solid - solid interaction between cobalt and manganese oxides and on surface and catalytic conversion of isopropanol over pure and variously doped solids. The techniques employed were XRD, N_2 adsorption at -196°C and conversion of isopropanol at 180 - 280°C using a flow method.

2. EXPERIMENTAL

2.1. Materials

Equimolar proportions of CoO/Mn_2O_3 were prepared by coprecipitation method of their mixed hydroxides from their nitrates solution using 1M NaOH solution at pH = 8 and temperature 70°C. The carefully washed precipitate was dried at 110°C till constant weight, then subjected to heating at 350, 400, 500, 600 and 700°C for 4 hrs. Four Li_2O - doped samples were prepared by impregnating a given dry weight of the mixed hydroxides with calculated amount of lithium nitrate dissolved in the least amount of distilled water sufficient to make paste. The paste were dried at 110°C and then calcined at 500 and 700°C for 4 hrs. The dopant concentrations in the calcined solids were 0.75, 1.5, 3, and 4.5 mol% Li_2O.

2.2. Techniques

X - ray powder diffractograms of various investigated samples calcined at 350, 400, 500, 600 and 700°C were carried out using a Bruker diffractometer (Bruker D8 advance target). The patterns were run with $CuK_{\alpha 1}$ with secondly monochromator (λ = 0.1545 nm) at 40 kV and 40 mA. The crystallite size of the crystalline phases present in the different solids investigated was calculated from the line broadening profile analysis of the main diffraction lines of these phases using Scherrer equation [30].

$d = K\lambda / \beta_{1/2} \cos\theta$

where d is the mean crystallite diameter, λ the X - ray wavelength, K the Scherrer constant (0.89), $\beta_{1/2}$ is the full - width at half maximum (FWHM) of the diffraction peaks of crystalline phases and θ is the diffraction angle. In broadening profile analysis the scanning rate was fixed at 0.2° in 2θ min^{-1}.

2.3. Surface Characteristics of Pure and Doped Solids

The specific surface area (S_{BET}), total pore volume (V_p), mean pore radius ($\bar{r}$) and pore volume distribution ($\Delta v/ \Delta r$)

of the various adsorbents were determined from nitrogen adsorption isotherms measured at -196°C using Quanta-chrome NOVA automated gas sorbometer. The values of V_p were calculated from the relation Vp = 0.95 15.45 X 10^{-4} V_{st} cm^3/g, where V_{st} is the volume from the equation

$$\bar{r} = \frac{2V_P}{S_{BET}} X \, 10^4 \, Å$$

2.4. Catalytic Dehydrogenation of Isopropanol

The dehydrogenation of iso-propanol was carried out in a conventional flow- type reactor under atmospheric pressure. The reactor tube is a Pyrex glass of 20 cm. long and 1cm internal diameter packed with beads glass except in the zone where the catalyst bed is located. The catalyst bed is placed in the middle of the reactor tube. The weight of the catalyst used was 100mg and a digital thermometer was used to measure the temperature of the catalyst. Both reactor and furnace are placed inside a Pyrex glass jacket of 5 cm diameter.

The catalysts investigated were activated in situ prior to exposure to the alcohol vapor by heating at 300°C for 1h in a current of argon flowing at rate of 30 ml min^{-1}. The reaction was carried out at temperature ranged from 180 to 280 °C.

The reaction mixture was analyzed using a gas chromatograph (Perkin Elmer Autosystem XL with flame ionization detector) equipped with TCD, fitted with a 2m Porapak Q stainless steel column suitable for gas analysis. The oven temperature set at 45 °C. Detector was kept at 220 °C.

3. RESULTS AND DISCUSSION

3.1. XRD Investigation of Pure and Doped Solids Calcined at Various Temperatures

The X - ray diffractograms of pure solids calcined at 350, 400, 500, 600, and 700°C were determined. Fig. (**1**) depicts the diffractograms of pure solids calcined at temperatures within 350 - 700°C. It is clearly shown from this figure the absence of all diffraction lines of CoO and Mn_2O_3 even in the solids calcined at 350°C. This finding suggested clearly the disappearance of the reacting oxides with subsequent formation of cobalt manganese oxides having the formula (Co, Mn) $(Co,Mn)_2O_4$ [31]. It can also be seen from this figure that the increase in calcination temperature of the solids investigated increased the degree of crystallinity and the crystal size of the produced phase.

The diffraction data of different solids investigated are cited in Table **1**. This table includes the computed values of crystallite size of the produced phase determined from the Scherrer equation. The degree of crystallinity of the phase produced was determined from the peak area of the main diffraction lines of the crystalline phase.

Figs. (**2**, **3**) depict the diffractograms of variously doped solids calcined at 500°C and 700°C, respectively. It is clearly shown from these figures that Li_2O - doping of the system investigated followed by calcinations at 500 and 700°C resulted in a progressive decrease in both the degree of crystallinity and crystallite size of the produced cobalt manganese oxide phase. Table **1** includes also the crystallite size and the degree of crystallinity of the produced phase as being influ-
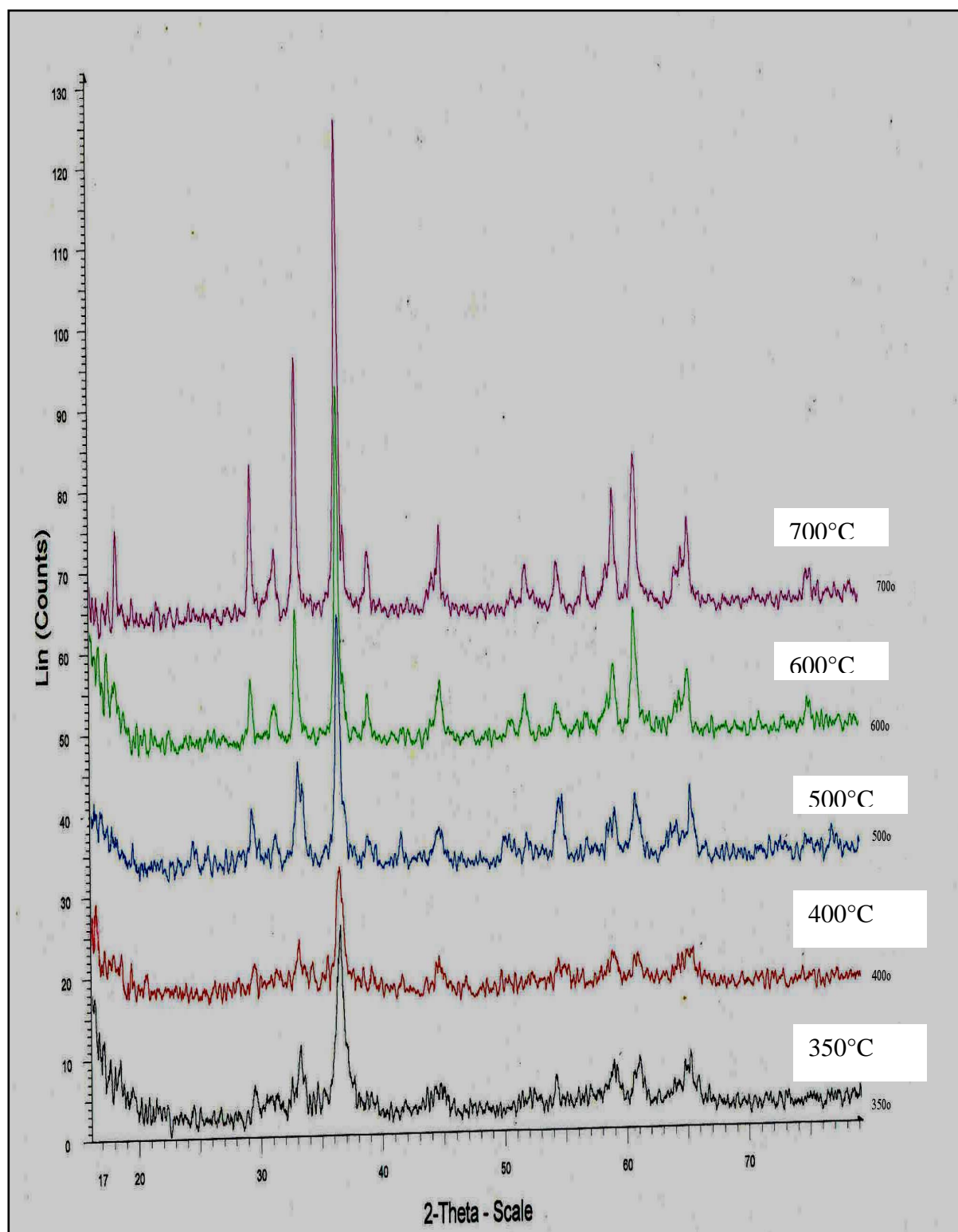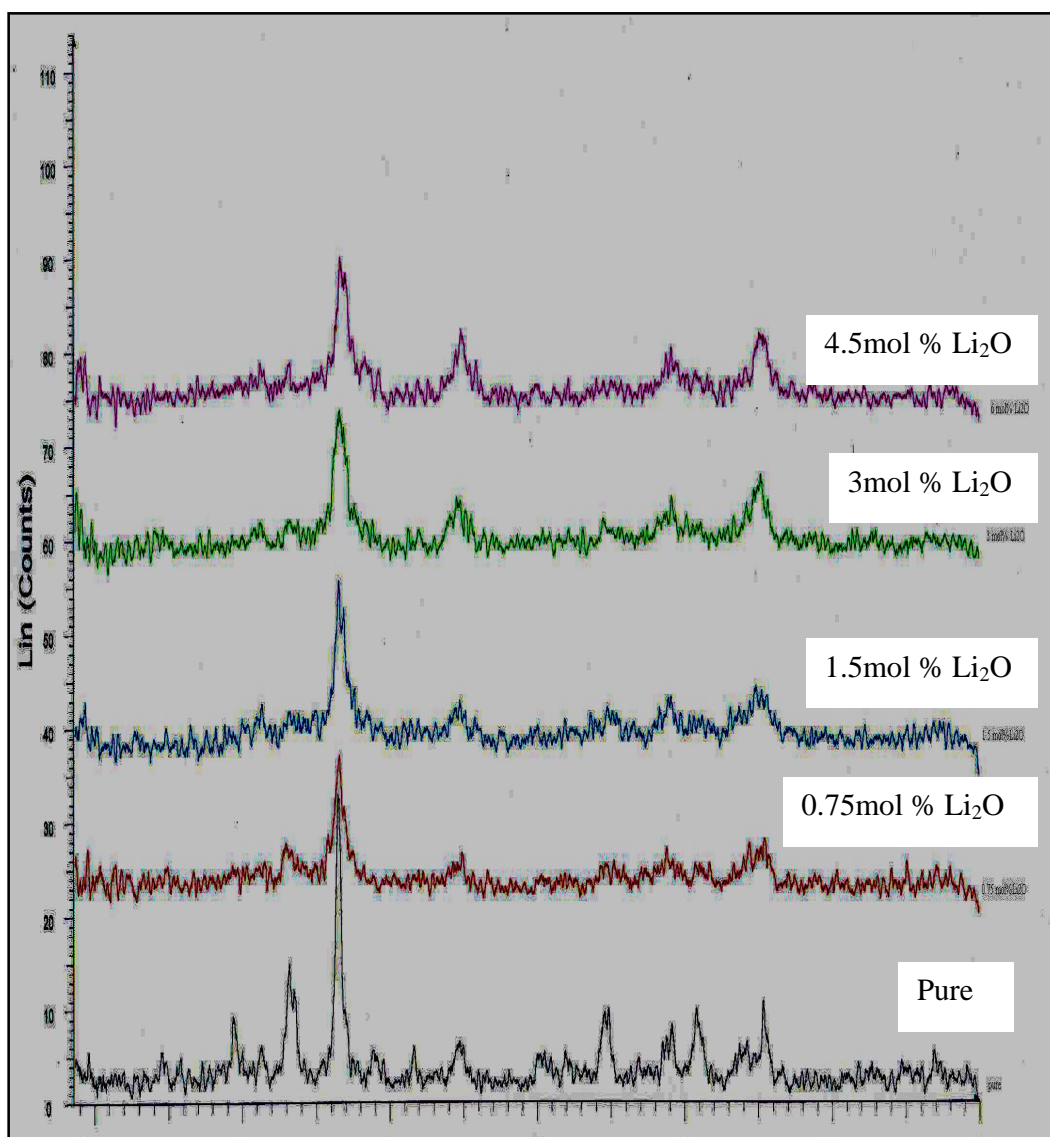
Fig. (1). X-ray diffractograms of pure solids calcined at various temperatures.

enced by Li_2O - doping. It is clearly shown from Table **1** that the crystallite size and degree of crystallinity of the produced cobalt manganese phase in pure solids increases progressively as a function of calcinations temperature. It can also be seen from Table **1** that the doping process conducted at 500°C and 700°C, generally, decreased both the crystallite size and degree of crystallinity of the phase produced. The produced decrease in the crystallite size due to Li_2O - doping is expected to increase the degree of dispersion of the produced phase leading to an increase in the concentration of the catalytically active phase. This increase might lead to an increase in the catalytic activity of the doped solids.

Table 1.   Crystallite Size and Degree of Crystallinity of Cobalt Manganese Oxides Phase in Pure and Doped - Solids Calcined at Different Temperatures

Solid	Calcination Temperature (°C)	Crystallite Size (nm)	Degree of Crystallinity (arb.units)
Pure	350	15	18
	400	18	25
	500	29	33
	600	31	45
	700	34	63
+0.75 mol% Li_2O	500	14	16
+1.5 mol% Li_2O	500	12	19
+3.0 mol% Li_2O	500	10	17
+4.5 mol% Li_2O	500	14	17
+0.75 mol% Li_2O	700	24	30
+1.5 mol% Li_2O	700	20	14
+3.0 mol% Li_2O	700	18	15
+4.5 mol% Li_2O	700	23	18

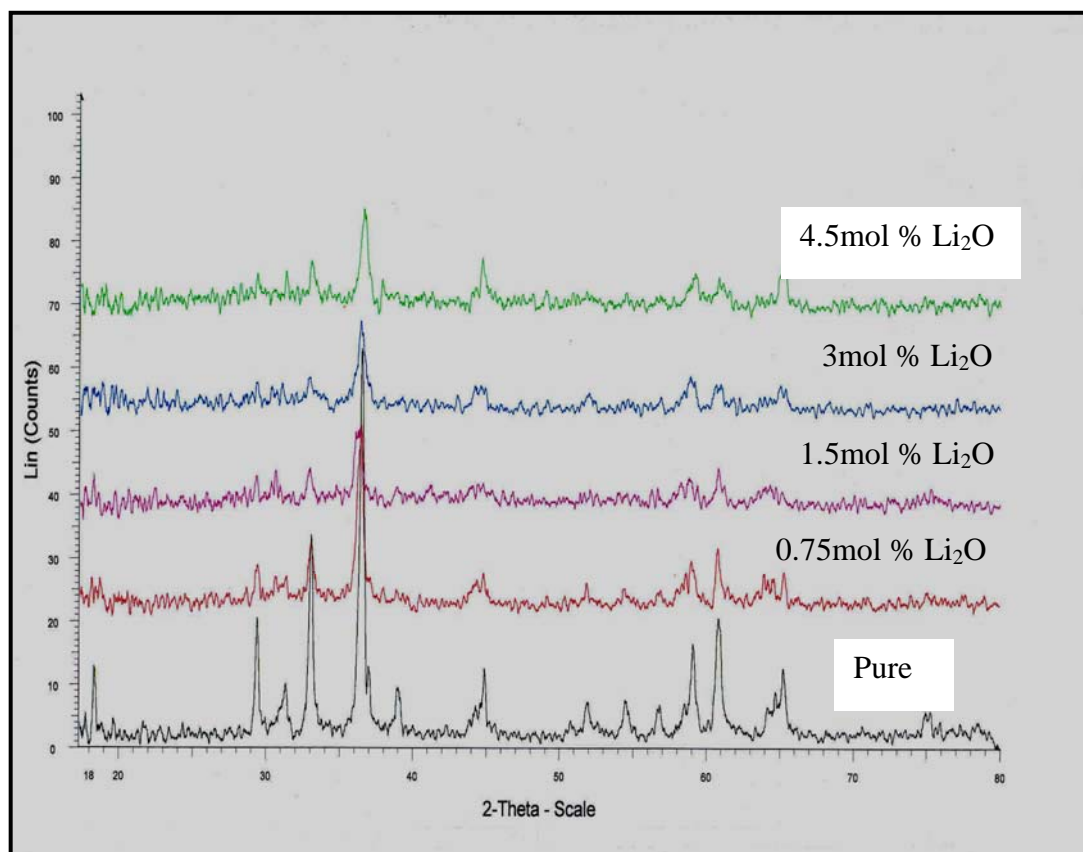**Fig. (2).** X-ray diffractograms of pure and different Li_2O - doped solids Calcined at 500°C.

Fig. (3). X-ray diffractograms of pure and variously doped solids calcined at 700°C.

The increase in the crystallite size of cobalt manganese oxide phase present in pure solids by increasing their calcination temperature within 350 - 700°C enabled us to calculate the activation energy of sintering of the produced phase by direct application of the Arrhenius equation.

Fig. (**4**) depicts the relationship between log crystallite size of the produced phase as a function of calcinations temperature. The slope of this plot determines readily ΔE_s value which measured 28 kJmol^{-1}.

3.2. Surface Properties of Pure and Doped Solids

The surface characteristics of pure and Li₂O - doped solids calcined at 500 and 700°C were investigated by analysis of N₂ adsorption isotherms carried out at -196°C over various adsorbents. These characteristics include specific surface area (S_{BET}), total pore volume (V_p), mean pore radius ($\bar{r}$) and pore volume distribution curves ($\Delta v/\Delta r$). Table **2** includes the computed S_{BET}, V_p, $\bar{r}$, and $\Delta v/\Delta r$ curves for pure and solids doped with 3 and 4.5mol% Li₂O followed by calcinations at 500 are given in Fig. (**5**). Examination of Table **2** and Fig. (**5**) shows the following: (i) The rise in calcination temperature of pure and doped adsorbents from 500 to 700°C decreased their specific surface area with subsequent increase in the V_p value. The significant decrease in the S_{BET} due to increasing the calcinations temperature from 500 to 700°C could be attributed, mainly, to pore widening. In fact,
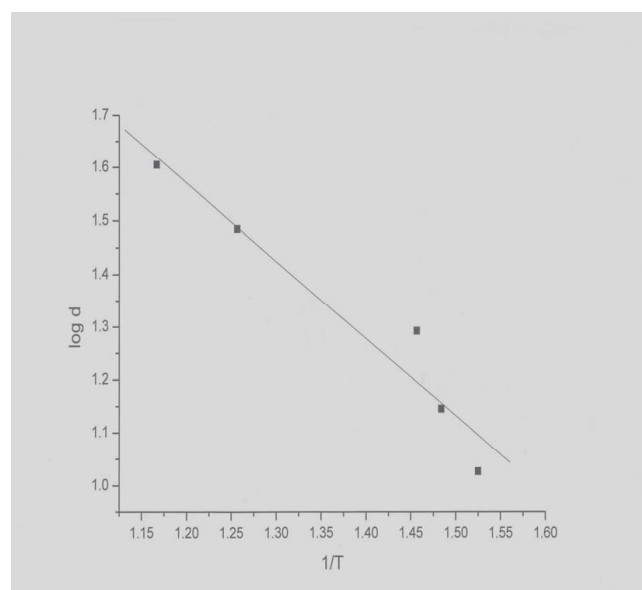

Fig. (4). Variation of logarithm crystallite size of cobalt / manganese mixed solids phase as a function of reciprocal of calcinations temperature (1/T).

$\bar{r}$ increases from 14Å to 40Å for pure sample upon increasing the calcinations temperature up to 700°C and increases from 16Å to 39Å for the heavily doped sample. (ii) Doping

Table 2. **Some Surface Characteristics of Pure and Li$_2$O - Doped CoO/Mn$_2$O$_3$ Solids Calcined at Different Temperatures**

Sample	Calcination Temperature (°C)	S$_{BET}$ (m^2/g)	Vp (ml/g)	$\bar{r}$ (Å)
CoO/Mn$_2$O$_3$	500	110	0.037	14
CoO/Mn$_2$O$_3$ + 3mol% Li$_2$O	500	113	0.047	17
CoO/Mn$_2$O$_3$ + 4.5 mol% Li$_2$O	500	146	0.058	16
CoO/Mn$_2$O$_3$	700	72	0.116	40
CoO/Mn$_2$O$_3$ + 3mol% Li$_2$O	700	82	0.127	39
CoO/Mn$_2$O$_3$ +4.5 mol% Li$_2$O	700	95	0.147	39

the system investigated with 4.5mol% Li$_2$O followed by calcination at 500 or 700°C increased the S$_{BET}$. This increase attained 33% and 32% upon doping with 4.5mol% Li$_2$O followed by calcination at 500 and 700 °C, respectively. (iii) The doping process did not much affect the $\bar{r}$ value while it increased the V$_p$ value. The increase attained 57% and 27% for the heavily Li$_2$O - doped adsorbents calcined at 500 and 700°C. (iv) Pure system showed wide pore distribution curve while the doped samples exhibited multimodal distribution curves having their maximum at smaller pore width values. This behavior might suggest the creation of narrow pores.

3.3. Catalytic Activity of Pure and Doped Solids

The catalytic conversion of isopropanol was carried out over pure and doped solids calcined at different temperatures. Acetone was only produced from the catalytic reaction conducted over all investigated solids. This finding indicates clearly the high selective nature of these solids towards dehydrogenation of the alcohol investigated.

Fig. (**6**) shows the percentage of dehydrogenation conversion of the investigated alcohol as a function of reaction temperature for pure solids calcined at 350 - 700 °C. It is clearly shown that the rise in calcination temperature of the solids investigated from 350 to 400°C led to a significant increase in their activity. The percentage increase in the catalytic activity measured at 240 due to this treatment attained 24%. Fig. (**6**) shows also that the maximum catalytic activity was attained for the solids calcined at 400°C, then decreased progressively by increasing the calcinations temperature above this limit. The decrease was, however, more pronounced, upon increasing the calcinations temperature from 600 to 700°C. The percentage decrease in the catalytic activity measured at 240°C, due to increasing the calcination temperature from 400 to 700°C attained 64%. The observed increase in the catalytic activity due to increasing the calcination temperature from 350 to 400°C might be attributed to an effective decrease in the crystallite size of the produced cobalt manganese oxides phase. In fact, this treatment led to a decrease of 66% and 42% in the crystallite size of cobalt - manganese oxides phase in the solids calcined at 500 and 700°C, respectively. While, the drop in the activity due to increasing the calcination temperature up to 700°C might result from an effective grain growth process of the produced cobalt manganese oxides phase whose crystallite size increased from 18.1 to 33.5 nm.

Fig. (**7**) depicts the percentage dehydrogenation of the alcohol investigated as a function of reaction temperature for the reaction carried out over variously doped solids calcined at 500 and 700°C. It is clearly shown from Fig. (**7**) that the catalytic activity increased progressively to an extent proportional to the amount of dopant added for the solids calcined at 500°C and 700°C. The maximum percentage increase in the catalytic activity, measured at 240°C, due to the addition of 4.5 mol% Li$_2$O attained 45% and 94% for the solids calcined at 500 and 700°C, respectively. This finding suggested that the effectiveness of doping much increased by increasing the calcinations temperature from 500°C to 700°C (the crystallite size of cobalt - manganese oxides phase decreased from 28.7 to 9.5 nm upon doping with 3 mol% Li$_2$O followed by calcinations at 500°C). The observed increase in the catalytic activity due to Li$_2$O - doping of the system investigated could be attributed to the enhanced formation of (Co,Mn)(Co,Mn)$_2$O$_4$ phase and to the significant decrease in the crystallite size of the produced phase. This decrease might increase the degree of dispersion of this phase, increasing thus the concentration of active sites (nanocrystalline cobalt manganese oxides phase). However, the decrease in the crystallite size seems to be not the only factor affecting the catalytic activity simply because the increase in the dopant concentration from 0.75 to 4.5 mol% Li$_2$O the solids calcined at 500°C did not much affect the crystallite size of cobalt manganese phase but much increased the catalytic activity. Furthermore, the crystallite size of cobalt manganese oxide phase in solids doped with 0.75 - 4.5 mol% and being calcined at 700°C measured almost the same value but having different catalytic activities. This factor might be the enhanced formation of nanocrystalline cobalt - manganese mixed oxides phase present in the solids being calcined at 500 and 700°C.

The effectiveness of doping process in increasing the catalytic activity of the system investigated increased by increasing the calcinations temperature from 500 to 700°C. This finding might suggest that the amount of Li$_2$O dissolved in the matrices of the solids investigated much increased by increasing the calcination temperature. This conclusion seems logical because of the effective increase in the mobility of the reacting Co, Mn and Li$^+$ cations.

Determination of the activation energy of the dehydrogenation of alcohol investigated might throw more light about the possible change in the mechanism of the catalyzed reaction. ΔE - values were readily determined from the change in the percentage conversion (below 20%) as a function of reaction temperature for the reaction carried over different solids.
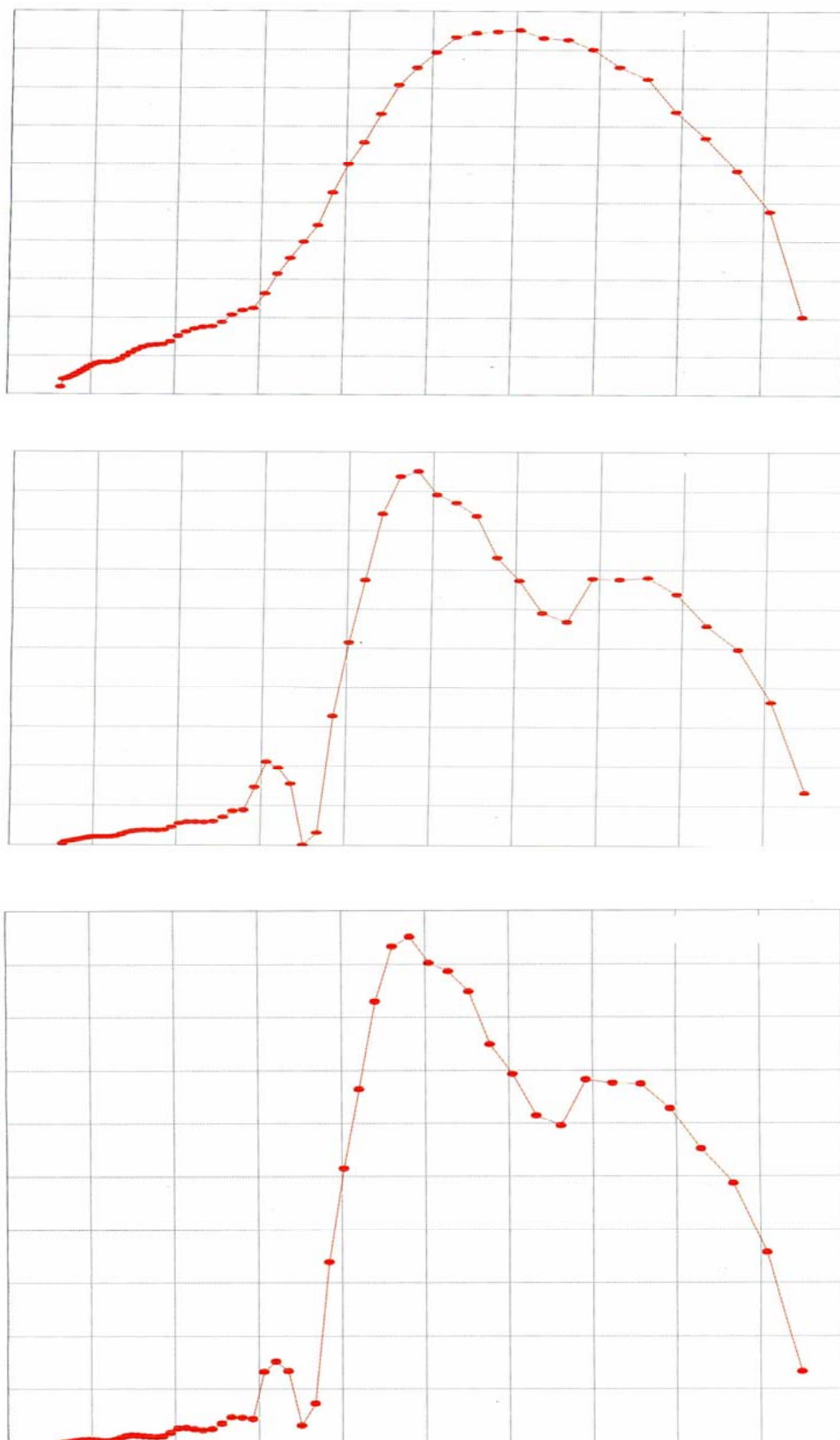
Fig. (5). Pore Volume distribution curves of pure and variously doped adsorbents calcined at $500^{o}C$.
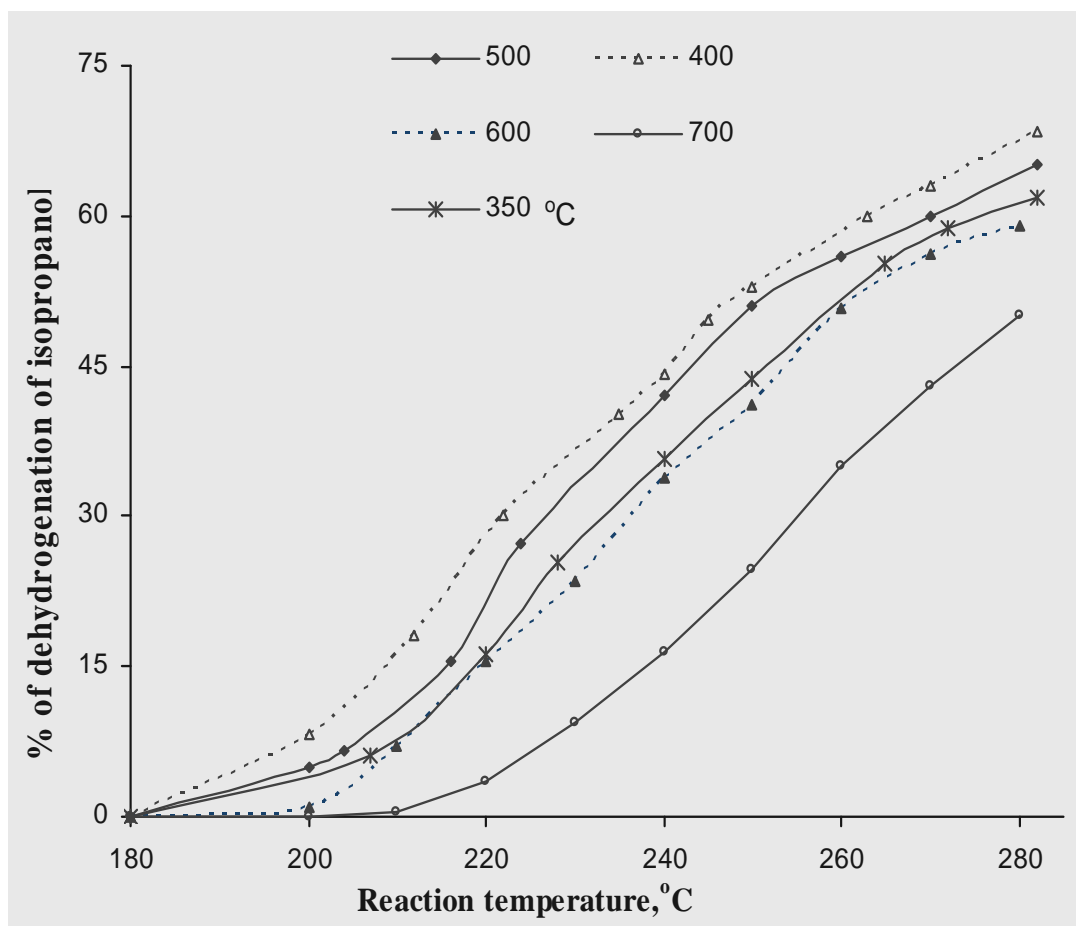
Fig. (6). Effect of reaction temperature on % of dehydrogenation of isopropanol carried out over pure solids calcined at 350-700 °C.

Table **3** includes the computed ΔE values for the catalyzed reaction conducted over pure and different solids. Also, Table **3** includes the values of logA (prexponential factor of the Arrhenius equation). Examination of Table **3** shows the following: (i) fluctuation in ΔE and log A values for pure and doped solids were observed (i.e. both increase and decrease in their values) took place. (ii) Li_2O - doping of the solids calcined at 500°C much increase ΔE values where ΔE increased from 59 to 99 kJmol^{-1} for the heavily doped solids calcined at 500°C. However, this treatment brought about an effective increase in the catalytic activity. So, the computed ΔE values for the doped solids calcined at 500°C did not express the observed increase in their catalytic activity. (iii) The calculated ΔE values for the doped solids calcined at 700°C did not also run parallel to the observed increase in their catalytic activity. In fact, ΔE values of the solids doped with 3 and 4.5 mol% are close to each other but having different catalytic activities.

The fact that ΔE and log A values for all solids investigated fluctuate in almost the same manner might suggest that the observed changes in ΔE values comes from a corresponding change in log A values. This speculation could be confirmed from recalculation of ΔE values for the reaction conducted over pure solids calcined at 350°C and 700°C adopting the log A value of the solids calcined at 350°C to the other solids. Similarly, ΔE values were recalculated adopting log A values of pure solids calcined at 500 and

700°C to the other solids calcined at the same temperatures. The recalculated values of the activation energies (ΔE*) are given in the last column of Table **3**. It is clearly shown from the data given in this column that ΔE* values of pure solids calcined at 350 - 700°C showed almost the same values (56 ± 2 kJmol^{-1}). This finding suggested clearly that the increase in calcination temperature of pure solids within 350 - 700°C did not change the mechanism of the catalyzed reaction but changed the concentration of active sites involved in the catalyzed reaction. Similarly, ΔE* values of variously doped solids calcined at 500 and 700°C showed almost the same values (58 ± 1) kJmol^{-1} and (60 ± 2) kJmol^{-1}, respectively. So, one may conclude that Li_2O - doping of the system investigated did not change the mechanism of the catalyzed reaction but increased the concentration of active sites participated in the catalyzed reaction. These assumptions find evidence from the plots of the equation

$$F(E_i) = a \exp (hE_i)$$

where E_i is the energy of the site (i) with the substrate.

$A = a \exp (h \Delta E)$ derived on the basis of dissipation function of active sites by their energy as a consequence of surface heterogeneity [32]. Fig. (**8**) shows the plot of log A versus ΔE* for pure solids calcined at 350 - 700°C and variously doped solids calcined at 500 and 700°C. The computed values of the constant "h" (slope) of the plot in Fig. (**8**) are 0.24 mol kJ^{-1} for pure solids calcined 350 - 700°C and 0.27
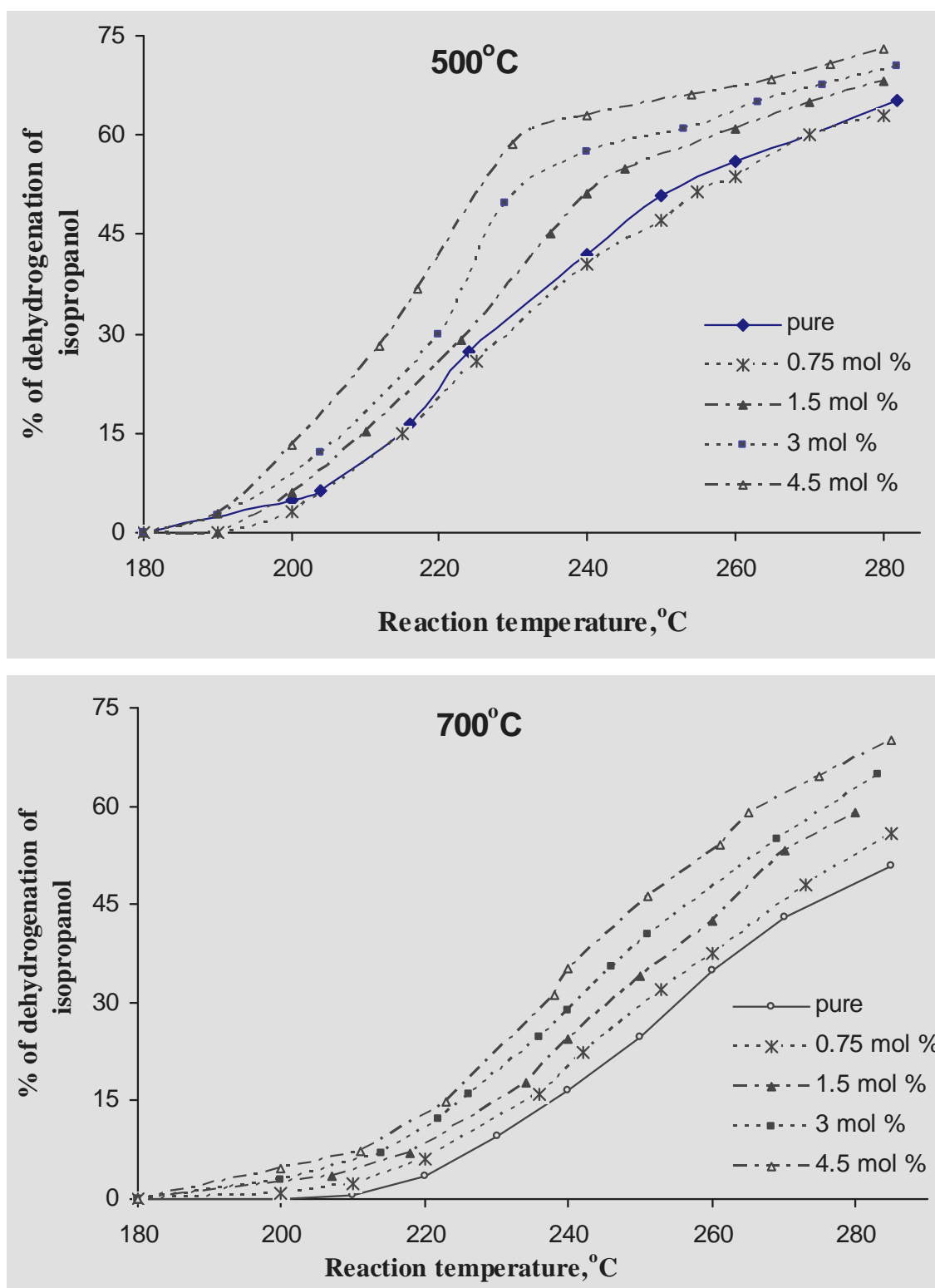
Fig. (7). Effect of reaction temperature on % of dehydrogenation of isopropanol carried out over Li$_2$O - doped solids calcined at 500 and 700 °C.

molkJ^{-1} and 0.25 mol kJ^{-1} for variously doped solids calcined at 500 and 700°C, respectively. The "a" value for pure solids was 8.4 min^{-1}. The "a" values for the variously doped solids calcined at 500 and 700°C were 0.86 min^{-1} and 13.9 min$^{-1.}$ The constants "h" and "a" values indicate that the increase in

calcination temperature and Li$_2$O - doping of the investigated system did not change the dissipation of active sites, i.e. the character of surface heterogeneity. In other words, these treatments did not change the energetic nature of active site but changed their concentration.

Table 3. Computed Activation Energies (ΔE, ΔE^*) and Logarithm Pre-Exponential Factor of the Arrhenius Equation for the Catalyzed Reaction Conducted Over Pure and Different Doped Solids

Sample	Calcination Temperature (°C)	ΔE (kJmol^{-1})	log A	ΔE^* (kJmol^{-1})
Pure CoO/Mn$_2$O$_3$	350	55.6	14.7	56
	400	68.8	11.6	54
	500	58.6	15.5	54
	600	76.6	19.9	56
	700	62.3	15.8	58
Pure solid	500	58.6	15.5	59
+0.75 mol% Li$_2$O	500	82.3	21.5	59
+1.5 mol% Li$_2$O	500	71.0	18.9	58
+3.0 mol% Li$_2$O	500	80.7	21.4	58
+4.5 mol% Li$_2$O	500	99.3	26.3	58
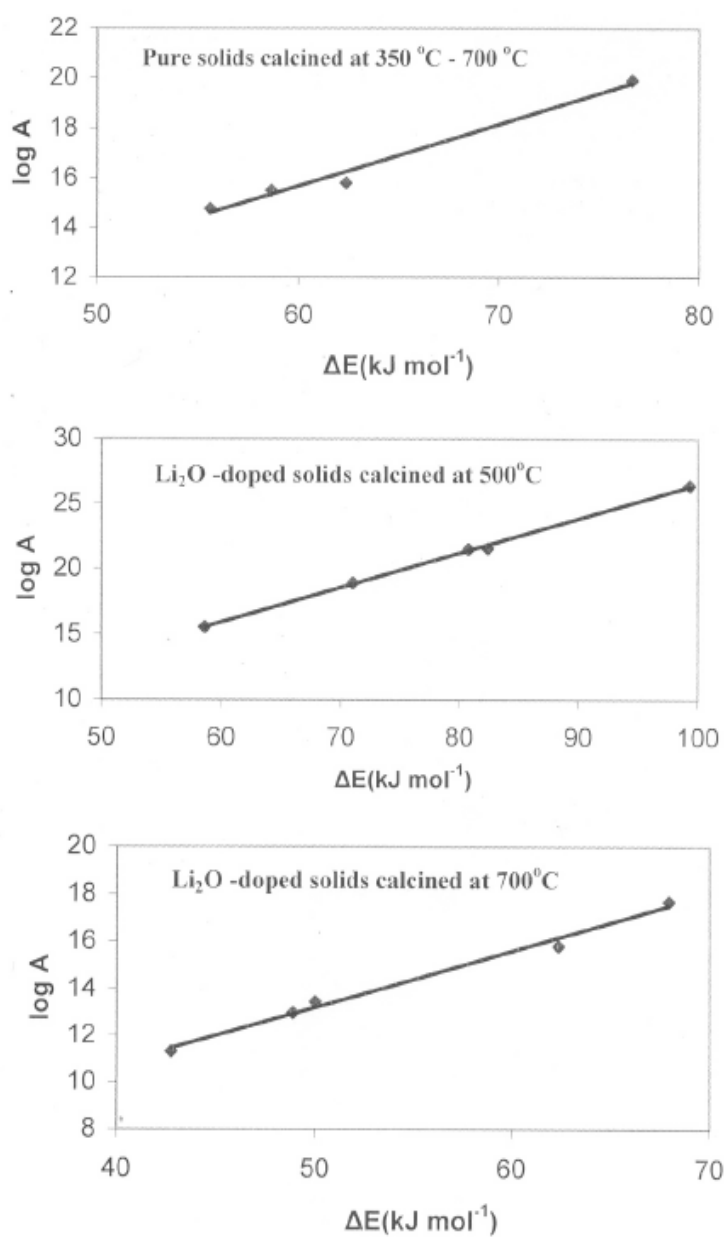
Fig. (8). Relationship between ΔE and log A for different solids investigated.

CONCLUSIONS

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

1. Heat treatment of CoO/Mn_2O_3 having equimolar proportion at temperature within 350 - 700°C led to the formation of nanocrystalline cobalt manganese oxide phase.

2. The degree of crystallinity and crystallite size of the produced phase increased progressively as a function of calcination temperature.

3. The computed value of the activation energy of sintering of pure solids determined from the increase in crystallite size of the phase produced was found to be 28 kJmol^{-1}.

4. Li_2O - doping of the system investigated decreased, generally, the crystallite size of the crystalline phase produced (cobalt manganese oxide phase).

5. The increase in calcination temperature of pure and doped adsorbents from 500 to 700°C decreased their specific surface areas and increased their total pore volume with subsequent increase in pore diameter. The doping process increased the S_{BET} and created a portion of narrow pores.

6. The increase in calcination temperature of pure solids from 350 to 400°C increased their catalytic activity in isopropanol conversion taking place *via* dehydrogenation of isopropanol to yield acetone only. The increase in the calcination temperature above 400°C led to a measurable decrease in the catalytic activity.

7. Li_2O - doping of the system investigated increased progressively its catalytic activity to an extent proportional to the amount of dopant added. The maximum increase in the catalytic activity measured, at 240°C, in presence of 4.5 mol% Li_2O attained 45 and 94 % for the solids calcined at 500 and 700°C, respectively.

8. The change in the calcination temperature of pure solids within 350 - 700°C and Li_2O - doping followed by calcinations at 500 and 700°C, did not modify the mechanism of the catalyzed reaction but changed the concentration of the active sites involved in the catalytic reaction.

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