

Synthesis, characterization and catalytic activity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3\pm\delta}$ in NO+CO reaction

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INTRODUCTION

In the process of lowering the cost of Pt-based catalysts and testing new catalytic materials on enhancing the typical NO reduction, perovskite materials are used since the early 1990. They proved to enhance the reduction of NO in the presence of CO and it is found that the catalyst performance is strongly depended on the preparation method and morphology of the materials [1-5]. Substantial research on catalytic behaviour has been done on perovskites of the general type LaMO_3 (M=Ni, Fe, Mn, Co, Cu) for deNO_x reactions [6-9]. La-Sr-Mn-Fe perovskites are promising as they have been tested for hydrogen peroxide decomposition exhibiting excellent catalytic stability for H_2O_2 decomposition [11]. In this study, we report the wet chemistry synthesis of nanostructured perovskites of the composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3\pm\delta}$ and we also examine the effect of Mn content at their catalytic activity on the reaction of NO+CO.

EXPERIMENTAL

A series of double substituted perovskites of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_y\text{Fe}_{1-y}\text{O}_{3\pm\delta}$ (y=0, 0.2, 0.5, 0.8, 1) compositions were synthesized using a modified citrate route. Nitrate salts of cations (Me) were mixed with citric acid (CA) and ethylene glycol (EG) at molar ratios Me:CA=1:1.2 and CA:EG 1:2. The precursors were dried at 120 °C for 3h until a yellowish gel was formed. A step of firing at 300 °C for 4h was followed by a final calcination step at 1050 °C for 10h and the final material was obtained. The crystallinity of the product was checked on a SIEMENS D5000 Diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and 2θ range from 10° to 100° with scan step of 0.01°. Results for Reitveld analysis and optical visualization were processed with FullProf and Crystal Impact Diamond software respectively. TGA measurements were performed by in air environment from 25°C to 1100°C with a 10K min⁻¹ rate. FTIR on 13mm KBr pellets from 2000-800cm⁻¹ study was carried out in a Jasco 4200 model in order to investigate the mechanism of the modified citrate route. Particle size measurements with a Malvern Mastersizer 2000 followed in order to retrieve information about the average particle size. The final materials were observed by SEM (Jeol6380LV) and their density was measured by Archimedes method.

The catalytic properties of LSMnF series were tested on a probe reaction of NO+CO in order to investigate the doping effect of Mn in the B-site. A catalytic bed of perovskite powder was placed in a plug flow quartz reactor. Prior to reaction the catalysts were pre-treated in 2 vol % O₂/He with 100ml min⁻¹ flow at 600°C for 1h. After cooling down to 100°C the feed gas switched to 1.00% NO/1.00% CO with He balance providing a GHSV of 60,000 h⁻¹ with total stream flow rate of 78ml min⁻¹. The temperature was increased from 100°C to 600°C at a rate of 2K min⁻¹ and the effluent gas was analysed by a properly setup of a BRUKER GC-436 gas chromatograph with TCD detector.

RESULTS

Thermogravimetric (TG) and FTIR studies provided significant information of the mechanism of synthesis of the catalysts. In all compounds the weight loss at 250 and ~400°C is attributed to the two-step dissociation of polymeric network whilst a weight loss at 700°C is attributed to the loss of carbonates (Figure 1). FTIR confirms the mono- and bi-metallic complexes of CA at (1640–1520 cm⁻¹) due to the two transition elements of Mn and Fe (Figure 2).

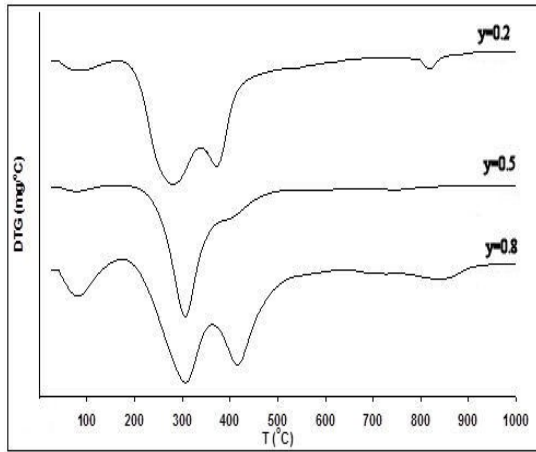


Figure 1. TGA of compounds with $y=0.2, 0.5, 0.8$

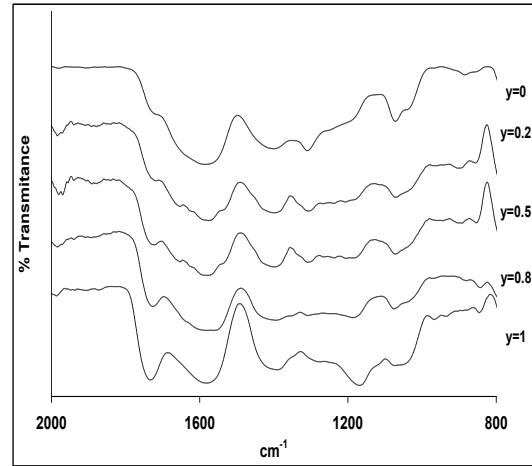


Figure 2. FTIR of LSMnF series

In figure 3 the XRD Reitveld analysis results are shown, with a typical rhombohedral picture of compound with $y=0.5$ as resulted from Crystal Impact Diamond software. A typical SEM picture and mean particle size are depicted at figure 4. All compounds provided an average particle size of 50nm. In Table 1 it is obvious that compounds with $y=1, 0.8, 0.5$ were crystallized at orthorhombic system with Pbnm (No 62) space group whilst compounds with $y=0.2, 0$ (Mn-rich) provided rhombohedral structure at R3c (No 167) space group.

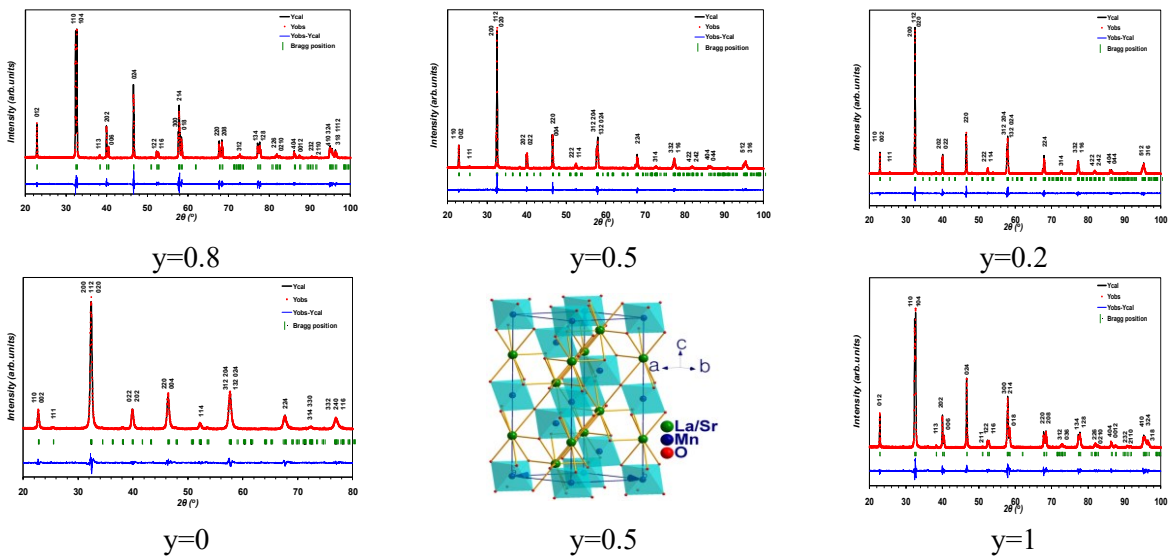


Figure 3. Reitveld analysis results

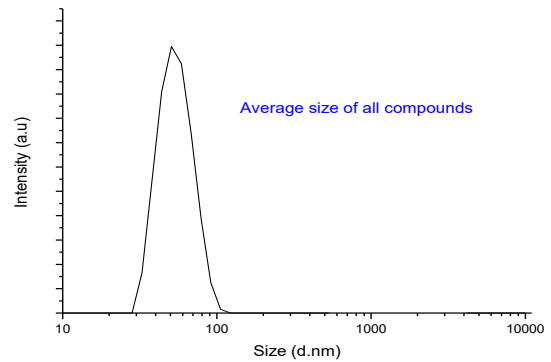
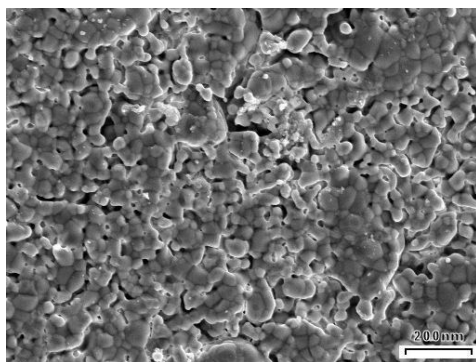


Figure 4. Typical SEM picture and particle size of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$

Table 1. Structural and physical properties of compounds

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$	y=1	y=0.8	y=0.5	y=0.2	y=0
Density ($\text{g}\cdot\text{cm}^{-3}$)	5.99	5.96	6.00	6.02	6.01
* S_p (m^2g^{-1})	20.03	20.13	20	19.93	19.96
Crystal System	Orthorhombic			Rhombohedral	
Space group	Pbnm (N° 62)			R3c (N° 167)	
Z	4	4	4	6	6
a (Å)	5.56	5.54	5.54	5.53	5.51
b (Å)	5.53	5.51	5.50	5.53	5.51965
c (Å)	7.82	7.80	7.79	13.37	13.3642
V/Z(Å ³)	60.25	59.66	59.43	59.14	58.769

*calculated

Results from Table 1 show that structural dimensions and molar volume of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_y\text{Fe}_{1-y}\text{O}_3$ series is gradually reduced with the increase of Mn doping. The ionic radii Mn^{4+} is 0,53Å and Fe^{4+} is 0.585Å, whilst radii of trivalent ions (on high spin state due to high temperature) are the same (0,645Å). Thus electronegativity is achieved with Mn^{4+} indicating that Mn is more easily oxidized than Fe. This fact is in accordance with literature results from Mössbauer studies [12] where the existence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ pairs rather than Fe^{5+} is verified in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_y\text{Fe}_{1-y}\text{O}_3$ compounds.

In Table 2 the results are depicting a better catalytic performance of the two $\text{La}_{0.8}\text{Sr}_{0.2}\text{MO}_3$ (M=Fe,Mn) compounds in comparison with other researchers [2,3,7] reporting the catalytic activity with different preparation methods as they appear active from 260°C

Table 2. Catalytic test results

Compound	T (°C)	X _{NO} Conversion factor (%)	CO ₂ yield (%)
La_{0.8}Sr_{0.2}FeO₃			
	260	11,35	19,51
	300	17,56	60,92
	400	39,04	80,91
	500	66,18	89,90
La_{0.8}Sr_{0.2}Mn_{0.2}Fe_{0.8}O₃			
	260	15,01	65,20
	300	22,10	88,51
	400	46,48	92,02
	500	70,95	93,00
La_{0.8}Sr_{0.2}Mn_{0.5}Fe_{0.5}O₃			
	260	27,46	17,48
	300	38,96	42,65
	400	56,32	92,32
	500	83,73	92,95
La_{0.8}Sr_{0.2}Mn_{0.8}Fe_{0.2}O₃			
	260	30,29	7,17
	300	40,70	15,08
	400	63,77	61,08
	500	86,46	93,05
La_{0.8}Sr_{0.2}MnO₃			
	260	37,26	35,76
	300	41,76	59,51
	400	91,99	74,16
	500	93,84	82,54

The correlation between the doping amount and NO conversion factor is obvious at Figure 5.

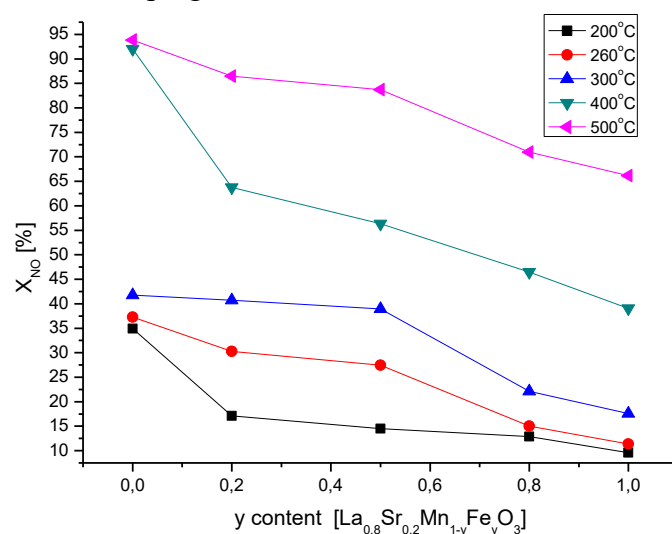


Figure 5. Correlation of y content and NO conversion factor at specific temperatures

The results of Table 2 and Figure 5 are reporting that Mn-rich compounds ($y < 0.5$) enhance the stoichiometric reaction path of NO-CO reaction to lower temperatures than reported in literature [2, 5, 10] whilst Fe-rich compound ($y > 0.5$) shows slightly better catalytic activity with similar structures [2, 4, 5, 6, 7] attributed firstly to their higher SSA.

CONCLUSIONS

Perovskite materials prepared with this modified nitrate method provided materials of large SSA. The effect of doping the perovskite lattice of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ with Mn lead to materials with high catalytic activity on the conversion of NO-CO reaction compared to other preparation methods. Mn-rich compounds ($y < 0.5$) have more positive effect on the stoichiometric reaction path of NO-CO reaction compared with the compounds with ($y > 0.5$) as they enhance it at lower temperatures. Further studies are pending in order to investigate the kinetics of the above reaction.

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