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Cu- and Pd-substituted nanoscale Fe-based perovskites for selective catalytic reduction of NO by propene

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Abstract

A series of Fe-based perovskites with high specific surface area was prepared by a new method, reactive grinding, and characterized by N_2 adsorption, XRD, SEM, H_2-TPR, TPD of O_2, TPD of $NO + O_2$, TPD of C_3H_6, and TPSR of $NO + O_2$ under C_3H_6/He flow. These materials were then subjected to activity tests in the selective catalytic reduction of NO by propene. The catalytic performance over $LaFeO_3$ is poor but can be improved significantly by incorporating Cu into its lattice, resulting in N_2 yields over $LaFe_{0.8}Cu_{0.2}O_3$ of 81% at 450 °C and 97% at 700 °C with a reactant mixture containing 3000 ppm NO, 3000 ppm C_3H_6, and 1% O_2 in helium at a space velocity of 50,000 h^{-1}. The enhanced NO reduction after Cu substitution is attributed to the easy formation of nitrate species, which have high reactivity toward C_3H_6. A mechanism was proposed with the formation of nitrate species as the first step and organo nitrogen compounds as important intermediates. Great catalytic performance at low temperature was also achieved over $LaFe_{0.97}Pd_{0.03}O_3$ with a N_2 yield of 67% and C_3H_6 conversion of 68% at 350 °C corresponding to the outstanding redox properties of this catalyst. O_2 can act as a promoter to oxidize NO into strongly adsorbed nitrate species, and also can accelerate the transformation of organo nitrogen compounds and isocyanate to get the desired products. In contrast, at higher concentrations O_2 has a detrimental effect, leading to consumption of the reducing agent by the complete oxidation of C_3H_6.

Keywords: SCR of NO; Propene; Reactive grinding; High surface area; Fe-based; Perovskite; TPR; TPD

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1. Introduction

Perovskite oxides, promising alternatives to supported noble metals, have attracted much attention for exhaust gas depollution because of their low cost, thermal stability at rather high temperatures, great versatility, and excellent redox properties. Most previous studies on the use of perovskites for the purification of motor vehicles exhaust gas from NO_x have involved the reaction between NO and CO [1–3]. Much less work has been reported on NO reduction using propene as a reducing agent in the presence of oxygen over perovskite-type oxides. Moreover, the limited data related to $NO + C_3H_6 + O_2$ reaction over perovskites shows poor catalytic performance, with maximal NO conversion to N_2 of $<25\%$ [4,5]. Consequently, new efforts are needed to improve the catalytic activity toward NO reduction by C_3H_6 in the presence of O_2 over perovskites, aiming to satisfy the requirements for their practical application.

It is well known that the catalytic characteristics of perovskites for various reactions and their redox properties depend primarily on the preparation procedure. The conventional method of perovskite preparation, the so-called "ceramic method," involves a calcination step with a temperature of at least 800 °C. As a result, large grain size and low specific surface area are usually obtained with a value of several m^2/g or even less [6]. Some other methods for preparing perovskites, including microemulsion [7], spray-drying [8], freeze-drying [9], citrate complexation [10], co-precipitation [11], and the sol–gel process [12], were developed to increase the specific surface area of perovskites by means of synthesis and calcination at relatively low temperatures (500–600 °C). The specific surface areas of perovskites generated by the foregoing methods can reach 10–30 m^2/g. Recently, a new method for perovskite preparation—reactive grinding—has been proposed

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by our group, generating a wide variety of perovskites at room temperature with extraordinarily high specific surface areas (on the order of 100 m^2/g) when grinding additives are used [13–15].

The selection of B-site cations is of essential importance in designing perovskite catalysts as well as in modifying their catalytic properties, because the catalytic properties of perovskite-type oxides are practically determined by the nature of their B-site cations [16,17]. Fe-based perovskites were thought to be suitable catalysts for air pollution control because of their great performance in interactions between CO and NO [1], despite the scarcity of investigations into selective catalytic reduction of NO by C_3H_6 in the presence of O_2. Moreover, B-site substitution of perovskites was also considered an effective way to improve their catalytic properties due to the generation of new lattice defects, mixed valence states, and nonstoichiometric oxygen [18]. Copper-containing catalysts are of special interest because they are active in the transformation of nitrogen oxides [19], with the low-coordination isolated Cu ions as active sites [20,21]. In addition, the activity of Pd-substituted lanthanum cuprates was found to be comparable to that of Pt-Rh/CeO_2-Al_2O_3 for NO reduction and higher for CO and C_3H_6 oxidation [22]. A special self-regeneration character on Pd-containing perovskite was also described by Nishihata et al., who showed that Pd can move back and forth between the B-site in the perovskite and the metal oxide when exposed to fluctuations in the redox characteristics of the emission exhaust [23]. Cu and Pd ions, with valence states different from those of Fe ions in a perovskite lattice, thus may be interesting candidates for partial B-site substitution in $LaFeO_3$.

In the present study, a parent $LaFeO_3$ and its corresponding Cu- or Pd-substituted perovskites ($LaFe_{0.8}Cu_{0.2}O_3$ and $LaFe_{0.97}Pd_{0.03}O_3$), synthesized by reactive grinding, were characterized by X-ray diffraction (XRD), temperature-programmed reduction by hydrogen (H_2-TPR), temperature-programmed desorption (TPD) of O_2, $NO + O_2$, and C_3H_6, and temperature-programmed surface reduction (TPSR) of $NO + O_2$ under C_3H_6/He flow. The samples were also tested in a fixed-bed reactor for NO reduction with propene in the presence or absence of 1% O_2. This research was carried out to identify the different physicochemical properties of $LaFeO_3$ before and after Cu or Pd substitution, as well as to illustrate the correlation between the modification of their structure and their catalytic behaviors. Another objective of this work was to propose a reaction mechanism for NO reduction over Fe-based perovskites.

2. Experimental

A series of Fe-based mixed oxides was synthesized by reactive grinding in a manner similar to that reported previously [13–15]. Desired amounts of La_2O_3 (Alfa, 99.99%), Fe_2O_3 (Baker & Adamson, 97.49%), CuO (Aldrich, 99%), or PdO (Aldrich, 99.98%) were fully mixed and milled inside a tempered-steel vial using three tempered-steel balls under an air atmosphere. Grinding was conducted in two steps of 8 h for synthesis and 10 h for refining, with ZnO as the grinding additive.

The specific surface area of the samples calcined at 500 °C for 5 h was determined using an automated gas sorption system (NOVA 2000; Quantachrome) through nitrogen adsorption equilibrium at −196 °C. Before measurements were done, samples of about 200 mg were outgassed at 300 °C under vacuum for 6 h to remove any remaining humidity. The chemical composition (Fe, Cu, Pd) of the catalysts was established by atomic absorption spectroscopy (AAS) using a Perkin-Elmer 1100B spectrometer after the samples were dissolved in a mixture of 25 ml of 10% HCl and 2 ml of concentrated HF at 60 °C for 24 h. The amount of La in the perovskites was measured using an inductively coupled plasma (ICP) spectrometer (Optima 4300DV; Perkin-Elmer) with the same pretreatment before analysis as used for AAS. The final products were characterized by XRD using a Siemens D5000 diffractometer with Cu-K_α radiation ($\lambda = 1.5406$ Å) in a range $20^\circ < 2\theta < 70^\circ$ with steps of $0.05^\circ(2\theta)$ each for 2.4 s. Crystallite sizes were determined using Scherrer's equation after considering the instrumental broadening, whereas the crystal phases were identified via the JCPDS reference. The morphology of the mixed oxides after calcination at 500 °C for 5 h was recorded at 100,000× magnification by scanning electron microscopy (SEM), using a JEOL JSM 840A at 110 kV.

H_2-TPR and TPD of O_2, $NO + O_2$, and C_3H_6 were conducted in a fixed-bed continuous-flow reactor. Before performing the H_2-TPR study, the sample (about 50 mg) was heated to 500 °C and maintained at this temperature for 1 h under 10% O_2. Before performing the TPD of O_2, $NO + O_2$, and C_3H_6-TPD, the sample was pretreated in 10% O_2, 3000 ppm $NO + 1\%$ O_2, and 3000 ppm C_3H_6, respectively, balanced by He, at 500 °C for 1 h, followed by cooling to room temperature under the same atmosphere and purging with He for 40 min. The sample was heated again from room temperature to 800 °C at a rate of 5 °C/min with a 20 ml/min 5% H_2/Ar flow in the TPR study, and the effluent gases were monitored on-line using a thermal conductivity detector (TCD). A cold trap was used to remove the water from effluent gas before it went through the TCD. The sample was flushed with 20 ml/min of He at a rising temperature up to 500 °C (800 °C for O_2-TPD) at a rate of 10 °C/min in the TPD analysis. The O_2, NO, N_2O, and N_2 desorbed during O_2-TPD and $NO + O_2$-TPD experiments were simultaneously detected and recorded on-line by mass spectrometry (MS) with mass numbers of 32, 30, 44, and 14, respectively. Moreover, C_3H_6, CO, and CO_2 desorbed during C_3H_6-TPD experiments were monitored with the mass numbers of 41, 28 and 44, respectively.

TPSR of $NO + O_2$ under C_3H_6/He flow over $LaFe_{0.8}Cu_{0.2}O_3$ was performed with the same sample pretreatment used for TPD of $NO + O_2$, but the thermodesorption was performed in 1000 ppm of C_3H_6/He instead of He. The desorbed C_3H_6, NO, and O_2 together with generated CO_2, N_2, and H_2O were monitored by MS with mass numbers of 41, 30, 32, 44, 14, and 18, respectively.

The selective catalytic reduction (SCR) of NO by C_3H_6 was conducted in a tubular fixed bed reactor at atmospheric pressure. A gas mixture of 3000 ppm of NO, 3000 ppm of C_3H_6, with or without 1% O_2, and the balance He, passed through