

Surface composition and catalytic activity of La-Fe mixed oxides for methane oxidation



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ABSTRACT

Four La-Fe oxide samples with La/Fe atomic ratio $y = 1.02 \sim 0.68$ (denoted as La_yFe) were prepared by the citrate method. The samples had a decreased specific surface area with the La/Fe atomic ratio decreasing. XRD pattern proved that the sample $\text{La}_{0.94}\text{Fe}$ is single phase perovskite $\text{La}_{0.94}\text{FeO}_{3-d}$. Phase composition of the samples was estimated by the Rietveld refinement method. XPS analyses indicate that La^{3+} ions are enriched on surface of crystallites for all the samples, and surface carbonate ions are relatively abundant on the samples $\text{La}_{1.02}\text{Fe}$ and $\text{La}_{0.94}\text{Fe}$. Catalytic activity for methane oxidation per unit surface area of the samples is in the order of $\text{La}_{0.68}\text{Fe} > \text{La}_{0.76}\text{Fe} > \text{La}_{0.94}\text{Fe} > \text{La}_{1.02}\text{Fe}$ both in the presence and in the absence of gaseous oxygen. A reason for this order would be the higher concentration of Fe^{3+} ion on the surface of the samples $\text{La}_{0.68}\text{Fe}$ and $\text{La}_{0.76}\text{Fe}$.

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1. Introduction

Perovskite-type oxide has a formula ABO_3 , where usually La^{3+} ions occupy at the lattice A-sites and ions of a transition metal (Mn, Fe, Co etc.) occupy at the lattice B-sites [1]. When La^{3+} ions were substituted partially by other metallic ions at a lower valence state such as Ca^{2+} and Sr^{2+} ions, lattice oxygen vacancy would be formed together with a part of transition metal ions changing into a higher valence state in the crystal structure to maintain electrical balance [1–5]. Oxygen in gas phase can adsorb at the surface lattice oxygen vacancy, forming adsorbed oxygen species either neutral or charged [1,3,6]. Charged adsorbed oxygen species are formed only when there are electrons that can be drawn from neighboring transition metal ions [1,3,6]. Surface metallic ions are also adsorbed by or bound with oxygen species or hydroxyls or carbonate ions due to exposure to the air atmosphere in the preparation process of the samples.

Perovskite-type oxides are effective catalysts for catalytic combustion of hydrocarbons and purification of exhaust gas of vehicles [1–8]. It is reported that the perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ can have a high catalytic activity similar to $\text{Pt}/\text{Al}_2\text{O}_3$ for methane combustion [8], and the perovskite $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ shows a higher durability than $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst in aging in engine exhaust [7].

The supported noble metal catalysts really can have high catalytic activities even below 350°C , but also have a sintering tendency above 500°C which is not good for stability [3]. Oxidation reaction on surface of metal oxide catalyst is generally believed to proceed on suprafacial mechanism or intrafacial mechanism or the mixed mechanism of the suprafacial mechanism with the intrafacial mechanism [1]. Suprafacial mechanism features with surface adsorbed oxygen species acting as catalytically active species, and operates at relatively low reaction temperature. Intrafacial mechanism goes on with participation of surface lattice oxygen as catalytically active species at high reaction temperatures that allow surface lattice oxygen to release feasibly. In most cases, the mixed mechanism takes effect. Arai et al. estimated the respective contribution of surface adsorbed oxygen species and surface lattice oxygen for methane oxidation at reaction temperatures $450 \sim 650^\circ\text{C}$, and argued that the contribution of surface lattice oxygen increased with reaction temperature increasing [8]. When charged oxygen species, including surface lattice oxygen and charged surface adsorbed oxygen, are catalytically active species, its consumption and regeneration is accompanied by cycling of valence state of neighboring transition metal ions such as $\text{B}^{3+} \leftrightarrow \text{B}^{4+}$ and/or $\text{B}^{2+} \leftrightarrow \text{B}^{3+}$ [1,3,6]. The ease at the cycling of valence state is dependent on kind of transition metal. Hence, kind of transition metal ions at the B-sites influences catalytic activity of perovskite-type oxides greatly [6,8].

There are many papers discussing effect of partial substitution of La^{3+} ions by Ca^{2+} or Sr^{2+} ions etc. [1–5,8–10]. Only a few

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of papers are published on preparation and characterizations of perovskite-type $\text{La}_x\text{FeO}_{3-d}$ oxides with La^{3+} deficiency ($x < 1$) to our knowledge [6,11,12]. In the present work, a series of La-Fe oxides with La/Fe atomic ratio = 1.02 ~ 0.68 (measured by XRF) were prepared. Phase composition and surface elemental composition of the samples, and especially the elemental composition at the different Ar^+ -etching depths for the sample $\text{La}_{0.94}\text{Fe}$, were analyzed. Catalytic activity for methane oxidation of the samples was discussed in view of the difference in surface elemental composition of the samples.

2. Experimental

2.1. Preparation of La-Fe oxides

Citrate method was adopted to prepare La-Fe mixed oxides in the present work, since citric acid were frequently used as complexing agent to produce uniform precursor of two kinds of metallic ions [2–5,9,10,13]. At first, an aqueous solution of mixture of lanthanum nitrate and iron nitrate (Guoyao Chemicals, China) was added dropwise into an aqueous citric acid solution (the molar ratio of the citric acid to the total metallic ions was fixed at 0.5) under rigorous stirring, and stirring was kept for 30 min after the addition completed. Then, the citrate solution was heated in a rotary evaporator at 80 °C and vacuum degree of 0.08 MPa for 30 min, where a viscous liquid was obtained. The viscous liquid was dried in an oven at 80 °C for 5 h and subsequently at 110 °C for 2 h. At last, the dried sample was calcined in a muffle furnace at 700 °C for 5 h. A series of samples were prepared by this way with atomic ratio of La/Fe at 1.02, 0.94, 0.76 and 0.68 (measured by X-ray fluorescence spectroscopy, XRF-1800, Shimadzu), respectively. These samples are thus denoted as La_yFe , in which the variable y is the atomic ratio of La/Fe of the samples.

In addition, ICP-AES method was also used to determine atomic ratio of La/Fe for the four samples. However, unfortunately the samples $\text{La}_{0.76}\text{Fe}$ and $\text{La}_{0.68}\text{Fe}$ were not completely dissolved in acid solution due to the presence of Fe_2O_3 phase in a notable amount (see XRD patterns in Fig. 1). The samples $\text{La}_{1.02}\text{Fe}$ and $\text{La}_{0.94}\text{Fe}$ were dissolved completely in acid solution and showed a value of La/Fe atomic ratio at 1.09 and 0.96, respectively, which are similar to those given by XRF measurements.

2.2. Characterizations

Phase identification of the samples was performed on an X-ray diffractometer (D8 Advance, Bruker) with $\text{Cu K}\alpha$ irradiation at 40 kV

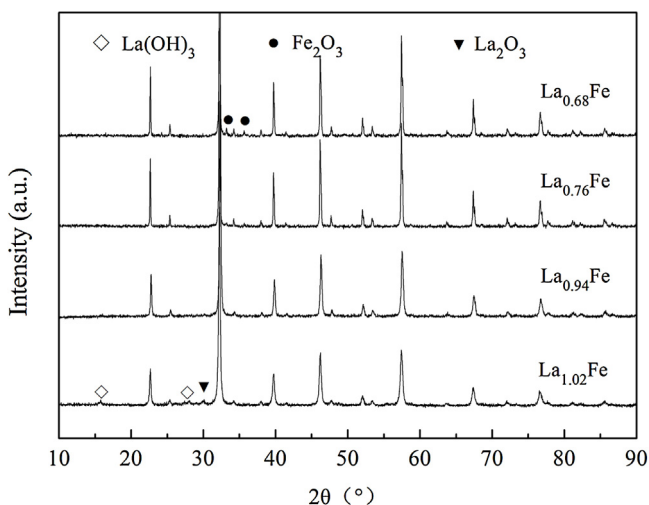


Fig. 1. XRD patterns of the four La-Fe oxide samples.

and 40 mA. The Rietveld refinement method implemented in the TOPAS software package was used to estimate phase composition of the samples and crystallite size of the perovskite phase.

Specific surface area (SSA) of the samples was measured on a SSA analyzer (JW-DA, Beijing JWGB, China). At first each the samples was degassed at 150 °C for 1 h in high vacuum, and then allowed to adsorb N_2 at liquid nitrogen temperature (–196 °C) under a relative pressure of $p/p_0 = 0.06 \sim 0.30$. The BET equation was used to calculate SSA value.

Reducibility of the samples was measured by temperature programmed reduction (TPR) technique on a TPR instrument (PX200, Tianjin Pengxiang, China) equipped with a thermal conductivity detector (TCD), where a reducing gas of 10% H_2/Ar was set at 40 ml/min, temperature was ramped to 700 °C at 10 °C/min, and sample powder was fixed at 50.0 mg at each run.

Surface elemental composition of the samples was analyzed on an X-ray photoelectron spectrometer (PHI Quantera) with monochromatized $\text{Al K}\alpha$ radiation. The base pressure of the instrument was 2×10^{-9} Torr. Ar^+ etching (1 keV) was applied for the sample $\text{La}_{0.94}\text{Fe}$ after the surface composition analysis in order to obtain elemental composition at the different (average) depths of 5 nm, 10 nm, 20 nm and 40 nm beneath the surface of crystallites for the sample. Curve-fitting for the XPS peaks, calibrated with the binding energy of adventitious carbon $\text{C}_{1s} = 284.8$ eV, was performed with a Gaussian–Lorentzian profile.

FT-IR spectra were recorded in the wavenumber range of 400–4000 cm^{-1} for the samples on an IR instrument (Thermo Fisher Scientific Nicolet iS10), where the thin disks for measurements were obtained by pressing mixture of each the samples with KBr powder.

2.3. Catalytic activity evaluations

Catalytic activity for methane oxidation of the La-Fe oxides as catalysts (200 mg granules in 40–60 mesh) was evaluated in a continuous flow fixed-bed quartz tube reactor (8 mm i.d.) at reaction temperature of 600 °C and atmospheric pressure. Total flow rate of the feed gas was 200 ml/min, in which methane gas was 2.0 vol%, oxygen gas 16.8 vol%, nitrogen gas as balance gas. Analyses of reaction products were carried out after 1 h stabilization of the reaction on a gas chromatograph (Shanghai Kechuang, China). Carbon dioxide was the sole carbon-containing product.

Pulse reaction of methane in the absence of gaseous oxygen over the La-Fe oxides (50.0 mg powder) was performed in a quartz tube reactor (4 mm i.d.) at reaction temperature of 600 °C. The reactor was connected between pressure valve and injector of a gas chromatograph (Beijing Jiafeng, China). Pressure of carrier gas (N_2) of the gas chromatograph was set at 0.06 MPa, so the pressure on the La-Fe oxide powder was actually 0.16 MPa. Pulse operation started after 30 min stabilization of each the samples at the reaction temperature. Pulse dose of 10 vol% CH_4/N_2 gas into the reactor was set at 0.2 ml, and the pulse was repeated 10 times with a fixed time interval of 15 min between any two successive pulses. Carbon dioxide was the sole carbon-containing product. It is observed that methane conversion decreased as pulse number increased for every sample. So the average value of methane conversion in the 10 times pulses is used to compare the catalytic activity of the four La-Fe samples for methane oxidation in the absence of gaseous oxygen.

3. Results and discussion

3.1. Phase composition and crystallite size

Fig. 1 shows XRD patterns of the four La-Fe oxide samples. All samples display clearly characteristic peaks of perovskite phase

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