

An investigation of NO/CO reaction over perovskite-type oxide $\text{La}_{0.8}\text{Ce}_{0.2}\text{B}_{0.4}\text{Mn}_{0.6}\text{O}_3$ (B = Cu or Ag) catalysts synthesized by reverse microemulsion

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Abstract

The perovskite-type oxides $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3$ prepared by reverse microemulsion and sol–gel methods (denoted as R and S, respectively), have been investigated on their catalytic performance for the (NO + CO) reaction, and characterized by means of temperature-programmed desorption (TPD), X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). XRD measurements proved the presence of the perovskite phase with a considerable amount of CeO_2 phase and the formation of CeO_2 phase was restrained with the reverse microemulsion method. TEM investigations revealed that the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ -R nanoparticles were uniform spheres in shape with diameters ranging from 40 to 50 nm, whereas an aggregation of particles was found for the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ -S catalyst. The activity of NO reduction with CO decreased in the order of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ -R > $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ -S > $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3$ -R > $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3$ -S. In NO-TPD experiments, the principal desorbed species detected in the effluent was NO with a trace amount of O_2 and N_2O , suggesting that the non-dissociated adsorption of NO on the surface of the perovskite-type oxides was dominant. The XPS results revealed that Ce^{4+} and Cu^+ was the predominant oxidation state for Ce and Cu components in $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3$ catalysts. The existence of Cu^+ ions and its redox reaction ($\text{Cu}^+ \leftrightarrow \text{Cu}^{2+}$) would benefit the NO adsorption and reduction by CO.

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1. Introduction

The reaction of NO and CO has been paid a great attention by many research groups due to its existence in exhaust gases of both mobile and immobile sources. The catalysts employed in the reaction are usually noble metals and perovskite-type oxides. Generally speaking, perovskite-type oxides do not show as good catalytic performance as noble metals. Nevertheless, they have comparable activity and been considered as potential depolluting catalysts in some cases [1].

The physicochemical properties of perovskite-type oxides (general formula ABO_3) can be regulated to meet the requirements of certain desired reactions by partially substituting A and/or B with other metals of different oxidation states

since the oxidation state of B cation and the structural defect (such as anionic or cationic vacancies) can be changed by the manipulation. During the past years, the perovskite-type oxides such as LaMO_3 , $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ (M = Fe, Co, Mn, Cr, Ni) [2,3], LaMnO_3 , $\text{LaMn}_{0.99}\text{Pt}_{0.01}\text{O}_3$ [4], $\text{La}_{1-x}\text{Sr}_x\text{Al}_{1-2y}\text{Cu}_y\text{Ru}_y\text{O}_3$ [5,6], LaCoO_3 [7,8], $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-2y}\text{Cu}_y\text{Ru}_y\text{O}_3$ [9], $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ [10,11], $\text{La}_2\text{Cu}_{1-x}\text{Fe}_x\text{O}_4$ [12], and $\text{La}_{1-x-y}\text{Sr}_x\text{Ce}_y\text{FeO}_3$ [13,14] have been intensively studied and used to catalyze the reaction of NO and CO.

Although perovskite-type catalysts have showed good performance in many reactions, the low surface area is always the disadvantage. Usually, perovskite-type oxides are prepared by calcination at high temperatures ($>800^\circ\text{C}$), resulting in a surface area of less than $10\text{ m}^2\text{ g}^{-1}$. In order to increase catalytic activity, various attempts to enhance the surface area have been made by using methods such as mist-drying, chelating and metal–citric–cellulose complexing, sol–gel process, and hydrothermal synthesis [15]. Recently, the reverse microemulsion

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technology has been investigated for preparing nanoparticles of pure metal, metal oxides as well as perovskite-type oxides. Giannakas et al. [16] reported that LaMnO_3 prepared via cetyltrimethyl ammonium bromide (CTAB)–butanol–octane–nitrate salt microemulsions possessed relatively high specific surface area of $20 \text{ m}^2 \text{ g}^{-1}$ and nanoparticle size of 20–100 nm, which was claimed to be a promising catalyst as a substitute for noble metals in the de- NO_x application.

In this work, the perovskite-type oxides $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3$ were prepared by reverse microemulsion and sol–gel methods. The performance of the two kinds of perovskite-type oxides for the reaction of NO and CO and the characterization of the materials using temperature-programmed desorption (TPD), X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) are reported.

2. Experimental

2.1. The preparation of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3\text{-S}$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3\text{-S}$

The $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3\text{-S}$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3\text{-S}$ catalysts were prepared by means of citric acid complexing sol–gel process [17]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Beijing Chemical Reagents Company, >99%), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Beijing Chemical Reagents Company, >99%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sinopharm Group Chemical Reagent Co, >99.5%) or AgNO_3 (Beijing Chemical Reagents Company, >99.8%), and $\text{Mn}(\text{NO}_3)_2$ hydro-solution (Beijing Yili Fine Chemical Reagents Company, >49%) at the appropriate ratio were mixed in aqueous solution. Citric acid (Aldrich, >99%) equimolar to the metals was added. The solution was then evaporated at 80°C to produce a viscous syrup. After subsequent evaporation at 120°C for 8 h and calcination at 850°C in air for 10 h, the material was in turn ground, tabletted, crushed, and sieved to a size range of 60–80 mesh.

2.2. The preparation of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Cu}_{0.4}\text{Mn}_{0.6}\text{O}_3\text{-R}$ and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ag}_{0.4}\text{Mn}_{0.6}\text{O}_3\text{-R}$

Two reverse microemulsions of CTAB/1-butanol/water/*n*-heptane with identical weight ratios of CTAB:1-butanol:water:*n*-heptane = 21:15:27:37 were prepared: one comprising desired amounts of chemicals same as those used in Section 2.1 (denoted as precursor solution A), the other comprising a precipitating agent of 0.5 M NaOH solution (denoted as precursor solution B). Equal amounts of the two precursor solutions A and B were mixed together with continuous stirring at 30°C for 2 h. After the particles were formed in water droplets, they were not precipitated and the mixed microemulsion containing the particles remained transparent due to the adsorption of surfactant molecules at the oil/water interface. After acetone was added, the reaction occurred and the result was the destruction of the microemulsion and the generation of co-precipitation. Then, the as-received precipitations were washed with acetone and water repeatedly to remove the oil, remained Na^+ , and surfactant molecules adsorbed on the

surfaces of particles. Finally, the washed particles were collected, dried at 120°C for 8 h and calcined at 850°C in air for 10 h. The obtained powders were in turn ground, tabletted, crushed, and sieved to a size range of 60–80 mesh.

2.3. Reaction and characterization

The catalytic activity of NO and CO reaction was evaluated in a quartz tube micro-reactor (i.d. = 10 mm) with a gas mixture of 1%NO + 1%CO + 98% He. The space velocity (SV) was $20,000 \text{ h}^{-1}$. Five hundred milligrams of the catalyst was packed in the middle of the reactor between two plugs of quartz. A thermocouple was placed in direct contact with the catalyst for accurate temperature measurement. Products were analyzed, usually 30 min after temperature stabilization, by an on-line gas chromatograph (Shimadzu GC-14C). A Porapak Q + R column, which was dipped in a acetone-water- $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ bath to keep the column temperature of -20°C , was used to separate NO, NO_2 , and N_2O . A 5A molecular sieve column was used (in parallel) to separate N_2 , O_2 , CO, and CO_2 .

The NO-TPD experiments were carried out in a similar micro-reactor. Before performing a TPD experiment, the samples (50 mg) were heated to 800°C in O_2 and maintained at the temperature for 1 h in order to clean the surface of the samples and then pretreated in situ in NO (30 ml min^{-1}) at 450°C for 1 h, followed by cooling to room temperature in the same atmosphere and purging with He for 10 min. After being cooled to room temperature, the sample was heated from 30 to 850°C at a rate of $15^\circ\text{C min}^{-1}$. The effluent gases were monitored and analyzed on-line by a mass spectrometer (Hiden, HPR20).

The crystal structures of the catalysts were determined by an X-ray diffractometer (D8 Advance) operating at 35 kV and 35 mA using Cu $\text{K}\alpha$ radiation. The patterns recorded were referred to the powder diffraction files—1998 ICDD PDF database for the identification. The specific surface areas of catalysts were measured using the BET method on an ASAP2020 apparatus.

XPS (Leybold Heraeus-Shenyang SKL-12) technique was used to determine the core-level binding energies of the cations in the catalysts, using monochromatic Al $\text{K}\alpha$ as the excitation source. Before carrying out the XPS experiments, the samples were treated in O_2 (30 ml min^{-1}) at 800°C for 1 h. The C 1s line at 284.6 eV was taken as a reference for binding energy calibration.

3. Results

3.1. Catalytic performance for the (NO + CO) reaction

The catalytic performance of the four catalysts for the (NO + CO) reaction at $\text{SV} = 20,000 \text{ h}^{-1}$ is shown in Figs. 1 and 2. Only N_2 , N_2O , and CO_2 were detected in the reaction effluents under the adopted reaction conditions. Over all the catalysts investigated in the present work, the NO conversion increased with the rise in temperature. From Fig. 2, one can see that the N_2O yield increased at first and then decreased with

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