Catalysis Letters 1 (1988) 299–306

COMPLETE OXIDATION OF METHANE OVER PEROVSKITE OXIDES

Zhen KAIJI, Liu JIAN and Bi YINGLI

Department of Chemistry, Jilin University, Changchun, China

Received 9 March 1988; accepted 17 August 1988

1. Introduction

The complete oxidation of methane is of significant importance not only for exhaust emission treatment, but also for tunnel cleaniless. In the recent years, many interesting attempts have been focused on this topics. As well known, for the mentioned reaction perovskite oxides have also been suggested. One of the determining factors for this type of oxides to be used in this reaction is a stable bulk structure of the compounds, which is denoted as ABO_3. In addition, both A and B atoms in the oxides can be substituted either by metal atoms with valence same as that in the original compounds or by metal atoms with variable valences [1–3].

In this paper, the authors report results of a study on a series of perovskite oxides formulated as $La_{1-x}Me_xMnO_3$, where Me denotes Ca, Sr, Ba atom, respectively. The catalytic properties for the total oxidation of methane were tested over this series of samples. XRD technique was used for determining the phase composition of the oxides. Mn^{4+}/Mn ratio in each of the strontium substituted samples was measured by chemical analysis. For some of this series of samples magnetic susceptibility determination was performed as well.

2. Experimental

PREPARATION OF SAMPLES

The samples used in this work were synthesized by the co-precipitation method. The needed stoichiometric nitrate solutions for the aim were prepared first. Ammonium hydroxide and ammonium bicarbonate were chosen as precipitants. Under stirring the precipitants were added quickly and during the precipitation procedure PH value of the solution was kept at 8–9. The formed precipitates were filtered, washed, dried at 393 K and finally decomposed at 873 K for several hours. The decomposed materials were compressed under a pressure of

200 kg/cm^2, followed by an additional calcination at 1373 K in air for 2 h. Before using the synthesized samples were pelletized and 60–80 mesh particles were collected for running experiments.

The used manganese nitrate solution was prepared from electrolyzed metallic manganese dissolving in nitric acid, the other reagents are of analytical purity.

CHARACTERIZATION OF SAMPLES

The crystal structure of the synthesized compounds was determined by XRD technique using a SHIMADZU-3DX diffractometer (CuK Ni filter). A scanning rate of 0.5 degree/min was set for these samples. The surface area was determined using flow air adsorption method and calibrated with a standard samples of known specific area.

The content of Mn^{4+} and the total amount of manganese in each of the perovskite compounds were determined by a traditional oxidation-reduction titration method using sodium thiosulphate solution according to the procedure suggested in [7]. The magnetic susceptibility of a part of the prepared perovskite compounds was measured using a magnetic balance. The catalytic activity of samples for complete oxidation of methane was performed using a fixed bed stainless-steel reactor, the inner diameter of which is 0.4 cm equipped with a manifold of gas line. 0.4 g of catalyst was loaded and supported by quartz pellets. The temperature range for running this reaction was 733–813 K. Typically in most of the experiments the composition of reactant was set: CH_4: air $= 6:94$ and the used GHSV $= 5000\ h^{-1}$.

The inlet and exit gases were analyzed gas-chromatographically. A thermoconductivity detector and a flame ionization detector were used, carbon molecular sieve was chosen as separation column.

In this work, the conversion of methane was calculated by the following formula:

$$\text{conv} = \frac{h_0 - h}{h_0} 100\%$$

where h_0 and h are the chromatographic peak height of methane in inlet and exit gases, respectively.

3. Results and discussion

Based on the XRD measurements of the samples it can be identified that all the prepared compounds have a perovskite type structure of cubic crystal. The diffraction peaks of the corresponding crystal phase were displayed in fig. 1 and the calculated space distances and the cubic lattice parameters of them are listed in table 1. One can easily find in the figure and the table that for different

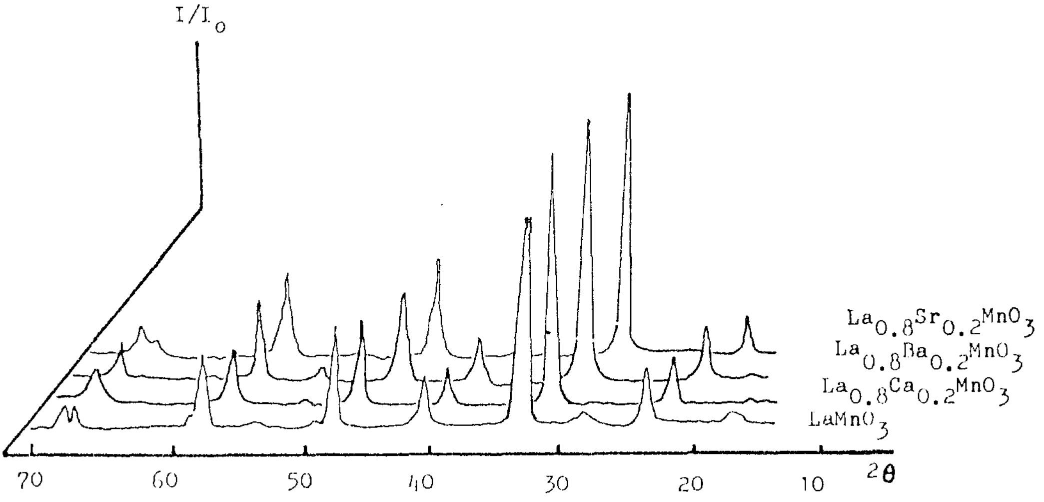

Fig. 1. XRD patterns of the synthesized perovskite oxides.

compound there is a slight shift of the diffraction peaks which is mainly caused by the difference in ion radius of alkaline-earth metal ions. In addition, the *d* values of the main diffraction peaks are in good agreement with that obtained using standard samples. The specific surface area and x, the substitution extent by strontium atom of samples are shown in table 2.

Figure 2 exhibits that substitution of part of lanthanum atoms by strontium atoms results in an obvious variation of the total conversion of methane and the larger the amount of the substituting strontium, the higher the conversion of methane total oxidation except the case where 0.2 mole of lanthanum was substituted, i.e. a minimum appears at $x = 0.2$ and at three temperatures (see fig. 3). The appearance of either a minimum or a maximum in an activity curve with respect to the substitution extent of lanthanum atoms by alkaline earth metal atoms in perovskite oxides is very common, for instance, in a paper of Teraoka et

Table 1
d values and lattice parameters of the perovskite oxides in Ångstrom

Sample	*d* value						Lattice parameter (a)
$LaMnO_3$	1.576	1.743	1.941	2.230	2.763	3.880	3.892
$La_{0.8}Ca_{0.2}MnO_3$	1.585	1.740	1.957	2.230	2.740	3.867	3.870
$La_{0.8}Ba_{0.2}MnO_3$	1.595	1.746	1.953	2.540	2.760	3.900	3.900
$La_{0.8}Sr_{0.2}MnO_3$	1.587	1.727	1.933	2.240	2.730	3.867	3.875
$La_{0.9}Sr_{0.1}MnO_3$	1.580	1.725	1.933	2.238	2.720	3.850	3.880
$La_{0.7}Sr_{0.3}MnO_3$	1.587	1.730	1.933	2.235	2.730	3.880	3.860
$La_{0.6}Sr_{0.4}MnO_3$	1.587	1.734	1.970	2.227	2.730	3.867	3.850

All these perovskite oxides have same crystal structure–cubic *d* values and lattice parameters are in Ångstrom.

Table 2
Specific surface areas and total activity of methane conversion of the perovskite oxides

x	S (m^2/g)	total activity of methane conversion		
		733 K	773 K	813 K
0	2.9	3.6	11.0	24.5
0.1	4.4	4.8	12.8	26.8
0.2	3.3	2.0	6.8	15.0
0.3	3.5	5.4	15.8	30.5
0.4	3.1	6.9	20.0	38.7

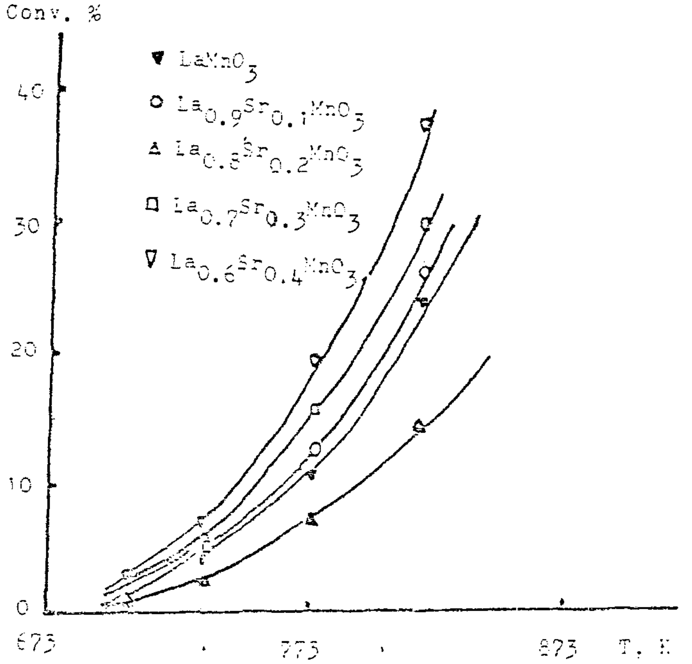

Fig. 2. Total activity of methane conversion of Sr-substituted lanthanum manganites at different temperatures.

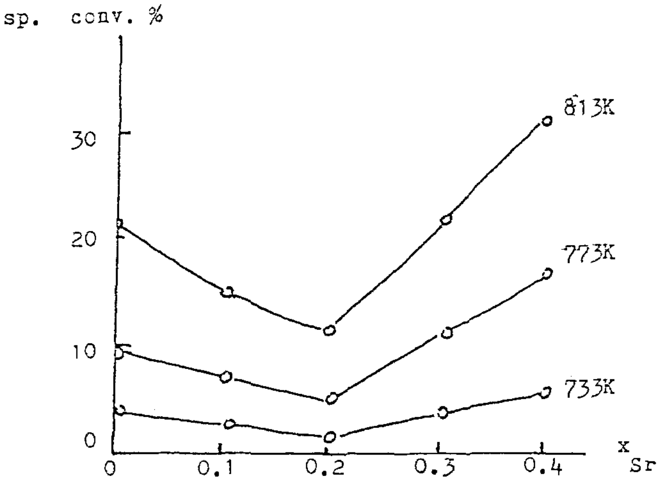

Fig. 3. Specific activity of methane conversion over the series of Sr-substituted lanthanum manganites at different temperatures.

al. [8] a maximum activity for propane oxidation was found at $x = 0.6$ in $La_{1-x}Sr_xMnO_3$ samples. In our case where specific activity for methane conversion of the series of samples was plotted against x, it can also be seen that a minimum specific conversion of methane appears at the three temperatures as shown in fig. 3. In addition the lower the reaction temperature, the wider the valley. It seems that at temperatures below 733 K the specific activity for methane total oxidation might become very low and there would not be obvious effect on the activity caused by strontium atom substitution in $La_{1-x}Sr_xMnO_3$ oxides.

Figure 4 shows that total activity of methane conversion over these strontium substituting lanthanum manganite depends paralellelly on the ratio Mn^{4+} to the total amount of manganese ion in the samples, for instance, the higher the ratio, the more active the catalyst. These results are in coincidence with that obtained by Jonker et al. [2]. However, this figure shows on the other hand, an exception that in case where 0.2 mole of lanthanum was displaced by strontium atoms the activity of the compound for methane total oxidation reduced apparently.

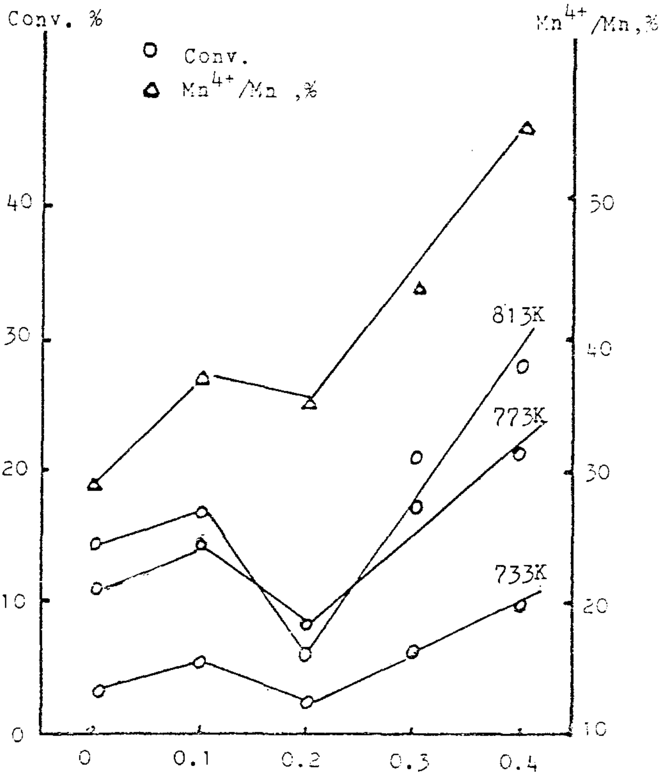

Fig. 4. Strontium-content dependence of methane conversion and Mn^{4+}/Mn ratio of the perovskite oxides.

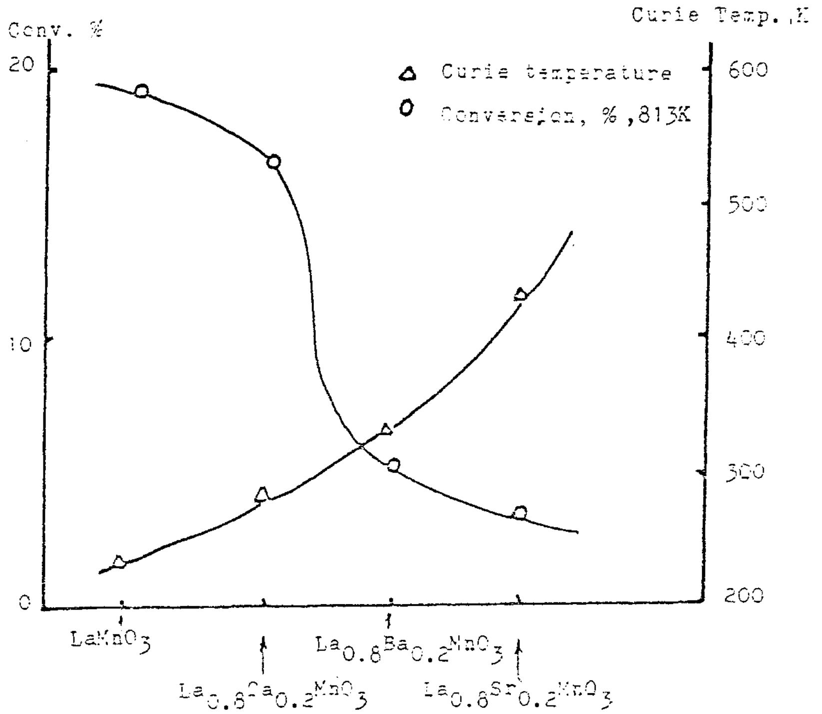

Fig. 5. Effect of alkaline-earth metal atoms on total activity of methane conversion and Curie temperatures.

Figure 5 shows a plot of the activity of methane conversion at 813 K and the Curie temperature against different alkaline-earth metal atoms (Ca, Sr, Ba) at the same x value (0.2) in La_{1-x} (Ca, Sr, Ba)$_x$$MnO_3$ oxides. From fig. 5 one can see that the higher the Curie temperature, the lower the total activity. Further investigation has to be done in order to make clear if this correlation exists at temperatures other than 813 K. As is known the Curie temperature is such a temperature, at which transformation from ferromagnet to paramagnet takes place i.e. at this temperature disordered magnetrons arrange instead of ordered distribution. According to Curie-Weiss formula

$$\chi = \frac{C}{T - T_c}$$

where χ denotes the magnetic susceptibility; C: a constant; T: the temperature and T_c; the Curie temperature. It is clear that a high T_c gives a large χ. If one considers Mn-O-Mn ion group as a magnetron then the magnetic susceptibility will depend on the type and the arrangement mode of the magnetron [9]. In our case Mn^{3+} and Mn^{4+} ions exist in the strontium substituting manganite of lanthanum. Thus, we dealt with different types of magnetrons, such as Mn^{4+}-O-Mn^{4+}, Mn^{3+}-O-Mn^{3+} and Mn^{4+}-O-Mn^{3+}. The magnetic exchange interaction as usual, may occur in these magnetrons. As a result, the magnetic exchange interaction between the lattice oxygen ion and manganese ions with different valency may be quite distinct. A combination of different types of magnetron possessing different magnetic properties gives rise to magnetic susceptibility of the bulk phase. Sequently, the Curie temperature of the sample depends strongly on its magnetic properties.

The results of the above comparison between the Curie temperature of the samples and the corresponding total activity of methane conversion can be explained as follows: activation of the methane molecule needs a suitable arrangement mode of the composed metal ion and oxygen ion in this type of oxide catalysts.

Acknowledgements

Senior engineer Yang Hongmao is greatly thanked for his XRD skill. Authors would also like to thank for the assistance from the Beijing Institute of Physics in magnetic susceptibility measurements.

References

[1] R.J.H. Voorhover, Perovskite-related oxides as oxidation and reduction catalysts, in: *Advanced Materials in Catalysis* (Academic Press, New York, 1973) p. 129.
[2] G.H. Jonker, Physica 16 (1950) 337, 599.
[3] Yung Fang and Yu Yao, J. Catal. 36 (1975) 266.
[4] K. Ichimura, Y. Inoue and I. Yasumori, Bull. Chem. Soc. Jap. 53 (1980) 3044.
[5] T. Nakamura, M. Misono and Y. Yoneda, Shakubai (Catalysts) 24 (1979) 310.
[6] G. Parraveno, J.A.C.S 75 (1953) 1497.
[7] T. Yamakuchi, Yogyo Kyokai Shi 88 (1980) 9.
[8] Y. Teraoka, M. Yoshimatsu, N. Yamazoe, T. Seiyama and Shakubai (Catalysis) 26(2) (1984) 106.
[9] John B. Goodenough, Phys. Rev. 100 (1955) 564.