



Influence of partial Mn-substitution on surface oxygen species of LaCoO₃ catalysts

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ARTICLE INFO

Article history:

Received 17 January 2012

Received in revised form 17 April 2012

Accepted 23 April 2012

Available online 15 July 2012

Keywords:

LaCoO₃

Surface oxygen species

Particulate matters

Partial substitution

ABSTRACT

A series of LaCo_{1-x}Mn_xO₃ ($x = 0.05, 0.1, 0.3, 0.5, 0.7$) perovskite-type catalysts were prepared by citric acid sol-gel method to study the influence of partial Mn-substitution on the catalytic performance and surface oxygen species of LaCoO₃ perovskite-type catalysts. Their catalytic performances for particulate matters (PM) oxidation were investigated by a technique of temperature-programmed oxidation reaction (TPO), indicating that the catalytic performance of LaCo_{0.95}Mn_{0.05}O₃ is better. The catalysts were characterized by XRD, BET, IR, H₂-TPR, O₂-TPD and XPS. The results show that LaCo_{1-x}Mn_xO₃ catalysts have perovskite-type structures after partially substituted by Mn. There are three kinds of oxygen species, lattice oxygen ion O₂⁻, peroxide ion O⁻ and superoxide ion O²⁻, are present on the surfaces of catalysts. The content of surface oxygen species varies with Mn-substitution amount. Superoxide ion O²⁻ and surface oxygen vacancy play an important role in the reaction of PM oxidation.

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1. Introduction

The particulate matters (PM) emitted from diesel engines are harmful to the environment and human health [1]. The legislation and standards become stricter so that the reducing of PM emitted from diesel engines becomes the main purpose of catalytic purification. Many reports demonstrated that perovskite or perovskite-like type [2,3], spinel type [4,5] and hydrotalcite type [6,7] mixed oxides have good candidate catalysts for diesel PM.

In perovskite-type oxides catalysts (ABO₃), B-ion is vital for reduction and catalysis. A-ion (normally rare-earth and alkaline-earth metals) is responsible for stabilizing structure. B-ion in the perovskite can be particularly active in oxidation catalysis if it can shift between two stable oxidation states to achieves electrical balance: (a) the insertion of O₂⁻ into a lattice from gas phase O₂, and (b) the formation of oxygen radicals. Meanwhile, catalytically active B-ion in the perovskite can be substituted by other elements to form oxygen vacancies. Oxygen absorbed from the gas phase and further incorporation of oxygen atoms into a lattice leads to three kinds of oxygen species, O₂⁻, O⁻ and O²⁻. Furthermore, producing high ratio of O₂⁻ to O²⁻ is important for preparing high activity perovskite oxidation catalyst [8]. Kondakiddi et al. [9] reported that partial substitution of A-ion or B-ion with other metal elements results in

the modification of valance states, and then the mobility of oxygen species in the lattice can be increased [9]. Mn-oxides always have high redox property, and Mn existing with different higher valance states is in favor of the absorption and mobility of oxygen species. In this work, Mn with several valances was used to partially substitute B-ion of LaCoO₃ catalysts. Many techniques were employed for catalyst characterization to study the influence of Mn-substitution on the catalytic performances and surface oxygen species of LaCoO₃ perovskite-type catalysts.

2. Experimental

2.1. Catalyst preparation

A series of LaCo_{1-x}Mn_xO₃ ($x = 0.05, 0.1, 0.3, 0.5, 0.7$) perovskite-type catalysts were prepared by citric acid sol-gel method. Nitrates of La, Co and Mn (II) were used as starting materials and citric acid was used as complexing agent. The nitrates and citric acid were dissolved in distilled water, and then were mixed. The mixed aqueous solution was heated and stirred to evaporate water in 80 °C water bath, then became sticky gel. After that, the gel was dried at 120 °C for 2 h in air dry oven, then calcinated at 700 °C for 4 h in muffle roaster.

2.2. Catalytic activity measurement

The catalytic activities of the prepared samples were evaluated with a temperature programmed reaction. A commercially

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available carbon black Printex-U from Degussa was used as a model of PM. The PM was mixed with the catalyst in a weight ratio of 1:9. The mixture was mixed with a spatula in order to reproduce the loose contact mode and then 555 mg mixture was placed in the quartz tube ($\Phi = 12$ mm, i.d.). Reactant gases containing 0.10 vol.% NO and 5 vol.% O₂ balanced with He were passed through a mixture of the catalyst and Printex-U at a flow rate of 100 ml/min. O₂, CO and CO₂ of the outlet gas was analyzed via an on-line gas chromatograph (Shanghai Kechuang, GC900A) with columns of TDX-01, equipped with thermal conductivity detector (TCD). The oxidation performances for catalysts were evaluated by the ignition temperature (T_i) and the maximum oxidation rate temperature (T_m) of PM.

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) experiments were performed on MSAL XD-3 diffractometer (Beijing Puxi) employing Cu K α radiation ($\lambda = 0.15418$ nm). The X-ray tube was operated at 36 kV and 20 mA. The X-ray powder diffractogram was recorded in the range of 5–90° with a scanning rate of 4/min.

FT-IR absorbance spectra were obtained in the wave number ranging between 4000 and 400 cm⁻¹ via a TENSOR27 spectrophotometer manufactured by Germer Burke Company. The measured wafer was prepared as KBr pellet with the weight ratio of sample to KBr, 1/100. The resolution was set at 4 cm⁻¹ during measurements.

Surface areas of the samples were measured via N₂ adsorption at 196 °C on a Micromeritics ASAP 2000 adsorption analyzer (America Microsoft) with the samples being outgases at 300 °C for 2 h under vacuum prior measurement. Surface areas were calculated according to Brunauer–Emmett–Teller (BET) method.

H₂-temperature-programmed reduction (H₂-TPR) measurements were measured in multi-function adsorption instrument (Tianjin Xianquan, TP5000-II). The measurements were carried out using a gas mixture of H₂-N₂ (10 vol.%) and the gas flow (40 ml/min), sample weight (50 mg), and heating schedule (10 °C/min).

The O₂-TPD experiments were performed with AutoChem II 2920 (America Microsoft). Catalyst (200 mg) was used. The sample was pretreated in O₂-He (5 vol.%, 40 ml/min) at 300 °C for 30 min, and then cooled down to 50 °C. The oxygen desorbed gradually from 50 °C to 950 °C at the rate of 10 °C/min in the He stream.

X-ray photoelectron spectra (XPS) were recorded with a VG Multilab 2000 spectrometer using Mg K α as X-ray source ($h\nu = 1253.6$ eV). The binding energies were calibrated using C1s peak of contaminant carbon (BE = 284.6 eV) as standard. Point peak fitting was carried out by XPS Peak 4.1.

3. Results and discussion

3.1. Influence of Mn-substitution amounts on PM oxidation

Curves of the relationships between the ignition temperature (T_i), the most combustion temperature (T_m) of PM and Mn-substitution amounts are illustrated in Fig. 1.

As shown in Fig. 1, T_i and T_m of PM are 338 °C and 540 °C catalyzed by LaCoO₃ without Mn-substitution. When Mn-substitution amount (x) is $0.05 \leq x \leq 0.1$, the catalytic performances of LaCo_{1-x}Mn_xO₃ are obviously improved, T_i and T_m decrease about 40 °C comparing with LaCoO₃. The catalytic performance of LaCo_{0.95}Mn_{0.05}O₃ is best with the lowest T_i (298 °C) and T_m (505 °C). An inflection point is present when Mn-substitution amount is $x = 0.1$. The catalytic performances of LaCo_{1-x}Mn_xO₃ are worse than LaCoO₃ when x is between 0.1 and 0.7. From the curves of T_i and T_m , we can know that the catalytic performances of LaCo_{1-x}Mn_xO₃

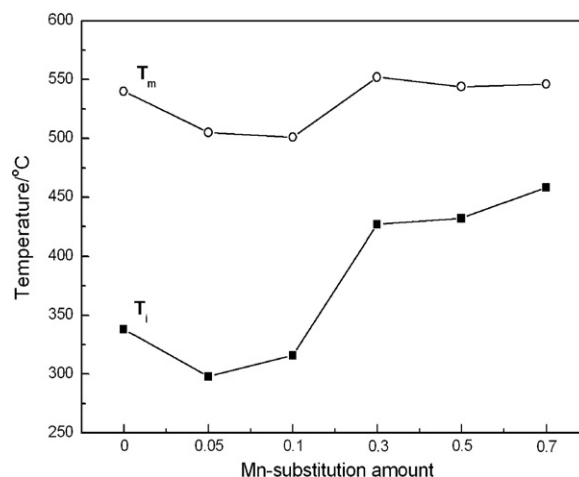


Fig. 1. The relationship between Mn-substitution amount and PM co.

become worse with the increase of x . It demonstrated that a small amount of Mn-substitution promotes PM oxidation, but a large amount impedes.

3.2. Results of XRD and BET

The XRD patterns of LaCoO₃ and LaCo_{1-x}Mn_xO₃ ($x = 0.05, 0.1, 0.3, 0.5, 0.7$) powders are illustrated in Fig. 2. The diffraction peaks of LaCoO₃ catalyst occurred at 23.2°, 32.9°, 40.7°, 47.5°, 58.6° and 69.1° (2θ), which are in great agreement with the JPCDS file. All the characteristic diffraction peaks belong to LaCoO₃ perovskite-type structure were observed in the spectra of all the catalysts substituted by Mn, and the diffraction angles (2θ) decrease with the increase of Mn-substitution amount. It indicated that LaCo_{1-x}Mn_xO₃ can form perovskite structure and their structures are influenced by Mn-substitution amount. The width of the main diffraction peaks become sharp as Mn-substitution amounts increase, demonstrating that average crystal particle sizes (D_c) increase as Mn-substitution amounts increase. It is in agreement with D_c calculated by Scherrer formula in Table 1. Comparing with the JPCDS file, we can know that Mn-oxides are mainly in the form of MnO₂ and Mn₂O₃ after calcinations. As shown in Fig. 1, LaCo_{1-x}Mn_xO₃ catalysts have not any characteristic diffraction peaks of Mn-oxides. It can demonstrate that Mn have entered the perovskite structure by replacing B-ion.

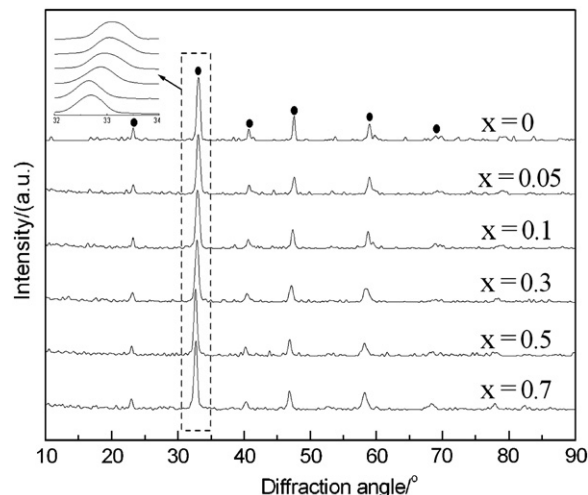


Fig. 2. XRD patterns of LaCoO₃ and LaCo_{1-x}Mn_xO₃ catalysts.

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