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Catalytic Behavior of Perovskite Nanoperovskites for NO+CO Reduction from Environment

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***Abstract*— In this paper, $LaMn_{0.6}B_{0.4}O_3$ (B= Cu and Fe) perovskite type mixed oxides were prepared by sol-gel method and characterized by X-ray diffraction and scanning electron microscope. Activity of synthesized catalysts were evaluated in catalytic reduction of NO with CO. XRD results show that the studied perovskites were synthesized in single phase perovskite structure. The activity of catalysts improved due to partial substitution of Mn by B cation. T50% of NO over $LaMnO_3$, $LaMn_{0.6}Cu_{0.4}O_3$ and $LaMn_{0.6}Fe_{0.4}O_3$ was 451, 358 and 366 ºC, respectively. $LaMn_{0.6}Cu_{0.4}O_3$ was the optimum catalyst in simultaneous reduction of NO with CO.**

Keywords— ***Perovskite Catalyst, Catalytic reduction, Sol-gel, NOx-CO, Environment***

I. Introduction

The emission of nitrogen oxides (NOx) and carbon monoxide (CO) from engines is an important problem in environmental and public health [1]. NOx and CO play important roles in global warming, acid rain and photochemical smog formation [2]. NO should be selectively converted to N_2 instead of NO_2 or N_2O, that are toxic or greenhouse gases. One of the effective ways to reduce NO and CO is catalytic reduction of NO with CO [3]. Precious metals Pt, Pd, and Rh supported on alumina and ceria have long been considered as the most efficient for the control of exhaust gas [4-5]. Due to the high cost and low stability of pecious metal, considerable efforts have been paid to the utilization of perovskite catalysts [6]. Perovskite mixed oxides with ABO_3 formula have high activity in reduction of exhaust gas emissions. Among various perovskite types with transition metal ions in B site, the mixed oxides containing iron [7], copper [8] and mangenese [9] are considered the most active catalysts in NO reduction with CO.

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In this paper, $LaMn_{0.6}B_{0.4}O_3$ (B= Cu and Fe) perovskite catalysts were synthesized by sol-gel method and their activities were evaluated in catalytic reduction of NO with CO. synthesized perovskites characterized by XRD and SEM.

II. Materials and method

The perovskites in this study have been synthesized using sol-gel method. The following salts were used for perovskites synthesis: $La(NO_3)_3.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Fe(NO_3)_3.9H_2O$, $Mn(NO_3)_2.4H_2O$ and Citric acid monohydrate. Nitrate solutions were prepared by dissolving salts in deionized water. Citric acid as the complexing agent was weighed out in the amount corresponding to the molar ratio of citric acid/total nitrate of 0.525 and was then added to the nitrate solutions. The solution was heated to 80 ºC with stirring until a sticky gel was obtained. The gel was dried at 200 ºC for 2 h and then calcined at 700 ºC for 5 h. The crystal structure of the samples was determined on an X-ray diffractometer (XRD, SIEMENS D500, Germany) with Cu Kα radiation of wavelength 0.15406 nm. The morphology of samples were analyzed using TESCAN (Czech Republic) scanning electron microscopy.

A fixed bed quartz reactor (i.d. = 9 mm) was used to evaluate the catalytic activities of the $LaMn_{0.6}B_{0.4}O_3$ perovskites at atmospheric pressure for the simultaneous reduction of NO and CO. The reactant feedstocks were: 3000 ppm NO + 3000 ppm CO + Ar (balance), total flow rate = 200 mL/min. 200 mg of the samples was used in each run. The inlet and outlet gas concentrations were analyzed online by a gas chromatograph (Shimadzu GC-2010) equipped with a TCD detector and a HP-Molesieve (Agilent, USA) column (l = 30 m, i.d. = 0.53 mm).

III. Results and discussion

The XRD pattern of samples in the range of 20º-80º are shown in Fig. 1. The comparison of pattern of samples with standard charts of $LaMnO_3$ (01-086-1226.CAF), $LaCuO_3$ (01-071-0872.CAF) and $LaFeO_3$ (01-075-0541.CAF) indicates that samples are synthesized in single phase

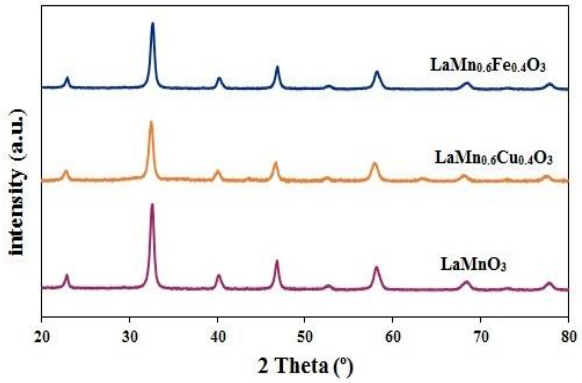

Fig. 1: XRD patterns of $LaMn_{0.6}B_{0.4}O_3$ samples

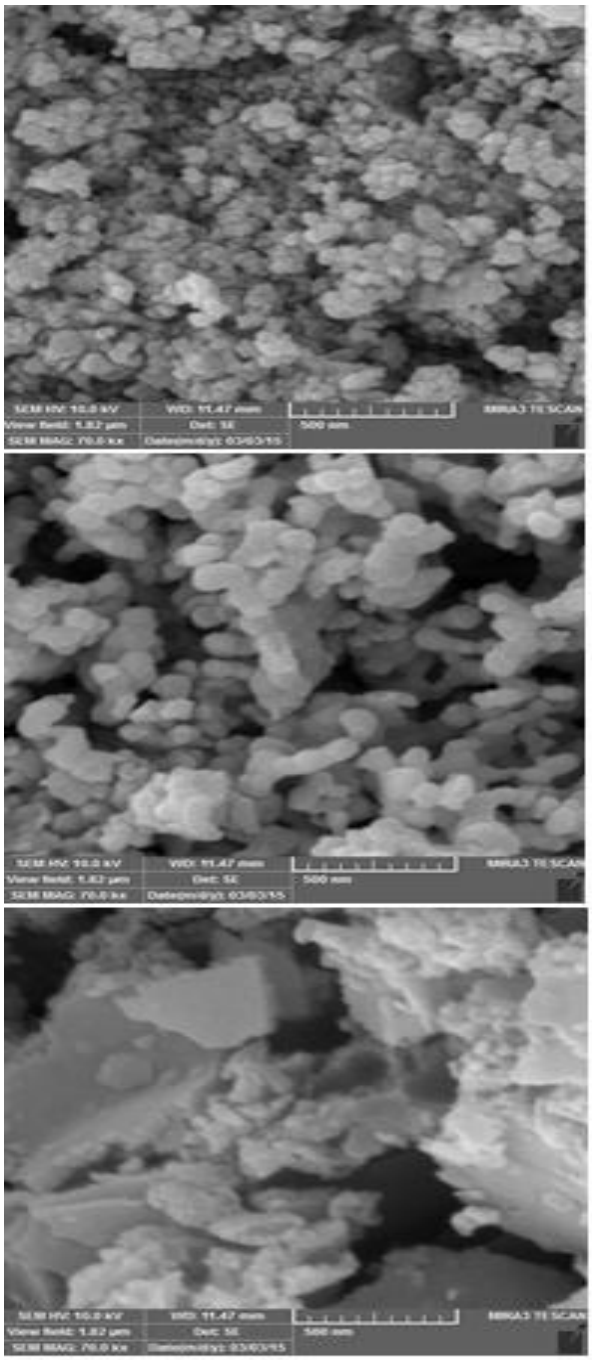

Fig. 2: SEM image of LaMn0.6B0.4O3

perovskite structure. From SEM images shown in Fig. 2, it is observed that sol-gel method has been capable of producing nanosize perovskite crystal close to 100 nm. Morphologies of samples were as irregular shaped grains.

Fig. 3 show the catalytic performance of the samples for simultaneous reduction of NO and CO. Based on results, NO and CO conversion increased with temperature. The T50% value for $LaMnO_3$, $LaMn_{0.6}Cu_{0.4}O_3$ and $LaMn_{0.6}Fe_{0.4}O_3$ were 451, 358, and 366 °C for NO conversion.

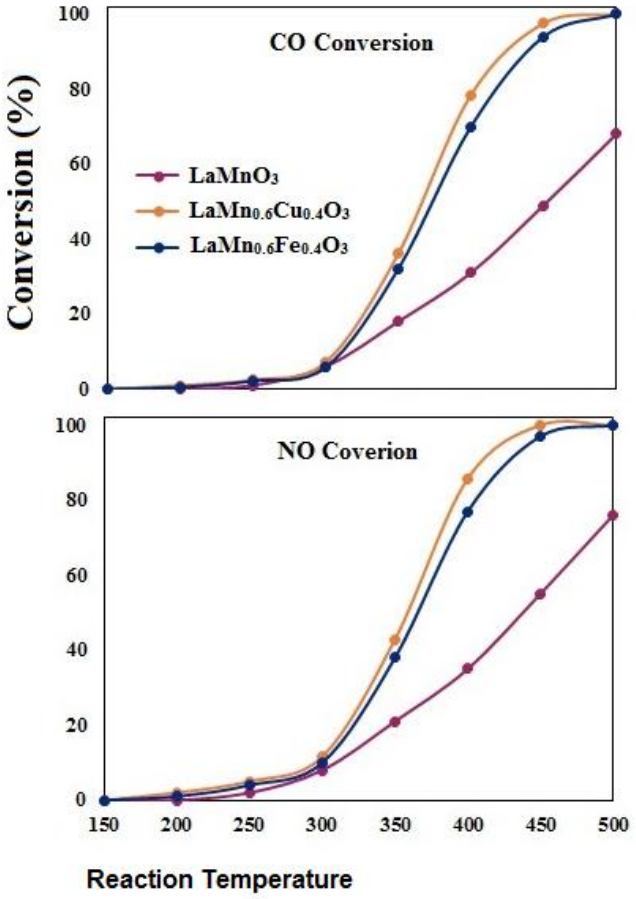

Fig. 3: Temperature profile for NO and CO conversion over LaMn0.6B0.4O3

Substitution of manganese by iron and cooper increased the activity of catalysts. The catalytic activity was in the order of $LaMn_{0.6}Cu_{0.4}O_3$ > $LaMn_{0.6}Fe_{0.4}O_3$ > $LaMnO_3$. So, it is resulted that $LaMn_{0.6}Cu_{0.4}O_3$ is the most active catalyst among the other studied perovskites, and means that copper exhibited the higher synergetic and cooperative behavior with manganese.

Fig. 4 shows the selectivity of N_2 and N_2O over synthesized perovskites. At temperatures higher than about 450 ºC, N_2 and N2O selectivity of catalysts is about unity and zero, respectively. Production of N_2O starts at low temperatures and reaches a maximum about 350 ºC and at higher temperatures its production decreases [10].

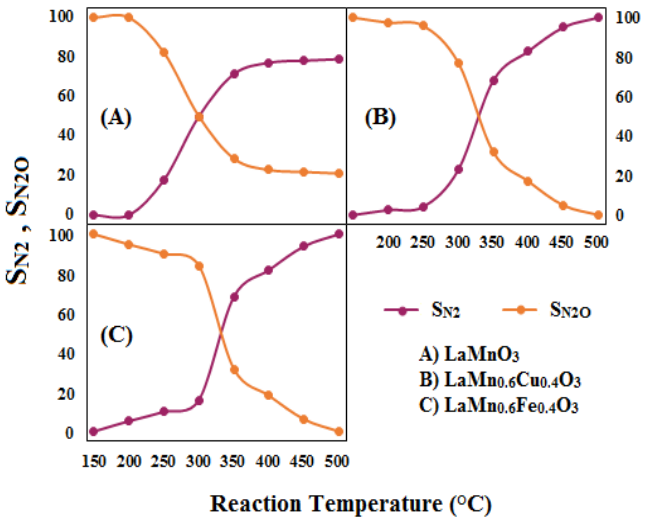

Fig. 4: Temperature profile for N2 and N2O selectivity over LaMn0.6B0.4O3

IV. Conclusions

The catalytic performance of $LaMn_{0.6}B_{0.4}O_3$ (B= Cu and Fe) perovskite catalysts obtained by sol-gel method was evaluated in catalytic reduction of NO with CO. Perovskite samples were characterized by XRD and SEM. XRD results show that single phase perovskite structure are obtained. SEM result shows that size of crystals is closed to 100 nm. Substitution of Mn by Fe and Cu increased the performance of catalysts in simultaneous reduction of NO with CO. $LaMn_{0.6}Cu_{0.4}O_3$ is the most active catalyst among the synthesized perovskites.

V. References

[1] Khristova, M.S., Petrović, S.P., Terlecki-Baričević, A., and Mehandjiev, D.R., "Catalytic reduction of NO by CO over Pd – doped Perovskite-type catalysts", Cent. Eur. J. Chem., 7, 857-863 (2009).

[2] Wang, Y., Zhu, A., Zhang, Y., Au, C.T., Yang, X. and Shi, C., "Catalytic reduction of NO by CO over NiO/CeO_2 catalyst in stoichiometric NO/CO and $NO/CO/O_2$ reaction", Applied Catalysis B: Environmental 81, 141–149 (2008).

[3] Glisenti, A., Pacella, M., Guiotto, M., Natile, M.M. and Canu, P., "Largely Cu-doped $LaCo_{1-x}Cu_xO_3$ perovskites for TWC: Toward newPGM-free catalysts", Applied Catalysis B: Environmental, 180, 94–105 (2016).

[4] Peter, S.D., Garbowski, E., Perrichon, V., and Primet, M., "NO reduction by CO over aluminate-supported perovskites", Catalysis Letters, 70, 27–33 (2000).

[5] Zhang, R., Villanueva, A., Alamdari, H. and Kaliaguine, S., "Reduction of NO by CO over nanoscale $LaCo_{1-x}Cu_xO_3$ and $LaMn_{1-x}Cu_xO_3$ perovskites", Journal of Molecular Catalysis A: Chemical, 258, 22–34 (2006).

[6] Peter, S.D., Garbowski, E., Perrichon, V., and Primet, M., "Activity enhancement of mixed lanthanum-copper-iron-perovskites in the CO+NO reaction", Applied Catalysis A: General, 205, 147–158 (2001).

[7] Leontiou, A.A., Ladavos, A.K. and Pomonis, P.J., "Catalytic NO reduction with CO on $La_{1-x}Sr_x(Fe^{3+}/Fe^{4+})O_{3\pm\delta}$ perovskite-type mixed oxides (x = 0.00, 0.15, 0.30, 0.40, 0.60, 0.70, 0.80, and 0.90) ", Applied Catalysis A: General, 241, 133–141 (2003).

[8] Teraoka, Y., Nii, H., Kagawa, S., Jansson, K. and Nygren, M., "Synthesis and catalytic properties of perovskite-related phases in the La-Sr-Co-Cu-Ru-O system", Journal of Materials Chemistry, 6, 97-102 (1996).

[9] Giannakas, A.E., Ladavos, A.K. and Pomonis, P.J., Preparation, "Characterization and investigation of catalytic activity for NO+CO reaction of $LaMnO_3$ and $LaFeO_3$ perovskites prepared via microemulsion method", Applied Catalysis B: Environmental, 49, 147-158 (2004).

[10] Ladavos, A.K. and Pomonis P.J., "Effects of substitution in perovskites $La_{2-x}Sr_xNiO_{4-\lambda}$ on their catalytic action for the nitric oxide+carbon monoxide reaction", Applied Catalysis B: Environmental, 1, 101-116 (1992).