



Simultaneous removal of NO_x and soot particulates over La_{0.7}Ag_{0.3}MnO₃ perovskite oxide catalysts

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ARTICLE INFO

Article history:

Available online 3 July 2010

Keywords:

La_{0.7}Ag_{0.3}MnO₃ catalyst
Simultaneous removal of NO_x and diesel soot
Solid state method

ABSTRACT

A highly active catalyst (La_{0.7}Ag_{0.3}MnO₃) for simultaneous removal of nitrogen oxides (NO_x) and diesel soot is synthesized by solid state method and the catalyst is characterized by XRD, FT-IR, H₂-TPR, and O₂-TPD. The results indicate that metallic Ag appears in the La_{0.7}Ag_{0.3}MnO₃ catalyst. The concentration of oxygen vacancy and the over-stoichiometry oxygen content also remarkably increase as the substitution increase of Ag⁺ for La³⁺ at A-site ions. The simultaneous removal of soot particulates and NO_x activities are evaluated by a temperature-programmed reaction (TPRe) technique. The superior performance of the La_{0.7}Ag_{0.3}MnO₃ catalyst for the reaction is probably due to lots of oxygen vacancy and over-stoichiometry oxygen in the perovskite lattice along with the zero-valence silver.

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1. Introduction

Perovskite-structured (ABO₃) oxides, as a potential catalyst for simultaneous removal of soot particulates and NO_x in diesel exhaust, have been investigated widely in academic and industry after the proposal of a catalyzed soot traps process [1]. The partial replacement of the A-site ions by alkali metal [2,3,4], alkali-earth metal [4] and rare-earth metal [5] in perovskite-structure will lead to structural defects in the crystal lattice, which might enhance the activity and selectivity for simultaneous removal of NO_x and soot. Silver could not only increase the carbon gasification rate [6], but also shows remarkable performances in NO_x abatement [7,8]. Silver supported alumina catalyst has also shown good performance on simultaneous removal of carbon particle and NO_x [9]. It is therefore possible to develop highly effective simultaneous removal of NO_x and soot catalysts by using Ag⁺ replaced A-site ions of perovskite oxides.

Herein, we partially replaced La³⁺ ions of LaMnO₃ perovskite oxide by Ag⁺ ions, and La_{0.7}Ag_{0.3}MnO₃ with prescribed stoichiometry was used as a catalyst for simultaneous removal of NO_x and soot. The results indicated that the structural defects produced by Ag⁺ ions replacement in the crystal lattice will affect the catalytic activity. Meanwhile, metallic silver in this catalyst might also promote the performance for simultaneous removal of NO_x and soot.

2. Experimental

2.1. Catalyst preparation

The La(NO₃)₃·6H₂O, AgNO₃·H₂O and Mn(CH₃COO)₂·4H₂O powders with a stoichiometric ratio were mixed and grinded continuously for 20 min in a mortar. Compared with the theoretical weight, 20% excessive NaOH was added into the mortar, and grinding the solid to react completely. Then the as-synthesized sample was washed with deionized water by filter. The solid product was dried at 100 °C for 24 h, followed by calcination at 600 °C for 10 h in air. After grinding, the catalyst powder (150–200 mesh) was obtained.

2.2. Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded at room temperature from 4000 to 400 cm⁻¹ by a Nicolet 6700 spectrometer, and 64 scans were collected with a resolution of 2 cm⁻¹. A self-supporting disk (10 mm diameter) prepared by pressing the mixture of sample powder and KBr was placed into a conventional metal cell with KBr windows.

The X-ray diffraction (XRD) patterns of the samples were measured on a powder X-ray diffractometer (PANalytical XRD Xpert pro. MPD) using Cu Kα radiation (λ = 0.1542 nm) in the 2θ range of 10–75° at a scanning rate of 2° per min. The tube voltage and current were set at 40 kV and 40 mA, respectively. The patterns were compared with JCPDS reference data for phase identification.

H₂-TPR measurements were carried out on a Quantachrome ChemBET-3000. Typically, 100 mg sample was pretreated at a

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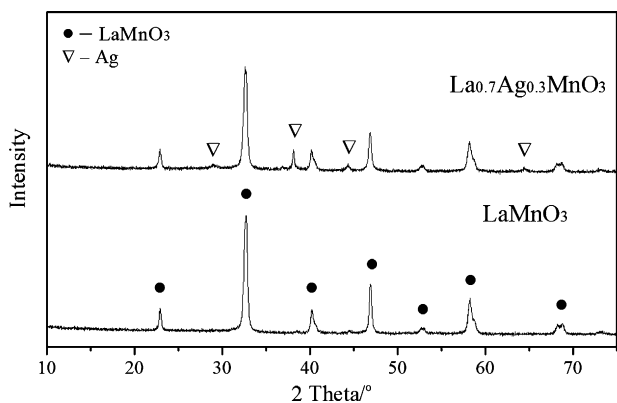


Fig. 1. X-ray diffraction patterns of catalysts.

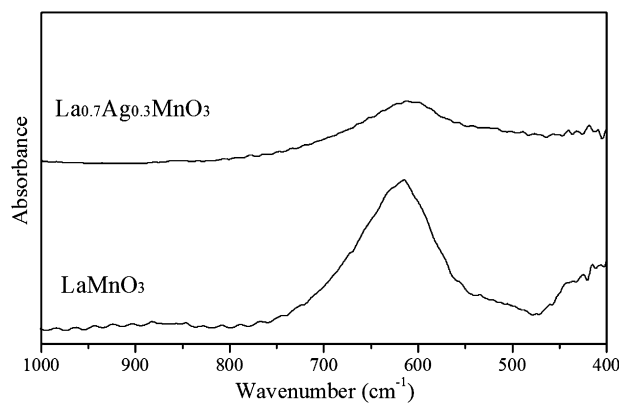


Fig. 2. FT-IR spectra of catalysts.

helium atmosphere at 500 °C for 1 h and subsequently cooled to 50 °C. Then, the H₂-TPR was carried out using 9.87% hydrogen in argon at a constant flow rate of 70 mL/min, from 100 °C to 800 °C at a heating rate of 10 °C/min.

The O₂-TPD experiments were performed on Quantachrome ChemBET-3000. 200 mg of the sample was pretreated using 4.16% O₂ in He (80 mL/min) at 600 °C for 30 min, and then cooled down to room temperature in the same atmosphere. The oxygen desorbed gradually from 100 °C to 850 °C at a heating rate of 10 °C/min in He stream.

2.3. Catalytic activity evaluation

The catalytic activities of the prepared samples were evaluated with a temperature-programmed reaction (TPRe) technique. The reaction temperature varied during each TPRe run from 200 °C to 600 °C at a 4 °C/min rate. The model soot particulates used was the Printex-U sample supplied by Degussa. 165 mg mixture of soot particulates and La_{0.7}Ag_{0.3}MnO₃ catalyst was carefully mixed, in the weight ratio of 1/10 for a “loose” contact between the soot particulates and the catalyst, and then placed into the center of a quartz reactor. The simulated exhaust consists of 0.2% NO, 5% O₂ with He as the major gas and the total flow rate is 60 mL/min. After reaction, the gas is automatically sampled and analyzed by a gas chromatograph (modified Agilent-6820 GC) equipped with a TCD and with a Porapak Q column for separating CO₂ and N₂O, and a molecular sieve 5A column for separating O₂, N₂ and CO. During the test of this work, N₂O and CO was not detectable.

The catalytic activity was evaluated by the values of T₁₀, T₅₀, and T₉₀, which were defined as the temperatures at which 10, 50, and 90% of the soot particulates were oxidized during the TPRe procedure, respectively. The maximum NO conversion into N₂ is another important parameter, which can be calculated by $2[N_2]_o/[NO]_i$, where [N₂]_o and [NO]_i are concentrations of N₂ in the outlet gas and NO in the inlet gas, respectively. In the TPRe experiments, the reaction was continuously run until the soot was completely burnt off.

3. Results and discussion

3.1. XRD

The X-ray diffraction patterns of La_{1-x}Ag_xMnO₃ (x=0, 0.3) catalysts are shown in Fig. 1. It reveals that the LaMnO₃ catalyst is rhombohedral perovskite phase in the present work. For La_{0.7}Ag_{0.3}MnO₃ catalyst, four additional peaks not belonging to the perovskite phase are observed at 29.1°, 38.1°, 44.3° and 64.4°, and they can be assigned to metallic Ag.

3.2. FT-IR

IR spectrum of LaMnO₃ perovskite presents two strong absorption bands around 600–650 cm⁻¹ and ~400 cm⁻¹, as shown in Fig. 2. Lavat and Baran [10] found that the BO₆ units dominate the spectroscopic behavior because, the B–O bonds of the BO₆ octahedral units are undoubtedly stronger than those of the 12-coordinated La(III)–O units. The bands in the range of 600–650 cm⁻¹ are assigned to the asymmetric stretching vibration of the BO₆ octahedra, while those at ~400 cm⁻¹ are ascribed to the deformation modes of the same polyhedral [11]. In the IR spectra of La_{0.7}Ag_{0.3}MnO₃ sample, the broadening of the bands at higher wave numbers and decreasing of their intensity, along with disappearing bands at lower wave numbers, were observed. It is plausible that BO₆ octahedral units in the structure of La_{0.7}Ag_{0.3}MnO₃ are more symmetric than that in LaMnO₃ because an amount of Ag⁺ substitutes La³⁺ at A-site getting into the lattice of perovskite oxide.

3.3. H₂-TPR

Fig. 3 shows the H₂-TPR patterns of La_{1-x}Ag_xMnO₃ (x=0, 0.3) catalysts. In all cases, two types of chemisorbed oxygen species, were observed: a low-temperature species, named α, desorbing below 600 °C, and a high-temperature one, named β, reacting in the region of 600–900 °C. The α peak depends strongly on the concentration of surface oxygen vacancies. In particular, its onset and intensity depend partly on the nature of the metal B of ABO₃ structure, but principally on the degree of substitution of the A-site ions with cations with lower valence [12]. Otherwise, nonstoichiometric excess oxygen appears, which is mostly weakly bonded in the perovskite lattice [13], and impacts on the α peak. A dramatic shift to low temperatures of the peak of α-oxygen species and the incre-

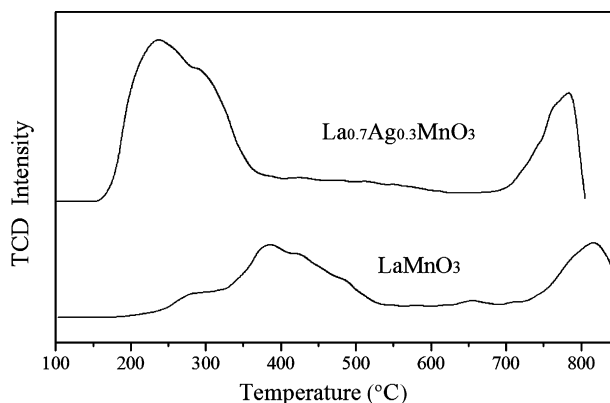


Fig. 3. The H₂-TPR patterns of catalysts.

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