Catal Lett (2008) 126:96–99
DOI 10.1007/s10562-008-9582-6

Properties and Catalytic Performance for Methane Combustion of $LaMnO_3$ Perovskite Prepared in Oil–Water Two-phase System

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Received: 10 May 2008 / Accepted: 4 July 2008 / Published online: 25 July 2008

Abstract $LaMnO_3$ catalysts with high catalytic activity for methane combustion have been prepared in an oil–water two-phase system. The procedure was carried out using oleic acid as phase-transfer agent, and ammonia as co-precipitation agent. In the meanwhile, H_2O_2 is employed to control the valence of Mn ions when precipitation. The control results in perovskites with similar phases having three O_2-TPD patterns, and induces the catalysts possessing distinct catalytic activities. The structure and properties of the catalysts were characterized by BET, TG-DSC, XRD and O_2-TPD techniques.

Keywords Perovskite · Methane · Catalytic combustion · Oil–water two-phase system

1 Introduction

In recent years, high-temperature catalytic combustion of methane has received considerable attention owing to the more efficient burning in wider air-to-fuel ratio and with lower NO_x emissions than the conventional thermal combustion [1–4]. The perovskitic samples of formula $ABO_{3+\delta}$ are considered as suitable catalysts due to their high thermal stability and good combustion activity. It is reported that the excellent performance of perovskitic catalysts depend mainly on the nature of A and B ions and on the valence state of the transition metal ion B, which can be altered partially by choosing a proper A ion. Moreover, by replacing part of A or B ions with A′ and B′ ions, it is possible to create or suppress oxygen vacancies on the catalyst [3–8]. On the other hand, further researches focus on the synthetic methods for preparing the perovskitic and/or the loaded perovskitic materials to improve the performance of the catalysts [9–14]. According to the literature [9], the $LaCoO_3$ catalysts prepared by a flame-spray pyrolysis method exhibited excellent thermo-stability. The MgO was introduced as a textural promoter and the composite catalyst possessed higher activity under a high temperature as reported by Saracco et al. [12].

In this work, the $LaMnO_3$ perovskitic catalysts were prepared in an oil–water two-phase system, which is an excellent method for preparing the other nano-materials developed in recent years [15, 16]. The influencing factors in the preparation procedure and their effects on the properties and catalytic performance for methane combustion are also studied.

2 Experimental

2.1 Catalyst Preparation

The $LaMnO_3$ perovskites were prepared in an oil–water two-phase system. In the synthesis, $La(NO_3)_3 \cdot 6H_2O$, 50 wt.% $Mn(NO_3)_2$ aqueous solution, 28 wt.% ammonia aqueous solution, 50 wt.% H_2O_2 aqueous solution, oleic acid, and isooctane were used. The preparation process was depicted in Fig. 1. The molar ratio of La:Mn:oleic acid was 1:1:0.5. Different catalysts were obtained by varying the

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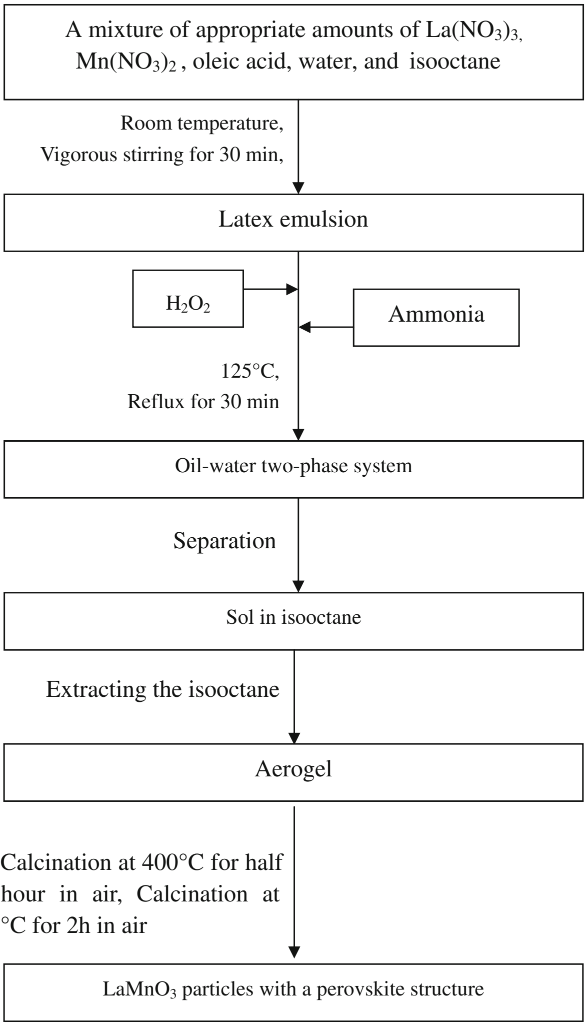

Fig. 1 Preparation procedure of catalysts

molar ratio of H_2O_2 to Mn. The catalysts with H_2O_2 to Mn ratio of 0.56, 0.63, 0.70, 0.77 and 0.84 were marked as LM1, LM2, LM3, LM4, and LM5, respectively.

2.2 Catalyst Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on the Shimadzu XD-3A diffraktometer using Cu Kα radiation.

TG and DSC were carried out on a NETZSCH STA 449 C analyzer. The Aerogel of the LM3 catalyst before calcination was heated from room temperature to 800 °C at the rate of 10 °C min^{-1} under static air.

Temperature programmed desorption (TPD) of O_2 were performed using a GC 7890 II gas chromatograph equipped with a TCD. The sample (50 mg) was preheated in flowing oxygen at 600 °C for 1 h before each test. After being cooled, the sample was heated to 800 °C at a programmed rate of 10 °C min^{-1} in flowing He(35 cm^3 min^{-1}).

Specific surface areas were calculated by the BET method from the N_2 adsorption isotherms, recorded at liquid nitrogen temperature on a ASAP-2010 micromeritics apparatus. Prior to the adsorption measurements, the samples were out-gassed at 473 K for 4 h.

2.3 Activity Tests

The reaction of methane combustion was carried out in a conventional flow system under atmospheric pressure. The catalyst (0.2 g) (20–40 mesh) and quartz powder (0.8 g, of the same particle size) were loaded in a quartz reactor (i.d. 10 mm), with quartz fiber packed at the end of the catalyst bed. Before each run, the catalyst was activated in flowing air (100 cm^3 min^{-1}) with the temperature increased at a rate of 10 °C min^{-1} to 600 °C, where it was maintained for 0.5 h. After cooling in the flowing air down to 350 °C, the activity tests were carried out by feeding 100 cm^3 min^{-1} of a mixture gas of 1 vol.% CH_4 (air as the balance). The inlet and outlet gas compositions were analyzed by an on-line gas chromatograph with a packed column of carbon molecular sieve and a thermal conductivity detector.

3 Results and Discussion

The XRD patterns of the $LaMnO_3$ catalysts are shown in Fig. 2. The single perovskite phase (JCPDS Number: 75-0440) is formed in LM3 and LM4, while γ-Mn_2O_3 (JCPDS Number: 06-0540) or La_2O_3 (JCPDS Number: 04-0856) are observed in the other catalysts. Furthermore, the amount of the other phases in different catalysts varies regularly. The formation of the perfect phase was attributed to the excellent disperse of the lanthanum and manganese ions, for the suppressing effect on the recrystallization by

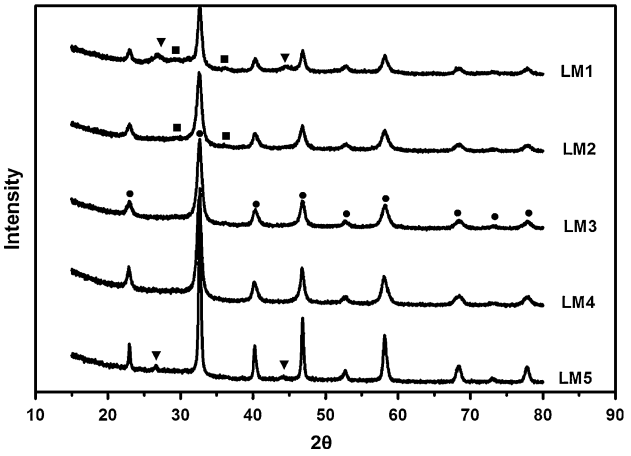

Fig. 2 XRD patterns of the catalysts: (●) $LaMnO_3$ (■) γ-Mn_2O_3 (▼) La_2O_3

transforming the precursors into the oil phase as soon as the formation of the precipitate, while, at that condition the phase was hard to be formed in a co-precipitation method using the same precipitator (ammonia) according to the literature [17] and our previous experiments. Furthermore, it is clear that a suitable ratio of the H_2O_2 to Mn is helpful to form the perovskite phase.

The mass transfer of reactants to the catalyst surface from the gas phase limits the reaction of catalytic combustion at high temperatures. The BET surface areas of $LaMnO_3$ catalysts are listed in Table 1. It can be seen that all the catalysts possess surface areas more than 11 $m^2\ g^{-1}$, the variation trend of the surface areas is identical to that of the ratio of H_2O_2 to Mn. Moreover, the average pore diameters vary to a lower size with the ratio. It's inferred that the higher surface area is due to the partially decomposition of MnO_x via the formation of the perovskite phase.

To determine the calcination temperature, a TG-DSC analysis of the LM3 catalyst precursor was carried out (Fig. 3). The TG curve indicates a weight loss from 180 °C to 450 °C which was mainly attributed to the removal of the exotic oleic acid. The DTA profile exhibits that the oleic acid can be burned up at about 370 °C. At that temperature the Mn ion in the catalyst is hardly reduced, suggesting that the decomposition of the oleic acid has no negative influence on the valence of the Mn ions. Moreover, the suitable temperature for removing guarantees a hindering effect on the conglomeration for the bonding of hydroxyl.

Table 1 Surface area and pore structure

Catalysts	S_{BET} ($m^2\ g^{-1}$)	V_{pore} ($cm^3\ g^{-1}$, BJH)	D_{pore} (nm, BJH)
LM1	11.1	0.059	15.2
LM2	15.3	0.088	16.4
LM3	14.6	0.051	9.3
LM4	19.5	0.070	9.3
LM5	22.1	0.072	7.8

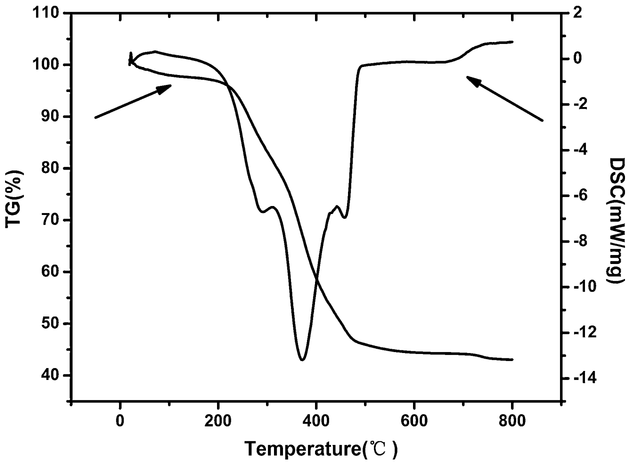

Fig. 3 TG-DSC curves of the LM3 catalyst before calcination

The catalytic activities for methane combustion over the catalysts are shown in Fig. 4. The sequence of the catalytic activity is as follows: LM3 ≫ LM2 ≈ LM4 > LM1 ≈ LM5. Relationship profile of Light-off temperature (T_{50}, corresponding to 50%) vs. the ratio of the H_2O_2 to Mn are shown in Fig. 5. The profile is a typical volcanic curve. It can be concluded that catalysts with different catalytic activities are easily obtained by altering the ratio of H_2O_2 to Mn. It is worth noting that the trend of the catalytic activities has no direct relation to that of the surface areas. The results can be explained by the more oxygen species depicted in the O_2-TPD shown below.

Temperature-programmed desorption (TPD) of oxygen is a powerful technique for the evaluation of catalyst affinity towards oxygen [18–20]. During the TPD analysis,

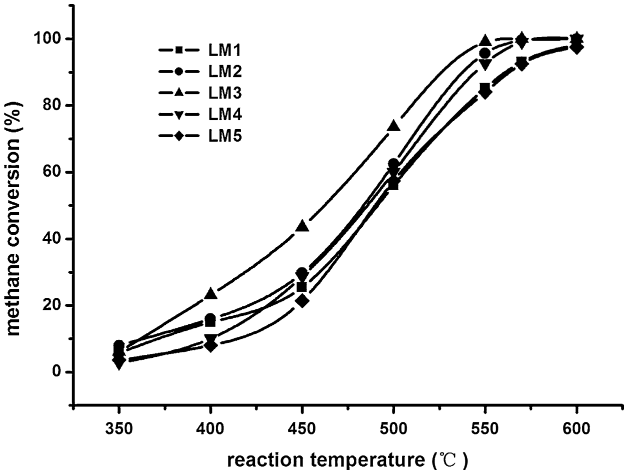

Fig. 4 Catalytic combustion of CH_4 over the catalysts

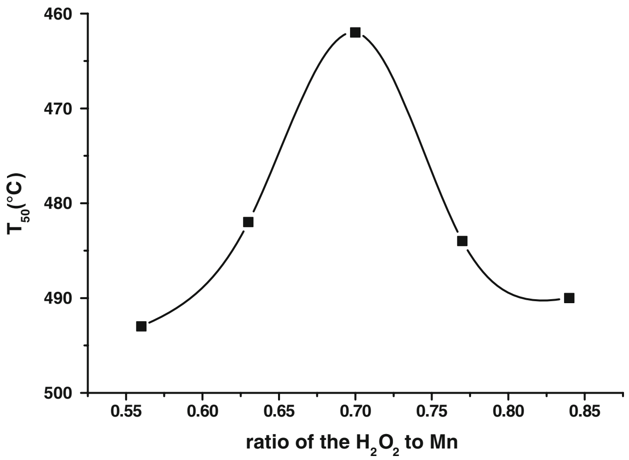

Fig. 5 Light-off temperature of the catalysts

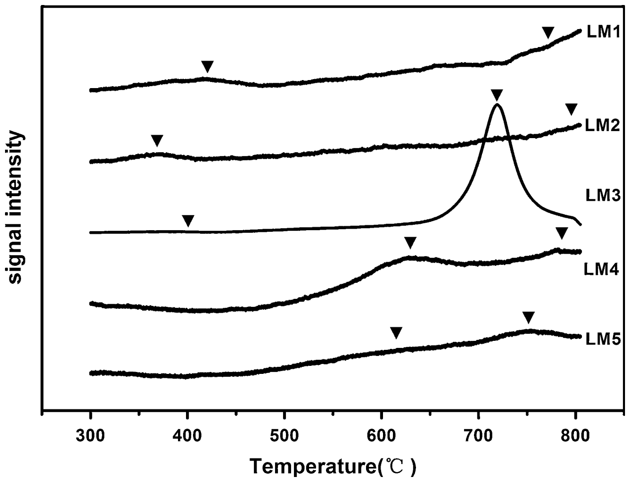

Fig. 6 O_2-TPD profiles of the catalysts: (▼) desorption peak

two desorption peaks, called α and β, can be observed, which were ascribed the release of oxygen, adsorbed on the surface or migrating from the bulk, respectively [8, 18, 20–23]. The set of catalysts show different TPD patterns, which are presented in Fig. 6. Though the catalysts have the same components ($LaMnO_3$), the profiles present three patterns: The first style, including LM1 and LM2, is similar to that of $LaCoO_3$ [20] or $La_{1-x}Ce_xMnO_3(x = 0.1–0.5)$ [23] reported in the literature. The first peak appears in a lower temperature area (350–400 °C), which leads to better initiative catalytic activities of LM1 and LM2. It is expected that the lower valence of the Mn ions accounts for more oxygen vacancies (α oxygen) because of deficient ligand numbers of Mn ion. The second style, including LM4 and LM5, is similar to that of $Nd_{1-x}K_xMnO_3(x = 0–0.15)$ reported in the literature [24]. In which two weak peaks are observed. The profile of LM3 is different from that of the other catalysts and is consistent with that of $LaMnO_3$ reported in the literature [24]. The first peak appears very tiny and the second peak appears very strong, resulting in the best catalytic activity of LM3 for methane complete conversion. It is inferred that the suitable valence of the Mn ions brings about a favorable perovskite with more lattice oxygen (β oxygen) and better transmission of the lattice oxygen. Though the theory developed by Voorhoeve et al. [25] and the Elay–Rideal mechanism were widely accepted, the catalytic mechanism of the catalyst has not been understood clearly. As for a perovskitic catalyst, partially substituting A or B ions are always considered as a favorable route, and most conclusions had been drawn based on this [12, 23, 24]. Here we present no-substitution $LaMnO_3$ and obtain the similar results. As a consequence, the simplified and controllable process is helpful to seek the relationship between the catalytic activity and the oxygen vacancies, the valence of the B ions, oxygen species mobility, oxygen species conductivity, etc.

4 Conclusions

A novel method of oil–water two-phase system for preparing high catalytic activity $LaMnO_3$ catalysts has been developed. H_2O_2 is used to control the valence of Mn ions by blocking the oxidation of oxygen through the transfer of sol into the oil phase, and this control works on the catalytic activity of the catalysts effectively. Meanwhile, the gel wrapped by oleate prevents particles from sintering when calcined, which leads to a high surface area.

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