THE PREPARETION AND CATALYTIC PROPERTIES OF $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4) PEROVSKITES in OXIDATION OF m–XYLEN

TỔNG HỢP VÀ NGHIÊN CỨU HOẠT TÍNH XÚC TÁC CỦA CÁC PEROVSKITE $LA_{1-X}SR_XMNO_3$ (X = 0; 0.2; 0.4) TRONG PHẢN ỨNG OXY HÓA M-XYLEN

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ABSTRACT

In this report, $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4) perovskite - type complex oxides have been done by sol-gel citrate method.The formation process of $La_{1-x}Sr_xMnO_3$ crystalline perovskites and characterization of these solids were examined by various physical, physico – chemical methods such as the Powder X-ray diffraction (XRD) and the Energy dispersive X-ray spectrocopy (EDXS). Results show that perovskite phases can be perfectly crystallized at the temperature of 600^oC and they have very small average particle size (14-20 nm). These perovskites exhibit a good catalytic activity in total oxidation of m-xylene at the relatively low temperature of reaction: the oxidative conversion of m-xylene over perovskites $La_{1-x}Sr_xMnO_3$ catalysts reaches a maximum (100%) at 300^oC temperature and be stable at this temperature . The results also indicate that partially substituting of La^{3+} with Sr^{2+} has not been effected exactly on the oxidative conversion of m- xylene.

TÓM TẮT

Bài báo trình bày tổng hợp các perovskite $La_{1-x}Sr_xMnO_3$ (x = 0; 0,2; 0,4) bằng phương pháp sol – gel citrat.Trên giản đồ nhiễu xạ tia X của các mẫu sau khi nung ở 600^oC cho các pic đặc trưng của pha perovskite rất cao và nhọn, chứng tỏ pha perovskite kết tinh tốt ở 600^oC và cho kích thước hạt nhỏ. Tính kích thước hạt trung bình theo công thức Scherrer dựa trên giản đồ nhiễu xạ tia X được kích thước hạt tinh thể trung bình từ 14 – 20 nm. Kết quả phân tích EDXS cho thấy các mẫu chỉ gồm có các nguyên tố La, Sr và Mn, tương ứng với thành phần các nguyên tố đưa vào mẫu. Hoạt tính xúc tác được nghiên cứu ở phản ứng oxy hoá m-xylen, kết quả: độ chuyển hóa m-xylen trên tất cả các perovskite đều đạt giá trị cao nhất (~ 100%) ở nhiệt độ thấp (300^oC) và độ bền xúc tác cao ở nhiệt độ này kể cả khi có mặt của hơi nước; sự thay thế Sr theo giá trị của x trong điều kiện nghiên cứu chưa gây ra ảnh hưởng rõ đến hoạt tính xúc tác của perovskite trong phản ứng oxy hóa m-xylen.

I. INTRODUCTION

Perovskite–type oxides (ABO_3) containing rare earth ions and transition metals are of interest for catalytic oxidation and reduction reactions associated with automotive exhaust emission control. They are known to exhibit a good catalytic activity in the total oxidation reaction of carbon monoxide or hydrocarbon and removal of nitrogen oxides [1,2,3]. By partially substitution of A and B ions of the perovskite with others, a wide variety of mixed oxides $A_{1-x}A'_xB_{1-y}B'_yO_3$ can be obtained, allowing the systematic modification of the catalytic properties [4,5].

In this present work, $La_{1-x}Sr_xMnO_3$ (with x = 0; 0.2; 0.4) perovskites complex oxides were prepared by sol-gel citrate method, perovskite phases can be perfectly crystallized even at the temperature of 600^{o}C and they have a good catalytic activity in total oxidation of m-xylene at low temperature of reaction.

II. EXPERIMENT

2.1 Catalysts preparation

The chemicals were used in this study, which are all analytical grade, consist of $La(NO_3)_3$, $Sr(NO_3)_2$, $Mn(NO_3)_2$, $C_6H_8O_7$ and NH_3 solution.

Solutions of $La(NO_3)_3$, $Sr(NO_3)_2$, $Mn(NO_3)_2$ were mixed with La^{3+}:Sr^{2+}:Mn^{2+} ((1-x) : x :1, respectively) molar ratio, then citric acid ($C_6H_8O_7$) solution was added in order to reach the citric acid : ΣM^{n+} molar ratio of 1,6 ; The pH of the solution was governed by NH_3 solution until the pH of mixture being 6,5-7 [6] at the same time the resulting mixture was

stirred and heated at 80°C until the pink–gel formed. After drying at 80°C in air for a day, the gel was converted into xerogel.Then xerogel was calcined at 500°C for 3 hours under air flowing by the rate of 33ml/min. Finally, the sample was calcined at 600°C in air enviroment for 4 hours, the perovskites powders were obtained.

2.2 Characterization of catalysts

The formation of perovskites phases were confirmed by X-ray powder diffractometry (XRD) D.5005.SIMENS, the samples were scanned over the 2θ range from 10° to 80° using Cu K_α radiation (λ =1.5406 Å). The average crystalline particle size (D) of was calculated from the XRD patterns according to Scherrer formula:

$$D = K\lambda / b\cos\theta \qquad (1)$$

where D is the average particle size, K is the Scherrer constant related to the shape and index (hkl) of crystals, λ is the wavelength (λ =0.15406 nm) of the X-rays, θ is Bragg angle and b is the additional broadening (in radians).

The chemical composition of material was determined by a Japan JEOL JSM -5410 SEM/EDS scanning electron microscopy.

The catalytic activity of complex oxides was examined in m-xylene total oxidation under codition below as:

- Amount of catalyst: 0.1 g; [m-xylene] = 200ppm

- The gas hourly space velocity (GHSV): 2857 h^{-1}

The inlet gas mixtures containing 200ppm m-xylens in synthetic air (air enviroment) were fed in the reactor system with blowing by the rate of 33 ml/min.

The oxidative conversion (α) of m-xylen are defined as:

$$\alpha\ \% = (S^o - S^1).100 / S^o$$

where S^o and S^1 are the inlet and outlet concentrations of m-xylene.

III- RESULTs AND DISCUSSION:

3.1 X-ray diffraction analysis and calculating the average particle size

Fig.1 shows the X-ray diffraction results of $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4) calcined at 600°C for 4 hours. It can be seen from Fig.1 that perovskite phases had been perfectly crystallized at the temperature of 600°C (the diffractionlines were high and sharp) and the sample with x = 0.2 possessed the best crystallinity; sample of x = 0 was crystallized worse.

Following fomula (1), the average crystalline particle size was calculated and listed in Table 1:

Table 1. The average crystalline particle size of $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4).

Sample	D (nm)
$LaMnO_3$ (x = 0)	13.97
$La_{0.8}Sr_{0.2}MnO_3$ (x =0.2)	16.46
$La_{0.6}Sr_{0.4}MnO_3$ (x = 0.4)	19.68

The average particle size of all samples is very small (about 14-20nm) and growning up with increasing of value of x.

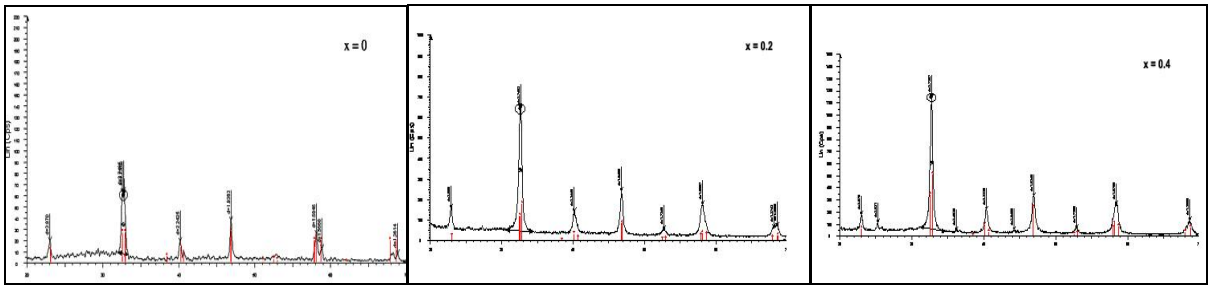

Fig.1 The X-ray diffraction patterns of $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4) calcined at 600°C for 4 hours.

3.2 Energy dispersive X-ray spectrocopy - DXS

The energy dispersive X-ray patterns of $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4) samples calcined at 600°C for 4 hours (Fig.2) show that three samples only consist of La, Sr, Mn elements and they have approxiametelly the proportion of initial prepared mixtures (Table 2):

Table 2- The composition of prepared perovskites $La_{1-x}Sr_xMnO_3$.

Sample	Atomic % EDXS
$LaMnO_3$ (x = 0)	La 52.41 %, Mn 47.59%
$La_{0.8}Sr_{0.2}MnO_3$ (x = 0.2)	La 41.79%, Sr 10.08% Mn 48.13 %
$La_{0.6}Sr_{0.4}MnO_3$ (x = 0.4)	La 30,18%, Sr 20,25% Mn 48,97%

3.3 The catalytic activity for the hydrocarbon oxidation of perovskites $La_{1-x}Sr_xMnO_3$ (x=0; 0.2; 0.4):

a. Effects of the temperature on oxidative conversion of m-xylene:

Effects of the temperature on oxidative conversion of m- xylene total oxidation reaction over perovskites $La_{1-x}Sr_xMnO_3$ **(x =** 0; 0.2; 0.4) catalysts are shown in Fig.3.

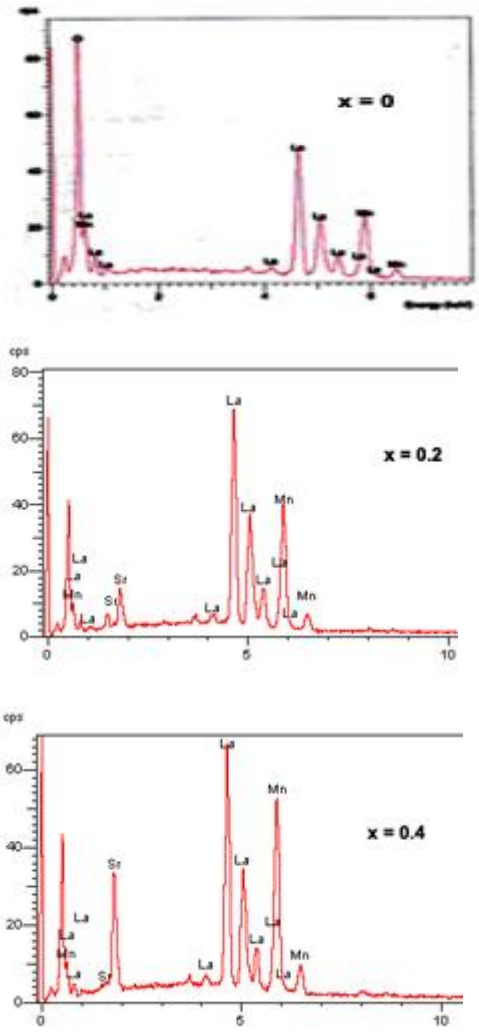

Fig.2 The Energy dispersive X-ray patterns of $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2; 0.4)

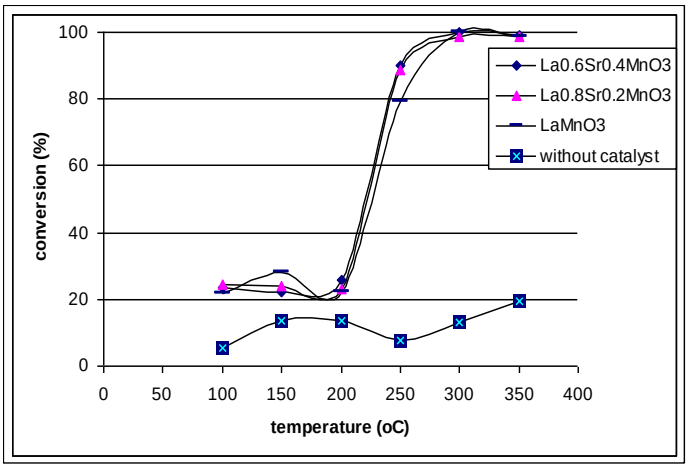

Fig. 3 Catalytic activities of m-xylene oxidation on $La_{1-x}Sr_xMnO_3$

When the reaction temperature increases that the reaction is promoted, so the oxidative conversion of m- xylene increases.

In case of the reaction without of catalyst, the oxidative conversion of m- xylene reaches low oxidative conversion (about 13%) in the temperature range from 100°C to 300°C and only reaches about 19% oxidative conversion at 350°C temperature.

The presence of $La_{1-x}Sr_xMnO_3$ (with x = 0; 0.2; 0.4) catalysts that makes the oxidative conversion of m- xylene increases exactly and reaches a maximal oxidative conversion (nearly 100%) at 300°C temperature of all samples. Special, their activity is poor at 200°C (about 22 – 26%) but they recover strongly at 250°C (about 79-90%) of all samples.

So, the $La_{1-x}Sr_xMnO_3$ (with x = 0; 0.2; 0.4) catalysts perovskite – type materials are very active in total oxidation of m- xylene reaction.

b. Effects of Sr^{2+} content on the catalytic activity of $La_{1-x}Sr_xMnO_3$:

In this study, the partial substitution of La^{3+} with Sr^{2+} in $LaMnO_3$ perovskite have been prepared. Catalytic activities of $La_{1-x}Sr_xMnO_3$ (x = 0; 0.2 and 0.4) catalysts were measured to assess the effect of the Sr^{2+} cation content on the activity in the m-xylene oxidation in the temperature range from 100°C to 350°C. Obtained results were shown in Fig.3. It can be noted that partially substituting of La^{3+} with Sr^{2+} has not been effected exactly on the oxidative conversion of m- xylene and it can be interestingly noted that althrough the sample $LaMnO_3$ (of x = 0) was crystallized the worst, but it possesses catalytic activity as other samples.

c. Effects of time on stream on the catalytic activity of $La_{1-x}Sr_xMnO_3$:

Figure 4 shows the resulting effects of time on stream on the oxidation of m-xylene over $La_{1-x}Sr_xMnO_3$.

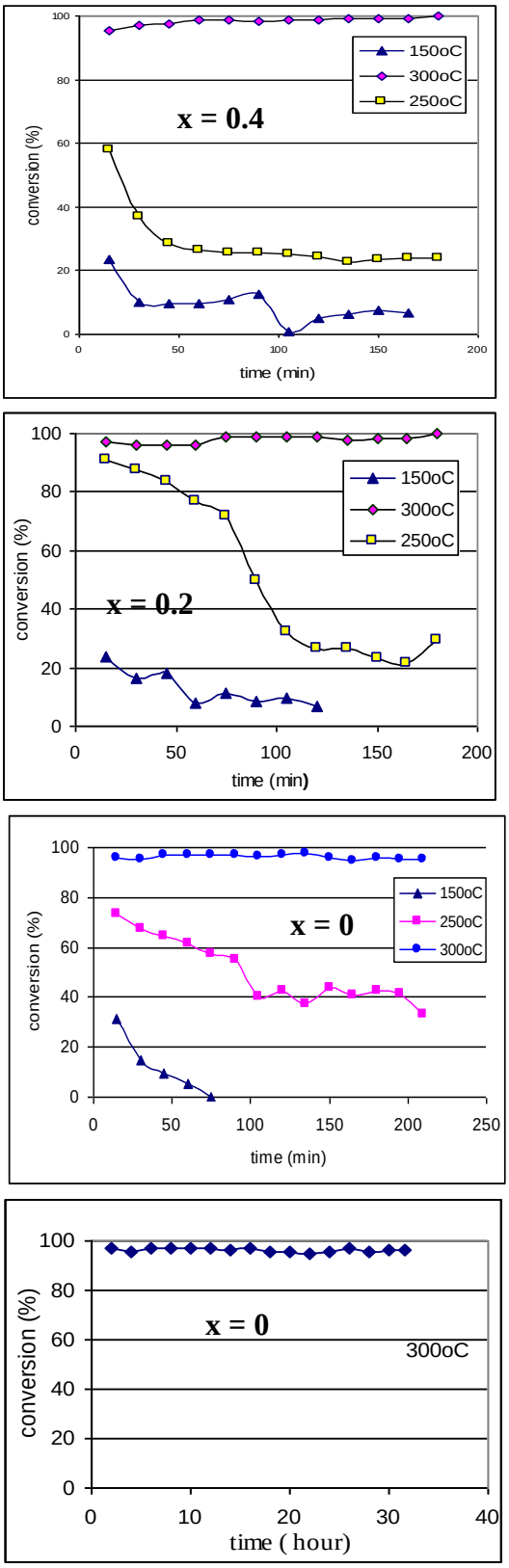

Fig.4 Effects of time on stream on the catalytic activity of $La_{1-x}Sr_xMnO_3$

The figure oxidation indicate at 150^{o}C and 250^{o}C temperatures, the conversion of m-xylene decreases quickly after the first 15 minutes of reaction of all samples.

When the reaction temperature increases to 300^{o}C, the oxidative conversion of m-xylene reaches a maximal oxidative conversion (nearly 100%) and remained actively for during 180 minutes of continuous reaction of all samples.

In oder to examine of the catalytic endurance, we increase the retention time on stream for during 33 hours over the sample $LaMnO_3$ of x = 0. The result reveals that the oxidative conversion of m- xylene still allways reaches a maximal oxidative conversion (nearly 100%) at 300^{o}C temperature and very be stable exactly for during 33 hours of continuous reaction. This means, the perovskite of $LaMnO_3$ is a good catalysts for reaction of m-xylene.

IV. CONCLUSIONS

1- Prepared perovskites of $La_{1-x}Sr_xMnO_3$ **(x =** 0; 0.2 ;0.4) by sol-gel citrate method with single phase, perfectly were crystallized at the relatively low temperature (600^{o}C) compared to other methods and they have small particle size (~14-20 nm).

2- The effects of the reaction temperature, Sr content and of time on stream on the catalytic activity of $La_{1-x}Sr_xMnO_3$ **(x** = 0; 0.2 ;0.4) in total oxidation of m- xylene reaction were investigated. From obtained results, it can be concluded that:

i) The oxidative conversion of m-xylene over perovskites $La_{1-x}Sr_xMnO_3$ catalysts reaches a maximum at 300^{o}C temperature .

ii) The partial substitution of La^{3+} with Sr^{2+} in $LaMnO_3$ perovskite has not been effected exactly on the oxidative conversion of m-xylene.

iii) The $La_{1-x}Sr_xMnO_3$ catalysts are very active and be stable at 300^{o}C temperature in total oxidation of m- xylene reaction.

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