



Di-metal-doped sulfur resisting perovskite catalysts for highly efficient H₂-SCR of NO

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Abstract

Lanthanide perovskite catalysts doped with limited palladium (to improve activity) and cerium (to improve sulfur resistance) were prepared using sol–gel method. In different B sites, lanthanide perovskites were studied at harsh conditions for H₂ selective catalytic reduction of NO. The activity sequence was as follows: LaCeMnPd > LaCeCoPd > LaCeFePd. LaCeMnPd had a high NO conversion of 96.6% at only 150 °C. And it also had a surprising SO₂ resistance in different SO₂ concentrations. After cutting out SO₂, NO conversion recovered rapidly to its original level, indicating that the slight deactivation was reversible. In addition, the effect of gas hourly space velocity, H₂/NO ratio, O₂, and SO₂ concentration was studied. And XRD, energy-dispersive X-ray, SEM, XPS, H₂-temperature programmed reduction, and NH₃-temperature programmed desorption were performed to characterize the catalysts.

Keywords SCR · NO_x · Catalyst · Hydrogen · Perovskite · SO₂

Introduction

NO_x pollution is a major problem in industries. Selective catalytic reduction (SCR) as a post-combustion NO_x control technology has been used widely for stationary sources (Radojevic 1998). The efficiency of SCR is influenced by many factors, such as reducing agent and catalyst. NH₃ is usually employed as a reducing agent to react with NO_x. However, NH₃ slip might produce new air pollution (Gomez-Garcia et al. 2005), and the formation of NH₄HSO₄ and (NH₄)₂SO₄ would deposit on catalyst surface and corrode air preheater (APH) (Forzatti 2001). Recently, hydrogen as a clean and economic alternative has been used in NO_x reduction and exhibits good efficiency. Therefore, environmentally friendly hydrogen has received increasing attention as an ammonia replacement for NO_x reduction.

Development of proper catalyst is critical for the successful application of H₂-SCR. The main catalysts used for reducing NO_x are as follows: supported noble metal catalysts (Pt/Al₂O₃; Acke et al. 1998), metal oxide catalysts (V₂O₅/TiO₂; Chen and Yang 1990), and metal ion exchanged zeolites-crystalline silicate (Cu-ZSM-5; Petunchi and Hall 1993; Skalska et al. 2010). While those catalysts are used widely in industries, some problems also exist such as highly cost, poor activity in low temperature, and sensitivity to sulfur dioxide.

Perovskite type catalyst is a promising solution for those problems (Lisi et al. 1999). Perovskite was mainly used as catalyst for the reaction NO + CO in motor vehicles' exhaust gas (Hosseini et al. 2018; Zhang et al. 2006a). Limited data are reported for perovskite in NO_x reduction with H₂. The general formula of perovskite is ABO₃, in which A ions are rare earth metal cations coordinated by 12 oxygens in octahedron and B ions are transition metal cations surrounded by six oxygens in octahedron (Rojas et al. 1990; Shi et al. 2017). A and B sites can be replaced partially by other metal cations with close atomic radius.

In this paper, we choose a series of perovskites in which lanthanum is the original occupier of A site. It has been proved that cerium can improve the SO₂ resistance in the catalyst. Wenqing Xu et al. studied the effect of SO₂ poisoning over Ce/TiO₂ catalyst in the SCR of NO_x with ammonia and

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obtained 90% conversion of NO in the presence of 100 ppm SO₂ at 350 °C for 48 h (Xu et al. 2009). So we doped certain percentage of cerium to substitute A site partially. However, perovskites always have a good activity at rather high temperature ($T > 450$ °C) (Zhang et al. 2006b), while some noble metals like Pt and Pd can exhibit good activity at much lower temperature. Qingqing Zhang et al. conclude that Pt/Pd-based catalysts can reduce NO completely at 150 °C (Zhang et al. 2013). A. Barrera et al. obtains 100% NO conversion over Pd/La and Pd/Al-La-15 at 150 °C (Barrera et al. 2001). To enhance the efficiency of NO_x reduction and obtain good NO_x conversion at relative low temperature, limited amount of noble metal palladium is added in the B site of perovskite. The doping components consisted of Pd²⁺ and Ce⁴⁺ will create vacancies (mainly oxygen vacancies) that depend on the doping contents and their special located sites (Das et al. 2018). The Pd²⁺ substitutes the Mn³⁺; it will create an oxygen vacancy by two Pd sites in the B sites. In contrast to A sites, it will generate a cation vacancy by two Ce sites. Meanwhile, it is observed that di-metal doping of cerium and palladium form a synergistic effect that can maintain a good efficiency under high oxygen concentration. The novel catalyst aims at having a special function of high efficiency, low cost, and good SO₂ resistance at low temperature and high oxygen content.

Experimental section

Catalyst preparation

All the catalysts are prepared via citric acid sol–gel method. All the chemicals are A.R. grade or better. Take La_{0.9}Ce_{0.1}Mn_{0.9}Pd_{0.1}O₃, for example; a stoichiometric quantity of La (NO₃)₃·nH₂O, Ce(NO₃)₃·6H₂O, MnCl₂·4H₂O, and PdCl₂ is dissolved in deionized water. And then, citric acid is added with a molar ratio of metal cations: citric acid = 1:1. The mixture is stirred constantly at 80 °C, 700 r min^{−1}, until deionized water is evaporated and wet gel is formed. Subsequently, the wet gel is dried in air at 100 °C for 12 h until the gel self-combusts to spongy residues. Then, the residues are calcined at 700 °C for 4 h to finish the process.

Characterization methods

X-ray diffraction (XRD) data is obtained by an X-ray diffractometer (D/max 2550 V) detected between 10° and 80° using a Cu Kα radiation at 40 kV and 100 mA. The element composition of catalysts is confirmed by energy-dispersive X-ray (EDX) spectrometer (Falion 60S system). The morphology of catalysts is characterized by scanning electron microscopy (SEM; NOVA NanoSEM 450). The surface properties of the catalysts are determined by X-ray photoelectron spectroscopy (XPS) analysis using ESCALAB 250Xi as instrument. The

experiment is carried out under an Al Kα radiation at an energy step size of 0.05 eV to obtain high-resolution XPS spectra, and the spectra is calibrated with respect to C 1s at a binding energy of 284.8 eV.

H₂-temperature programmed reduction (H₂-TPR) and NH₃-temperature programmed desorption (NH₃-TPD) experiments are tested with a chemisorption analyzer (Micromeritics, AutochemII2920). For further experiments, each sample is treated at 300 °C for 60 min with He before experiment and then is analyzed from room temperature to 800 °C with the mixture of 10% H₂/Ar for 40 mL min^{−1} at a heating rate of 10 °C min^{−1}. For the latter experiment, the samples are pretreated at 50 °C for 60 min with 10% NH₃/He at a flow rate of 40 mL min^{−1}, and then the samples are swept continually with He flow for 60 min at a flow rate of 40 mL min^{−1}. Subsequently, the samples are heated from room temperature to 800 °C at 10 °C min^{−1} under a 50-mL min^{−1} flow of He to record the desorption curve.

Catalyst activity evaluation

The selective catalytic reduction (SCR) of NO by H₂ is performed in a fixed bed flow reactor at atmospheric pressure. Catalyst powder (0.2 g) is loaded in a quartz tube with calcined silicon dioxide for support. Silicon dioxide is calcined at 600 °C until it is stable before experiment. The gas outlet of the reactor is connected with an online chemiluminescent NO–NO₂–NO_x Analyzer (Thermo, Model 42i) to monitor the concentration of NO and NO_x.

The activity of catalysts is evaluated by changing the composition of simulated flue gas, including NO (900–1400 ppm), H₂ (10000–14,000 ppm), O₂ (0%–6%), SO₂ (100–300 ppm when used), N₂ (as the balance gas), and the space velocity of the reaction. The simulated flue gas firstly flows into the reactor and contacts the catalyst bed to have a reaction at setting temperature and flow rate. The temperature is controlled by a K-type thermocouple unit inside and outside the fixed bed at the range of 50–400 °C. The flow rate is controlled by Brooks thermal mass flowmeter to maintain the gas hourly space velocity (GHSV) at fixed value (32,000 h^{−1}). The effluent gas is then analyzed to determine NO concentration.

Results and discussion

Catalyst characterization

The XRD patterns of the synthesized samples with diverse B site cations are shown in Fig. 1a. LaMnO₃, La_{0.9}Ce_{0.1}Mn_{0.9}Pd_{0.1}O₃ (LaCeMnPd), and La_{0.9}Ce_{0.1}Co_{0.9}Pd_{0.1}O₃ (LaCeCoPd) exhibit similar intense diffraction peaks of (110), (104), (024), and (214), and other weak crystal planes are marked in the figure with symbol “.”.

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