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PEROVSKITE-TYPE $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ AS CATALYSTS: SYNTHESIS AND CHARACTERIZATION

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The main objective of this work was to study the effect of Ce doping on the structure, surface and absorption properties of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$. In this work, Cerium doped lanthanum manganese perovskites $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ were prepared by the sol-gel method and characterized by different methods. Moreover, diffraction patterns also contain extra peaks which are attributed as CeO_2 impurity peaks. Structural studies show that cerium addition up to 0.4 mol has no effect on the phase formation. Crystallite sizes are in the range of 14–27 nm.

Keywords: perovskite, crystal structure, specific surface area.

Introduction

Perovskite type oxides with general formula ABO_3 may potentially replace noble metal catalysts due to their high activity, thermal stability and low costs. The catalytic properties of ABO_3 basically depends on the nature of A and B ions. Noble metals as palladium and platinum are well known and highly active catalysts for the full oxidation of carbon mo-

noxide, methane, and olefins. Compared with noble metals, base metal catalysts show a lower but still sufficient activity as oxidation catalysts, their advantage being the lower costs [1–2]. Perovskite form is an interesting category of mixed oxides that have been studied widely in view of their activity in full oxidation, their hydrothermal stability and favorable costs. Therefore, these materials have received increased attention in the last decades [3–5]. The main objective of this work was to study the effect of Ce doping on the structure, surface and absorption properties of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$. In this work, Ce doped perovskite type oxides ($\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$), with x ranging from 0 to 0.4, were synthesized by sol-gel method. The prepared powder samples were characterized by XRD, EDS, BET and FT-IR methods.

Experimental

Synthesis of sol –gel method. $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0, 0.2, 0.4$) perovskites were prepared by the solgel method [6]. Precursors $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Roth, 99.995%), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.95%), $\text{Mn}(\text{NO}_3)_2 \cdot x \text{H}_2\text{O}$ (Roth, 99.995%) in appropriate quantities were dissolved in distilled water. Citric acid was added into the mixture in 10 wt% excess over the stoichiometric quantity to assure the complexation of metal ions. Water was removed at 80°C until a viscous gel was formed. The gel was dried in a vacuum oven set at 100°C [7] The precursor was then milled and calcined in air at 750°C for 5h to obtain the perovskite powders.

Characterization Measurement. Structural parameters of perovskites were determined by Maxima_X, XRD-7000 equipment with CuK_α radiation (0.15418nm) at room temperature. XRD measurement data were fitted by Rietveld analysis of the diffraction profiles, using the FullProf program. The specific surface areas were obtained by N_2 -physorption, evaluated using the BET equation on ASAP 2020. The formation of the samples was confirmed by an Oxford Instruments on Energy Dispersive X-ray spectrometry (EDS). The obtained perovskite oxides characterized by Fourier Transform Infrared Spectroscopy (FT-IR) using Shimadzu IR Prestige-21 equipment, in region of $400\text{--}4000 \text{ cm}^{-1}$ by KBr pellets.

Results and discussion

The XRD patterns of the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ samples of this study, calcined 5h at 1023K are shown in Fig.1. The XRD patterns of the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0, 0.2, 0.4$) samples are shown in Fig. 1. According to XRD patterns, all samples are having rhombohedral R-3c crystalline

structure with primitive lattice. In the XRD patterns of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0.2, 0.4$) samples, the sharp peaks at 28.55° , 56.4° corresponding to

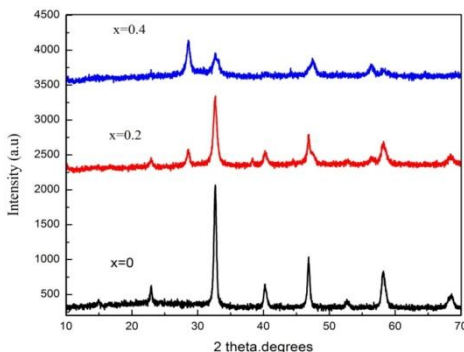


Fig. 1. XRD patterns of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0, 0.2, 0.4$) samples calcined 5h at 1023K

CeO_2 coexists in addition to the perovskite phase [7]. This means that all Ce is completely substituted into LaMnO_3 crystal structure. The intensity of CeO_2 peak increased with Ce doping content increases. The result from calculation of crystal structure was performed by FULLPROF using Rietveld method was shown in Table 1.

Table 1. XRD and BET analysis results of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0, 0.2, 0.4$) perovskite samples. Lattice parameters enlarged due to lattice relaxation and the crystallite size decreased with the increase of doping concentration

Samples	Lattice parameter (Å)	Crystallite size (nm)	SSA (m^2g^{-1})
LaMnO_3	$a=b=5.5007,$ $c=13.3638$	22.69	19.28
$\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$	$a=b= 5.5675,$ $c=13.3433$	14.81	27.26
$\text{La}_{0.6}\text{Ce}_{0.4}\text{MnO}_3$	$a=b=5.5690, c=13.3456$	27.91	20.32

Among the samples calcined at 1023K, only those of compositions LaMnO_3 formed a well crystallized perovskite phase, the patterns showing no other peaks. Also it is observed that cerium is not totally incorporated in the perovskite lattice. Beyond $x=0.2$ a separate CeO_2 phase is

formed. The crystallite size of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0, 0.2$) samples was found to be in the range of 22.69 to 14.81 nm, which it decreases with increasing Ce content. The specific surface areas (SSA) of samples were relatively low, about 19.28–27.26 m^2g^{-1} due to calcinations of perovskites. The specific areas of the catalyst series demonstrate that the specific BET surface area increases quite substantially for a higher degree of substitution x of La for Ce, with a maximum at $x=0.2$. Calcination at high temperature is necessary to obtain the perovskite-type oxide catalyst, but such treatment often results in a dramatic decrease in the specific surface area [8]. However, the enhancement was not linear with the substitution and SSA was highest for $x=0.2$. The obtained lattice parameter, crystallite size from diffraction data and the specific surface area from BET analysis were summarized in Table 1.

Table 2. Energy Dispersive Spectroscopy elemental analysis of samples

Element	LaMnO_3		$\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0.2$)	
	N (wt%)	M (wt%)	N (wt%)	M (wt%)
La	57.42	57.02	45.89	50.05
Mn	22.73	19.95	22.71	22.82
O	19.84	23.02	19.82	21.76
Ce			11.57	5.36
N — nominal, M — measured				

Table 2. The EDS pattern of LaMnO_3 shows only three elements La, Mn and O while the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ pattern shows four elements: La, Ce, Mn and O and. The EDS analysis show the composition is almost the same (within experimental error) as the nominal composition of the samples.

FT-IR spectroscopic results support the above structure analysis by XRD. As shown in Fig. 2, LaMnO_3 perovskite had vibration band around 600 cm^{-1} , which could be attributed to the characteristic absorption band of the stretching vibration of Mn-O band in MnO_6 octahedron. All the $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ catalysts also had vibration band around 600 cm^{-1} indicating that formation of the perovskite-type structures. This peak is found to be shifted towards higher frequency with increases Ce doping concentration. Moreover, the intensity of this vibration band increases for $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$, suggesting that the vibration bands become strong and up-shifting.

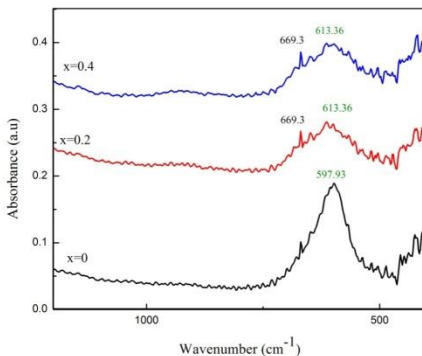


Fig. 2. FT-IR spectra of pure and Ce doped LaMnO_3 samples

The IR spectrum of LaMnO_3 presents an intense band around 600 cm^{-1} that could be assigned to vibration of Mn-O bond in octahedral coordination and a band from 418.02 cm^{-1} assigned to vibration of O-Mn-O bond in rhombohedral coordination. In the IR spectra of doped samples appears a shoulder at around 670 cm^{-1} may be due to Mn^{4+} ions formation. The appearance of this band at higher frequencies could be explained by the increasing of constant force of Mn-O as result of increasing of manganese ions electrical charge [9]. It can be noticed also the splitting of characteristic vibration of $\nu_{(\text{La-O})}$ that might be assigned to the presence of dopant ions.

Conclusion

A series of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ samples were synthesized at high temperature by sol-gel method. The effect of Ce-substitution for LaMnO_3 perovskite was investigated by EDS, XRD, BET and FTIR. XRD and FT-IR results show the phase segregation does not happen by the addition of cerium. Among all samples, $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ exhibited the best properties with the higher specific surface area, smaller crystallite size and more symmetrical structures which correspond for the enhancement of catalytic activity.

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ПЕРОВСКИТ La_{1-x}Ce_xMnO₃ КАТАЛИЗАТОРЫ:
СИНТЕЗ И ХАРАКТЕРИСТИКА

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Основная цель данной работы заключалась в изучении влияния Се легирования на структуру , поверхностных и абсорбционных свойств La₁₋

$x\text{Ce}_x\text{MnO}_3$. В этой работе, катализаторы из церий лантаната, легированного марганцем перовскитов $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0, 0,2, 0,4$) были получены золь-гель способом и исследованы методами рентгеновской дифракции (XRD), энергодисперсионной рентген спектроскопии (EDS), Фурье ИК- спектроскопии (FT-IR)и анализами площадь поверхности BET.

Анализ (РД)показал, что синтезированные образцы имеют ромбоэдрическую структуру. Кроме того, дифракционные картины также содержат дополнительные пики, приписываемые в качестве примесных пиков CeO_2 . Структурные исследования показывают, что церий до 0.4 моль не оказывает никакого влияния на формирование фазы. Размеры кристаллитов находятся в диапазоне от 14–27 нм.

Ключевые слова: перовскит, кристаллическая структура, удельная поверхность.