The influence of La$_2$O$_3$-doping on structural, surface and catalytic properties of nano-sized cobalt–manganese mixed oxides

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Received: 20 August 2015 / Accepted: 11 December 2015 / Published online: 3 March 2016
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Abstract Structural, textural and catalytic activity of CoO–Mn$_2$O$_3$ system as being influenced by La$_2$O$_3$-doping (0.75–3 mol%) and calcination temperatures (300–500 °C) were investigated. The techniques employed were XRD, N$_2$-adsorption–desorption at −196 °C, EDX and catalysis of H$_2$O$_2$-decomposition in aqueous solution at 30–50 °C. The results revealed that the investigated system consisted of nano-sized Co$_2$MnO$_4$ as a major phase together with unreacted portion of Co$_3$O$_4$ and γ-Mn$_3$O$_4$. Doping with the smallest amount of La$_2$O$_3$ greatly increased the surface molar ratio of Mn/Co (88 %) for the solid calcined at 500 °C with subsequent increase of the catalytic activity more than 12-fold for solids calcined at 500 °C. The increase of La$_2$O$_3$-dopant above 0.75 mol% decreased progressively the surface molar ratio of Mn/Co with subsequent decrease in the catalytic activity which still measured higher values than that measured for the un-doped catalyst.

Keywords Cobalt manganite · La$_2$O$_3$-dopant · Coprecipitation · Catalytic decomposition of H$_2$O$_2$

Introduction

Manganese oxides are reported to be considered as environment-friendly materials. MnO$_2$ and Mn$_3$O$_4$ were found to be active and stable catalysts for the combustion of organic compounds [1, 2].

Nanocrystalline manganese oxide powders were synthesized in previous study by an inert gas condensation technique [3]. The manganese oxide, which is prepared, is a mixture of MnO and Mn$_3$O$_4$. The particle size of manganese oxides is greatly dependent on their preparation conditions. Dimesso et al. [4] claimed that manganese oxides can be prepared by an inert gas condensation technique followed by annealing in air and oxygen at various temperatures. The predominant phase of MnO and Mn$_3$O$_4$ are obtained after annealing in air at 400 °C.

Mixed oxides containing transition metal oxides are used to design the catalytic materials to replace noble metal catalysts. Lahousse et al. [1] have found that γ-MnO$_2$ and Pt/TiO$_2$ catalysts measured high catalytic activities as compared to noble metals catalysts.

Mixing manganese with transition metal oxides in many catalytic systems modify the catalytic activity of individual components [5, 6]. Mixed oxide materials are active for oxidation–reduction reactions and combustion processes. For example, cobalt–zinc manganites, manganese–CeO$_2$ mixed oxides and Co-containing mixed oxides prepared from hydrotalcite-like precursors were active catalysts in the reduction of nitrous oxide [7–9]. Also, Co–Mn mixed oxides were found to be active catalysts for oxidation of ethanol [10] and conversion of synthesis gas to light olefins [11]. However, Ag–Mn, Ag–Co and Ag–Ce composite oxides supported on Al$_2$O$_3$ have been reported as catalysts for oxidation of volatile organic compounds [12]. In a previous study, Mn–Cu mixed oxides have been reported to...
be catalytically more active towards ethanol oxidation as compared to individual Mn$_2$O$_3$ and CuO [6]. Both copper and manganese mixed oxides catalysts were found to be more active catalysts in many industrial oxidation processes, such as CO oxidation by O$_2$, combustion of toluene, methanol, ethylene, ammonia, NO$_2$ and other combustion reactions [13–16]. However, Mn–Zr mixed oxide samples are active towards dehydrogenation of isopropanol, giving rise to acetone with high selectivity at partial conversion [17].

Hydrogen peroxide and its solutions find use as antiseptic in medicine [18, 19], other applications such as bleach in the textile and paper/pulp industry, in treatment of waste water [20]. However, the literature survey reveals that mixed oxide catalyst is more active in H$_2$O$_2$ decomposition. These catalysts have attracted much attention of chemists due to their application as low-cost fuel cells, their stability and high activity [21, 22]. The decomposition of hydrogen peroxide in presence of some metal oxides as LaMnO$_3$ at room temperature and nanocrystalline LaCrO$_3$ was investigated by Khetre et al. [23]. They found that the catalytic activity was increased by increasing both the amount of the catalyst and pH. The probable reaction mechanism has been suggested in which an intermediate surface complex is thought to be responsible for the enhancement of the decomposition of hydrogen peroxide.

The present work aimed at studying the effect of La$_2$O$_3$-doping of CoO/Mn$_2$O$_3$ system prepared by coprecipitation method on its structural, surface and catalytic properties. The techniques employed were XRD, EDX, N$_2$-adsorption isotherms carried out at −196 °C and catalytic decomposition of H$_2$O$_2$ in aqueous solution at 30–50 °C.

**Techniques**

X-ray powder diffractograms of various investigated samples calcined at 300, 400 and 500 °C were determined using a Bruker diffractometer (Bruker D 8 advance target). The patterns were run with copper K$_\alpha$ with secondly monochromator (λ = 1.5405 Å) at 40 kV and 40 mA. The scanning rate was 0.8° in 2θ min$^{-1}$ for phase identification and line broadening profile analysis, respectively. The crystallite size of the phases present in pure and variously La$_2$O$_3$-doped solids was determined using the Scherrer equation [24]:

$$ d = \frac{k\lambda}{\beta \cos \theta}, $$

where $d$ is the mean crystallite diameter, $\lambda$ is the X-ray wave length of the X-ray beam, $K$ is the Scherrer constant (0.89), $\beta$ is the full width at half maximum (FWHM) of the main diffraction peaks of the investigated phases, in radian and $\theta$ is the diffraction angle.

Energy dispersive X-ray analysis (EDX) was carried out on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The parameters were as follows: −15 kV accelerating voltage, 100 s accumulation time, 8 µm window width. The surface molar composition was determined by the Asa method (Zaf-correction, Gaussian approximation).

Different surface characteristics, namely specific surface area ($S_{BET}$), total pore volume ($V_p$), mean pore radius ($r^-$) and pore volume distribution curves ($\Delta V/\Delta r$) of various solids were determined from nitrogen adsorption–desorption isotherms measured at −196 °C using NOVA Automated Gas sorbometer. Before undertaking such measurements, each sample was degassed under a reduced pressure of 10$^{-5}$ Torr for 3 h at 200 °C. The values of $V_p$ were computed from the relation:

$$ V_p = 15.45 \times 10^{-4} \times V_d \text{cm}^3/\text{g}, $$

where $V_d$ is the volume of nitrogen adsorbed at $P/P^\alpha$ tends to unity. The values of $r^-$ were determined from the equation:

$$ r^- = \frac{2V_p}{S_{BET}} \times 10^4 \AA. $$

The catalytic activities of pure and variously La$_2$O$_3$-doped solids were determined by studying the decomposition of H$_2$O$_2$ in their presence at temperatures within 30–50 °C using 25, 50 and 100 mg of a given catalyst sample with 0.5 ml volume of H$_2$O$_2$ of known concentration diluted to 20 ml with distilled water (initial concentration of H$_2$O$_2$ = 0.01 mol/L). The reaction kinetics was monitored by measuring the volume of oxygen liberated at different time intervals until no further O$_2$ was liberated. The volume of the liberated oxygen was recalculated under STP.

**Experimental**

**Materials**

Equimolar proportions of CoO/Mn$_2$O$_3$ were prepared by coprecipitation method of their mixed hydroxides from their nitrates solution using 1 M NaOH solution at pH 8 and a temperature of 70 °C. The carefully washed precipitate was dried at 110 °C till constant weight, and then subjected to heating at 300, 400, and 500 °C for 4 h. Three La$_2$O$_3$-doped samples were prepared by impregnating a given dry weight of the mixed hydroxides with calculated amount of lanthanum nitrate dissolved in the least amount of distilled water sufficient to make pastes. The pastes were dried at 110 °C and then calcined at 300, 400 and 500 °C for 4 h. The dopant concentrations in the calcined solids were 0.75, 1.5, and 3 mol% La$_2$O$_3$. 

Equation

$$ K \alpha = \frac{}\text{cm} $$

Equation

$$ \beta = \text{cm} $$

Equation

$$ \theta = \text{cm} $$

Equation

$$ A = \text{cm} $$

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$$ B = \text{cm} $$

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$$ C = \text{cm} $$

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$$ D = \text{cm} $$

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$$ E = \text{cm} $$

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$$ F = \text{cm} $$

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$$ G = \text{cm} $$

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$$ H = \text{cm} $$

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$$ I = \text{cm} $$

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$$ J = \text{cm} $$

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$$ K = \text{cm} $$

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$$ M = \text{cm} $$

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$$ N = \text{cm} $$

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$$ O = \text{cm} $$

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$$ P = \text{cm} $$

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$$ Q = \text{cm} $$

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$$ R = \text{cm} $$

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$$ S = \text{cm} $$

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$$ T = \text{cm} $$

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$$ U = \text{cm} $$

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$$ V = \text{cm} $$

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$$ W = \text{cm} $$

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$$ X = \text{cm} $$

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$$ Y = \text{cm} $$

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$$ Z = \text{cm} $$

Equation
Results and discussion

X-ray investigation of various solids

X-ray diffractograms of un-doped and variously La$_2$O$_3$-doped solids calcined at 300–500 °C were determined from the recorded diffractograms of these solids are illustrated in Figs. 1, 2, 3 for the solids calcined at 300, 400 and 500 °C, respectively. The different structural characteristics of the solids investigated are given in Table 1. Table 1 includes the peak area of the main diffraction lines of different phases present and the crystallite size of CoMn$_2$O$_4$ phase formed calculated from the Scherrer equation.

Examination of Figs. 1, 2, 3 and Table 1 shows the following: (1) pure and variously La$_2$O$_3$-doped solids calcined at 300–500 °C consisted of nano-sized cobalt manganite (Co$_2$MnO$_4$) (02-1061-JCPDS-ICDD, Copyright, 2001) as a major phase together with un-reacted Co$_3$O$_4$ (42-1467-JCPDS-ICDD, Copyright, 2001) and γ-Mn$_3$O$_4$ (18-0803-JCPDS-ICDD, Copyright, 2001) phases. (2) The peak area of the main diffraction lines of Co$_2$MnO$_4$ phase decreases progressively by increasing the amount of La$_2$O$_3$-added in different solids. For example, the peak area of the main diffraction peak of cobalt manganite for the solids calcined at 500 °C measured 73.5, 55.1, 37.7 and 28.9 (a.u.) for pure sample and those treated with 0.75, 1.5 and 3 mol% La$_2$O$_3$, respectively. (3) The crystallite size of the produced Co$_2$MnO$_4$ varies between 21.3 and 75.7 nm depending on the dopant concentration and calcination temperature. (4) The increase in calcination temperature of various solids investigated within 300–500 °C increased progressively the peak area of the main diffraction line corresponding to the produced Co$_2$MnO$_4$. (5) No diffraction peak of lanthanum or lanthanum-manganite and lanthanum-cobaltite composites were detected in the diffractograms. This finding suggested clearly that La$_2$O$_3$ acted only as a doping agent.

These results show clearly the role of La$_2$O$_3$ in hindering the solid–solid interaction between cobalt and manganese oxide to yielding cobalt manganite. The increase in calcination temperature within 300–500 °C stimulated the formation of Co$_2$MnO$_4$. The formation of Co$_2$MnO$_4$ took place according to the reaction:

$$4\text{Co}_3\text{O}_4 + 3\text{Mn}_2\text{O}_3 \xrightarrow{300-500\, ^\circ\text{C}} 6\text{Co}_2\text{Mn}_3\text{O}_14 + 1/2\text{O}_2$$

The addition of smallest amounts of La$_2$O$_3$ (0.75–3 mol%) followed by heating at 300–500 °C hindered Co$_2$MnO$_4$ formation to an extent proportional to its amount added.
The retardation effect of La\textsubscript{2}O\textsubscript{3} might be attributed to dissolution of some of La\textsubscript{2}O\textsubscript{3} (La\textsuperscript{3+}) cation in the lattices of Co\textsubscript{3}O\textsubscript{4} and/or Mn\textsubscript{3}O\textsubscript{4} assuming that Co\textsubscript{3}O\textsubscript{4} consisted of (2CoO and Co\textsubscript{2}O\textsubscript{3}, i.e., cobalt cations existed in di- and/or tetra-valent states. The dissolution of La\textsubscript{2}O\textsubscript{3} in Co\textsubscript{3}O\textsubscript{4} lattices could be simplified adopting Kroger’s notations \cite{25} according to:

\[
\begin{align*}
\text{La}^{3+} + \text{Co}^{4+} + \text{Co}^{2+} & \rightarrow \text{La} \left( \text{Co}^{4+} \right) + \text{Co}^{3+} + 1/2\text{O}_2 \\
\text{La}^{3+} + \text{Co}^{2+} + 1/2\text{O}_2 + \text{Co}^{4+} & \rightarrow \text{La} \left( \text{Co}^{2+} \right) + \text{Co}^{3+}
\end{align*}
\]

where La (Co\textsuperscript{4+}) is lanthanum cation located in the position of host tetravalent cobalt cation lattice and La (Co\textsuperscript{2+}) is lanthanum cation located in the position of host divalent cobalt lattice cation in Co\textsubscript{3}O\textsubscript{4}. It is clear from Eqs. 1 and 2 that incorporation of La\textsuperscript{3+} in cobaltic oxide lattice decreased the concentrations of divalent and tetravalent cobalt cations converting them into Co\textsuperscript{3+} ions. The trivalent cobalt cations did not participate directly in the formation of CoMn\textsubscript{2}O\textsubscript{4} which involved divalent cobalt and trivalent manganese cations. So, the incorporation of lanthanum cation in Co\textsubscript{3}O\textsubscript{4} lattice according to mechanism 1 decreased the number of divalent cobalt involved in the formation of CoMn\textsubscript{2}O\textsubscript{4} phase. Consequently, the retardation of La\textsubscript{2}O\textsubscript{3} dopant in CoMn\textsubscript{2}O\textsubscript{4} formation could be understood.

Surface characteristics of various prepared solids

Nitrogen adsorption–desorption isotherms measured at \(-196 \, ^\circ\text{C}\) were determined for pure and variously La\textsubscript{2}O\textsubscript{3}-doped Co\textsubscript{3}O\textsubscript{4}/Mn\textsubscript{3}O\textsubscript{4} solids calcined at 300, 400 and 500 \(^\circ\text{C}\). All isotherms belong to type II of Branauer classification \cite{26} having hysteresis loops of small areas closing at \(P/P_0\) at about 0.5. Figure 4 depicts representative N\textsubscript{2}-adsorption–desorption isotherms measured over pure and variously doped solids calcined at 500 \(^\circ\text{C}\). Figure 5 depicts \(\Delta V/\Delta r\) curves of various solids calcined at 300 and 500 \(^\circ\text{C}\). Analysis of the recorded adsorption–desorption isotherms permitted us to calculate different surface characteristics, namely specific surface area (\(S_{\text{BET}}\)), total pore volume (\(V_p\)) and mean pore radius (\(r^-\)). The computed values of \(S_{\text{BET}}, V_p\) and \(r^-\) are given in Table 2.

Examination of Table 2 and Fig. 5 shows the following: (1) the \(S_{\text{BET}}\) and \(V_p\) values of pure and variously doped solids increased progressively by increasing the calcination temperature within 300–500 \(^\circ\text{C}\). The increase was, however, more pronounced for pure mixed solids which attained 113 and 295 \% for \(S_{\text{BET}}\) and \(V_p\), respectively \cite{27}. (2) The \(r^-\) values cited in the last column of Table 2 show that the investigated solids are mesoporous adsorbents measuring \(r^-\) values varying between 30 and 88 Å. (3) La\textsubscript{2}O\textsubscript{3}-doping decreased effectively the \(S_{\text{BET}}\) to an extent directly proportional to its amount present. The doping process did not affect the \(r^-\) values which remained almost constant for heavily doped sample (3 mol\% La\textsubscript{2}O\textsubscript{3}). (4) Most of the investigated solids exhibit bimodal pore volume distribution curves except the heavily doped sample (3 mol\% La\textsubscript{2}O\textsubscript{3}) exhibited tri-modal distribution curves (c.f. Figure 5). The maximum hydraulic pore radius was located at 11.5 and 27.5 Å for pure solids and found at 10 and 23 Å for solids doped by 0.75 mol\% La\textsubscript{2}O\textsubscript{3} and 9.5 and 30 Å for solids doped by 1.5 mol\% La\textsubscript{2}O\textsubscript{3} and 10, 16 and 26 Å for solids doped by 3 mol\% La\textsubscript{2}O\textsubscript{3} being calcined at 500 \(^\circ\text{C}\).

### Table 1

Peak area of different phases present in pure and variously doped Co\textsubscript{3}O\textsubscript{4}–Mn\textsubscript{3}O\textsubscript{4} solids calcined at 300–500 \(^\circ\text{C}\) and the crystallite size of Co\textsubscript{2}Mn\textsubscript{2}O\textsubscript{4} phase

| Solids | Calcination temperature (\(^\circ\text{C}\)) | Peak area (a.u.) of diffraction lines of | Crystallite size (nm) |
|--------|------------------------------------------|----------------------------------------|-----------------------|
|        |                                          | Co\textsubscript{2}Mn\textsubscript{2}O\textsubscript{4} phase | Co\textsubscript{3}O\textsubscript{4} phase | \(\gamma\)-Mn\textsubscript{3}O\textsubscript{4} phase | Co\textsubscript{2}Mn\textsubscript{2}O\textsubscript{4} phase |
| Pure (0.5 mol CoO + 0.5 mol Mn\textsubscript{3}O\textsubscript{4}) | 300 | 47.6 | 11.2 | 17.8 | 51.3 |
|        | 400 | 70.3 | 13.9 | 27 | 59.7 |
|        | 500 | 73.5 | 14.5 | 26.5 | 75.7 |
| +0.75 mol% La\textsubscript{2}O\textsubscript{3} | 300 | 39 | 7 | 10.8 | 26.3 |
|        | 400 | 45.9 | 11.7 | 20.5 | 27.5 |
|        | 500 | 55.1 | 14.3 | 21.3 | 31.5 |
| +1.5 mol% La\textsubscript{2}O\textsubscript{3} | 300 | 31.6 | 11.1 | 15.4 | 28.7 |
|        | 400 | 31.7 | 10.8 | 15.4 | 30.4 |
|        | 500 | 37.7 | 8.6 | 15.3 | 31.5 |
| +3 mol% La\textsubscript{2}O\textsubscript{3} | 300 | 25.2 | 9.3 | 11.6 | 21.3 |
|        | 400 | 21.3 | 7.8 | 9.8 | 23.5 |
|        | 500 | 28.9 | 9.8 | 15.2 | 30.8 |
These results show clearly the role of La$_2$O$_3$-doping in modifying the various surface characteristics of the system investigated. Comparison of ($r^{-}$) values of pure and variously doped solids calcined at 300–500 °C decreased effectively the calculated ($r^{-}$) values. This decrease might be followed by an increase in the $S_{BET}$ values opposite to what was found. So, one might expect that the dopant process decreased the concentration of the narrowest pore located at 11.5 Å.

**Energy dispersive X-ray analysis of various solids**

EDX investigation of pure and doped solids calcined at 300–500 °C was determined. The relative atomic abundance of manganese, cobalt, oxygen and lanthanum species present in the uppermost surface layers of the calcined solids is given in Table 3. It is well known that EDX technique supplies an accurate determination of relative atomic concentration of different elements present on their outermost surface layers [28–34]. In fact, this technique (EDX) has been successfully employed in determining the surface composition of a big variety of catalytic systems such as CuO/Mn$_2$O$_3$ [28], CuO/ZnO [29, 31, 33], TiO$_2$/Al$_2$O$_3$ [30], CuO/NiO [32] and Co$_3$O$_4$/Fe$_2$O$_3$ [34]. The thickness of these layers is bigger than those measured by using XPS technique. XPS is a well-known surface-sensitive technique that supplies very accurate relative atomic abundance of cationic and anionic species on the surfaces of investigated solids. Surface and bulk compositions of various solids are given in Table 3. Inspection of the results given in Table 3 reveals the following: (1) the surface composition of pure and variously doped solids is different from those of their bulk. (2) The surface concentration of cobalt species is always smaller than that presents in the
Table 2 Surface characteristics of pure and variously treated solids being calcined at 300–500 °C

| Solids                      | Calcination temperature (°C) | $S_{BET}$ (m²/g) | Total pore volume $V_p$ (cc/g) | Mean pore radius $r_-$ (Å) |
|-----------------------------|-----------------------------|-------------------|-------------------------------|---------------------------|
| Pure (0.5 mol CoO          | 300                         | 16                | 0.038                         | 48                        |
| +0.5 mol Mn₂O₃             | 400                         | 17                | 0.045                         | 52                        |
|                             | 500                         | 34                | 0.15                          | 88                        |
| +0.75 mol% La₂O₃           | 300                         | 13                | 0.021                         | 32                        |
|                             | 400                         | 14                | 0.022                         | 31                        |
|                             | 500                         | 16                | 0.024                         | 30                        |
| +1.5 mol% La₂O₃            | 300                         | 12                | 0.011                         | 18                        |
|                             | 400                         | 14                | 0.015                         | 21                        |
|                             | 500                         | 15                | 0.016                         | 21                        |
| +3 mol% La₂O₃              | 300                         | 10                | 0.016                         | 32                        |
|                             | 400                         | 12                | 0.020                         | 33                        |
|                             | 500                         | 14                | 0.023                         | 33                        |

Fig. 5 Pore volume distribution curves $\Delta v/\Delta r$ for pure and variously doped solids calcined at 500 °C
Table 3  Surface molar composition of pure and variously treated solids determined by EDX

| Solid                  | Calcination temperature (°C) | Element | Atomic abundance (at.%) | Mn/Co ratio |
|------------------------|-----------------------------|---------|-------------------------|-------------|
|                        |                             |         | Bulk                    | Surface     |            |
| Pure (0.5 mol CoO + 0.5 mol Mn$_2$O$_3$) | 300                         | Mn      | 28.57                   | 37.0        | 33.6       |
|                        |                             | Co      | 14.29                   | 1.1         |            |
|                        |                             | O       | 57.14                   | 62.0        |            |
|                        |                             | Mn      | 28.57                   | 38.6        | 35.1       |
|                        |                             | Co      | 14.29                   | 1.1         |            |
|                        |                             | O       | 57.14                   | 60.3        |            |
|                        |                             | Mn      | 28.57                   | 56.0        | 37.3       |
|                        |                             | Co      | 14.29                   | 1.5         |            |
|                        |                             | O       | 57.14                   | 42.5        |            |
| +0.75 mol% La$_2$O$_3$ | 300                         | Mn      | 28.39                   | 38.3        | 47.9       |
|                        |                             | Co      | 14.19                   | 0.8         |            |
|                        |                             | O       | 57.21                   | 60.64       |            |
|                        |                             | La      | 0.21                    | 0.26        |            |
|                        |                             | Mn      | 28.39                   | 48.2        | 53.5       |
|                        |                             | Co      | 14.19                   | 0.9         |            |
|                        |                             | O       | 57.21                   | 50.54       |            |
|                        |                             | La      | 0.21                    | 0.36        |            |
|                        |                             | Mn      | 28.39                   | 63.3        | 70.3       |
|                        |                             | Co      | 14.19                   | 0.9         |            |
|                        |                             | O       | 57.21                   | 35.44       |            |
|                        |                             | La      | 0.21                    | 0.4         |            |
| +1.5 mol% La$_2$O$_3$  | 300                         | Mn      | 28.21                   | 38.0        | 46.5       |
|                        |                             | Co      | 14.11                   | 0.8         |            |
|                        |                             | O       | 57.26                   | 60.74       |            |
|                        |                             | La      | 0.42                    | 0.46        |            |
|                        |                             | Mn      | 28.21                   | 38.9        | 47.4       |
|                        |                             | Co      | 14.11                   | 0.82        |            |
|                        |                             | O       | 57.26                   | 59.74       |            |
|                        |                             | La      | 0.42                    | 0.54        |            |
|                        |                             | Mn      | 28.21                   | 42.2        | 48.0       |
|                        |                             | Co      | 14.11                   | 0.88        |            |
|                        |                             | O       | 57.26                   | 56.34       |            |
|                        |                             | La      | 0.42                    | 0.58        |            |
| +3 mol% La$_2$O$_3$    | 300                         | Mn      | 27.85                   | 37.6        | 41.8       |
|                        |                             | Co      | 13.93                   | 0.9         |            |
|                        |                             | O       | 57.38                   | 60.4        |            |
|                        |                             | La      | 0.84                    | 1.1         |            |
|                        |                             | Mn      | 27.85                   | 38.6        | 42.0       |
|                        |                             | Co      | 13.93                   | 0.92        |            |
|                        |                             | O       | 57.38                   | 59.28       |            |
|                        |                             | La      | 0.84                    | 1.2         |            |
|                        |                             | Mn      | 27.85                   | 40.9        | 43.1       |
|                        |                             | Co      | 13.93                   | 0.95        |            |
|                        |                             | O       | 57.38                   | 56.95       |            |
|                        |                             | La      | 0.84                    | 1.2         |            |
bulk of pure and variously doped solids. (3) The concentration of surface manganese was several folds that of cobalt. This finding might suggest that cobalt hydroxide was precipitated much earlier than manganese hydroxides. This conclusion seems logical because of the significant difference between the values of the solubility products of Co(OH)3 and Mn(OH)2 which measured 5.9 × 10−15 and 1.6 × 10−44, respectively. (4) Lanthanum species present in the uppermost surface layers of all doped solids calcined at temperature within 300–500 °C is bigger than the amount present in the bulk of solids. This finding is expected because all doped solids were prepared by wet impregnation method [35, 36]. Furthermore, the surface concentration of lanthanum increases by increasing the calcination temperature of the doped solids. (5) The addition of the smallest amount of La2O3 (0.75 mol%) much increased the surface concentration of manganese present in all solids calcined at 300–500 °C. The increase in surface concentration of manganese species attained 4, 25 and 13 % for the solids calcined at 300, 400 and 500 °C, respectively. The increase of the dopant concentration above 0.75 mol% La2O3 decreased the surface concentration of manganese which still remained bigger than that measured for the un-doped samples calcined at the same temperatures.

It is well known that manganese species present in the uppermost surface layers in pure and doped solids are considered as the most catalytically active constituent involved in H2O2-decomposition. This assumption is based on the possible presence of manganese cations in different oxidation states varying between di- and hepta-valence states leading to a significant increase in the concentration of manganese ion pairs participating in the catalytic decomposition process. So, the bigger the surface concentration of manganese the bigger will be the concentration of the most catalytically active constituent and the bigger the catalytic activity. This speculation will be confirmed in the next section of the present work dealing with the catalytic decomposition of H2O2 on pure and variously La2O3-doped solids calcined at 300–500 °C.

Catalytic activity of pure and variously doped solids

The catalytic decomposition of H2O2 in aqueous solution was studied at 30, 40 and 50 °C over pure and variously doped solids precalcined at 300, 400 and 500 °C. First-order kinetics was observed in all cases. In fact, straight line was found upon plotting ln a/a − x against the time intervals t, where a is the initial concentration of H2O2 and a − x is its concentration at time t. The slopes (d ln a/a − x/ dt) of plots determine the reaction rate constant (k) for the reaction conducted at a given temperature over a given catalyst sample. The reaction kinetics were monitored using

![Fig. 6 First-order plots for catalytic decomposition of H2O2 at 50 °C, over pure and variously doped solids calcined at 500 °C](image)

![Fig. 7 First-order plots for catalytic decomposition of H2O2 at 50 °C, over pure and variously doped solids calcined at 300 °C](image)

25, 50 and 100 mg of catalyst sample. The results, not given, showed that k value increases linearly by increasing the catalyst mass indicating the absence of any possible solid gas diffusion of liberated oxygen. Figures 6 and 7 depict representative first-order plots of the catalyzed reaction conducted at 30 and 50 °C over pure and variously La2O3-doped solids precalcined at 300 and 500 °C, respectively. The values of the reaction rate constant per unit mass for the reaction carried out at 30, 40 and 50 °C were calculated from the slope of the first-order plots. Table 4 includes only the computed values of k50 °C. Inspection of Table 4 reveals the following: (1) the catalytic activity, expressed as reaction rate constant per unit mass, measured for pure and variously doped solids increased by increasing the calcination temperatures of all solids investigated calcined at 300–500 °C. (2) The presence of the smallest amount of La2O3 (0.75 mol%) increased considerably the (k) values. The increase reached about 103-fold for the catalytic reaction carried out at 30 and 50 °C. So, the comparison between the role of ZrO2, as shown in our
previous studied [27], and La2O3-doping of Co3O4–Mn3O4 system showed clearly that the increase in the catalytic activity due to the doping process was much more pronounced by doping with La2O3 as compared to ZrO2-doping [27]. (3) Increasing the dopant concentration above 0.75 mol% decreased the catalytic activity to an extent proportional to the amount of La2O3 added. (4) The observed increase in the catalytic activity of pure and variously doped solids by increasing their calcination temperature within 300–500 °C might be attributed to the observed increase in surface concentration of manganese species (considered as the most catalytically active constituent) and the observed increase in the specific surface areas (c.f. Tables 1, 2, 3). (5) The observed significant increase in the catalytic activity due to doping with 0.75 mol% La2O3 could be also attributed to the observed decrease in the crystallite size of Co2MnO4 phase (c.f. Table 1). (6) The decrease in the catalytic activity of the heavily doped solids might result from the observed increase in the crystallite size of Co2MnO4 (the major phase present in pure and doped solids) and also due to the observed decrease in surface concentration of manganese species besides the significant decrease in the S_BET (c.f. Tables 1, 2, 3).

In order to throw more light about the role of both calcination temperature and dopant concentration (La2O3) in the mechanism of the catalyzed reaction the activation energy of which (ΔE) was determined for pure and doped solids calcined at 300–500 °C. ΔE values were calculated from the values of k measured for the reaction carried out at 30, 40 and 50 °C by direct application of the Arrhenius equation. The computed ΔE values are given in Table 4. Examination of Table 4 shows that ΔE values for pure and variously doped solids decreased progressively as a function of dopant concentration. This trend ran parallel to observed increase in the catalytic activity, expressed as k50 °C values (c.f. Table 4). This finding expresses the observed increase in the catalytic activity of sample of 0.75 mol% La2O3-doping. On the other hand, increasing the dopant concentration above this limit increased ΔE values which remained almost smaller than ΔE values measured for the pure catalyst samples.

**Conclusions**

The main conclusions derived from the results obtained can be summarized as follows:

1. The role of La2O3-doping on structural, textural, surface composition and catalytic activity was investigated.
2. The prepared mixed solids consisted of nano-sized Co2MnO4 as a major phase together with un-reacted portion of Co3O4 and γ-Mn3O4.
3. Doping with La2O3(0.75 mol%) much increased both surface molar ratio of Mn/Co with (0.75 mol%) about 88 % with subsequent increase in the catalytic activity more than 12-fold.
4. The apparent activation energy of the catalyzed reaction measured 5.2, 1.5, 2.0 and 2.7 kJ/mol for the un-doped and catalyst doped with 0.75, 1.5 and 3 mol% La2O3.

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**References**

1. Lahousse C, Bernier A, Grange P, Delmon B, Papaefthimiou P, Ioannides T, Very Kios X (1998) Evaluation of γ-MnO2 as a VOC removal catalyst: comparison with a noble metal catalyst. J Catal 178:214–225
2. Baldi M, Escribano VS, Amores JMG, Milella F, Busca G (1998) Characterization of manganese and iron oxides as combustion catalysts for propane and propene. Appl Catal B 17:L175
3. Chen C-Y, Lin C-K, Tsai N-H, Tsay C-Y, Lee P-Y, Chen G-S (2008) Characterization of nanocrystalline manganese oxide powder prepared by inert gas condensation. Ceram Int 34:1661
4. Dimesso L, Heider I, Hahn H (1999) Synthesis of nanocrystalline Mn-oxides by gas condensation. Solid State Ion 123:39–46
5. Li W, Lin Y, Zhang Y (2003) Promoting effect of water vapor on catalytic oxidation of methane over cobalt, manganese mixed oxides. Catal Today 83:239–245
6. Morales MR, Barbero BP, Cadis LE (2006) Total oxidation of ethanol and propane over Mn–Cu mixed oxide catalysts. Appl Catal B 67:229
7. Fierro G, Iacono ML, Inversi M, Dragone R, Ferraris G (2001) Preparation, characterization and catalytic activity of Co–Zn-based manganites obtained from carbonate precursors. Appl Catal B 30:173
8. Chmielarz L, Kustrowski P, Rafalska-Lasocha A, Majda D, Dziembaj R (2002) Catalytic activity of Co–Mg–Al, Cu–Mg–Al and Cu–Co–Mg–Al mixed oxides derived from hydrotalcites in SCR of NO with ammonia. Appl Catal B 35:195
9. Qi G, Yang RT, Change R (2004) MnOx–CeO2 mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH3 at low temperatures. Appl Catal B 51:98–107
10. Kovanda F, Rojka T, Dobesová J, Machovic V, Bezdicˇka P, Obalová L, Grygar T (2006) Mixed oxides obtained from Co and Mn containing layered double hydroxides: Preparation, characterization, and catalytic properties. J Solid State Chem 179:812
11. Mirzaei AA, Faizi M, Habibpour R (2006) Effect of preparation conditions on the catalytic performance of cobalt manganese oxide catalysts for conversion of synthesis gas to light olefins. Appl Catal A: Gen 306:98–107
12. Luo M-F, Yuan X-X, Zheng X-M (1998) Catalyst characterization and activity of Ag–Mn, Ag–Co and Ag–Ce composite oxides for oxidation of volatile organic compounds. Appl Catal A: Gen 175:121–129
13. Liu Y, Luo MF, Wei ZB, Xin Q, Ying PL, Li C (2001) Catalytic oxidation of chlorobenzene on supported manganese oxide catalysts. Appl Catal B 29(1):61
14. Ferrandon M, Bjornbom E (2001) Hydrothermal stabilization by lanthanum of mixed metal oxides and noble metal catalysts for volatile organic compound removal. J Catal 200(1):148–159
15. Alvarez-Galvan MC, O’Shea VADP, Fierro JLG, Arias PL (2003) Alumina-supported manganese- and manganese-palladium oxide catalysts for VOCs combustion. Catal Commn 4(5):223–228
16. Zimowska M, Michalik-Zym A, Janik R, Machej T, Gurgul J, Socha RP, Podobiński J, Serwicka EM (2007) Catalytic combustion of toluene over mixed Cu–Mn oxides. Catal Today 119:321
17. López EF, Escribano VS, Resini C, Gallardo-Amores JM, Busca G (2001) A study of coprecipitated Mn–Zr oxides and their behaviour as oxidation catalysts. Appl Catal B 29:251
18. Khetre SM, Jadhav HV, Bangale SV, Jagdale PN, Bamane SR (2011) Use of mixed metal oxide as a catalyst in the decomposition of hydrogen peroxide. Ind J Chem 2(2):232–259
19. Shivankar VS, Thakkar NV (2006) Chiral mixed ligand Co (II) and Ni (II) complexes: synthesis and biological activity. Ind J Chem 46A:382–387
20. Wood A (2004) Life after ACC: little change for most firms’ EH&S efforts. Chem Week 166:27
21. Afmin B, Roberts MW (1992) Surface structure and the instability of the formate overlayer at a Pb(110) surface. Catal Lett 13(3):277–282
22. Kga Y, Oho Y, Tsukamoto K, Nakajima T (1990) Relationships between the gas permeabilities and the microstructures of plasma sprayed oxide layers. Solid State Ion 40/41:1000
23. Khetre SM, Jadhav HV, Bangale SV, Jagdale PN, Bamane SR (2011) Synthesis, characterization and hydrophilic properties of nanocrystalline ZnCo2O4 oxide by combustion route. Der Chemica Sinica 2(4):303–311
24. Cullity BD (1978) Publishing Cos, 2nd edn. Addison-Wesley, Reading
25. Kroger FA (1964) Chemistry of imperfect crystals. North-Holland, Amsterdam
26. Rouquerol F, Rouquerol J, Sing K (1999) Adsorption by powders and porous solids: principles, methodology and applications. Academic Press, San Diego
27. Ibrahim SM, Badawy AA, El-Shobaky GA, Mohamed HA (2014) Structural, surface and catalytic properties of pure and ZrO2-doped nanosized cobalt–manganese mixed oxides. Can J Chem Eng 92:676–684
28. El-Shobaky GA, El-Shobaky HG, Badawy AA, Fahmy YM (2011) Physicochemical, surface and catalytic properties of nanosized copper and manganese oxides supported on cordierite. Appl Catal A: Gen 409–410:234
29. El-Shobaky GA, Hassan HMA, Yehia NS, Badawy AA (2010) Effect of CeO2-doping on surface and catalytic properties of CuO–ZnO system. J Non-Cryst Solids 356:32–38
30. El All SA, El-Shobaky GA (2009) Structural and electrical properties of γ-irradiated TiO2/Al2O3 composite prepared by sol–gel method. J Alloys Compd 479:91–96
31. El-Shobaky GA, Yehia NS, Hassan HMA, Badawy AA (2009) Catalytic oxidation of CO by O2 over nanosized CuO–ZnO system prepared under various conditions. Can J Chem Eng 87:792–800
32. El-Shobaky GA, Radwan NRE, El-Shall MS, Turky AM, Hassan HMA (2009) Physicochemical, surface and catalytic properties of nanocrystalline CuO–NiO system as being influenced by doping with La2O3. Colloids Surf A: Physicochem Eng Asp 345:147–154
33. El-Shobaky GA, Yehia NS, El-Hendawy AA, Abo-Elenin RMM, Badawy AA (2009) Effects of preparation conditions on surface and catalytic properties of copper and zinc mixed oxides system. Open Catal J 2:45–53
34. Fagal GA, Badawy AA, Hassan NA, El-Shobaky GA (2012) Effect of La2O3-treatment on textural and solid–solid interactions in ferric/cobaltic oxides system. J Solid State Chem 194:162–167
35. Radwan NRE, Fagal GA, El-Shobaky GA (2001) Effects of CeO2-doping on surface and catalytic properties of Cu4Al2O7 solids. Colloids Surf A 178:277
36. El-Shobaky GA, Fagal GA, Mokhtar M (1997) Effect of ZnO on surface and catalytic properties of CuOAl2O3 system. Appl Catal A: Gen 155:167