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Effect of Ce on NO direct decomposition in the absence/presence of O_2 over $La_{1-x}Ce_xSrNiO_4$ ($0 \le x \le 0.3$)

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Abstract

Effect of cerium ions on the activity of $La_{1-x}Ce_xSrNiO_4$ ($0 \le x \le 0.3$) for NO decomposition was investigated both in the absence and presence of oxygen. The amount of Ce in the frame reached 30 at.% ($x = 0.3$) in the present case without destroying the matrix structure. The Ce-substituted samples showed high activity for NO decomposition not only in the absence of O_2 but also in the presence of O_2, and the specific activity reached 1.59 μmol s^{-1} m^{-2} even 6.0%O_2 was fed to the reactant gas ($La_{0.7}Ce_{0.3}SrNiO_4$, $T = 1123$ K), indicating that the Ce addition can enhance the oxygen forbearance of catalyst. In addition, a new highly active site, which facilitates oxygen mobilization and desorption, might be formed in the sample due to the Ce addition, which thus resulted in the high activity for NO decomposition.

Keywords: Nitrogen oxide; Direct decomposition; Ce; Active site; Oxygen forbearance

1. Introduction

Nitrogen oxides (NO_x), one of the serious pollutants in the earth's atmosphere, have been received much attention even a century ago because of the harm to environment and human body. Their removal from all sources remains great challenge, in spite of all progress made over the years [1–3]. Catalytic NO decomposition is the most desirable way of removing NO_x from exhaust gas streams since it does not involve the addition of a supplemental reductant and the products of the reaction (N_2 and O_2) are nontoxic [4]. However, it is known that in the process of NO decomposition, the oxygen produced from NO dissociation is often strongly bonded to the catalyst surface, poisoning NO dissociation site and preventing NO dissociation further [5]. Hence, to promote the oxygen desorbing from the active site is one of the effective ways to improve the activity of NO decomposition.

Among the catalysts for NO decomposition, Cu-ZSM-5 is the most excellent one and exhibits high activity even at low temperatures (∼773 K) [6,7]. But the shortcomings of Cu-ZSM-5 are the narrow temperature range with high activity and the unstable structure at high temperatures. When O_2 and/or H_2O, especially SO_2 coexisted in the reactant, the activity of NO decomposition decreased abruptly. Another sort of interesting catalysts for NO decomposition are perovskite(-like) mixed oxides with ABO_3 or A_2BO_4 structure [2], in which the valence of B-site transition metal, as well as the number of oxygen vacancies are controllable by partial substitution of A- and/or B-sites ions, without destroying the matrix structure. Here, the active site is thought to be F-center, described as: $[\,]M^{n+} \Leftrightarrow [e^-]M^{n+1}$ [8].

Recently, cerium received much attention in designing catalyst for NO decomposition because of its excellent performance for oxygen storing/scavenging. Delmon and co-workers [9] found that the activity of $LaCoO_3$ was significantly improved when CeO_2 doping in $LaCoO_3$. Pomonis and co-workers [10,11] found that the NO decomposition rate accelerated with the increase of CeO_2 content in La–Sr–Ce–Fe–O system. Misono and co-workers [12,13] investigated the property of Sr-, Ce- and Th-substituted $LaMO_3$ (M = Mn, Fe, Co) in detail and found that only

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the Ce-substituted samples showed improving property for oxygen mobility. All these results showed that catalytic performance of catalyst could be improved by cerium addition.

In this paper, based on our previous works [14–16] we investigated the transformation of active site as well as the effect of Ce content on the catalytic performance of $La_{1-x}Ce_xSrNiO_4$. The high activity of $La_{1-x}Ce_xSrNiO_4$ ($x \leq 0.3$) for NO decomposition suggests that a new highly active site, which facilitates oxygen mobilization and desorption, is formed due to the Ce addition.

2. Experiment

2.1. Preparation

$La_{1-x}Ce_xSrNiO_4$ with x from 0 to 0.7 was prepared by the conventional citrate method [17]. Briefly, to an aqueous solution of La^{3+}, Ce^{3+}, Sr^{2+} and Ni^{2+} nitrates (all are in A.R. pure grade) with appropriate stoichiometry, a solution of citric acid 50% in excess of stoichiometry was added. The resulting solution was evaporated to dryness, and then the precursors obtained were decomposed in air at 573 K, calcined at 873 K for 1 h and finally pelletized and calcined at 1173 K in air for 6 h, the synthesized pellets were pulverized to 40–80-mesh size to be used.

2.2. Characterization

Powder X-ray diffraction (XRD) data were obtained from an X-ray diffractometer (type D/MAX B, Rigaku) operated at 40 kV and 10 mA at room temperature, using Cu Kα radiation combined with nickel filter. The diffraction angle 2θ falls between 20° and 80°.

Specific surface areas (SSA) of catalyst were measured by N_2 adsorption at 77 K with a Micromeritics ASAP2010 instrument.

Infrared spectra (IR) in the range 1800–400 cm^{-1} were recorded on a Nicolet-5DX FT-IR spectrometer with a TGS detector. Samples were produced in the form of KBr pellets.

Temperature programmed desorption of oxygen (O_2-TPD) was carried out on conventional apparatus equipped with a thermal conductivity detector (TCD). The samples (0.2 g) were first treated in O_2 at 1073 K for 1 h and cooled to room temperature in the same atmosphere, then swept with helium at a rate of 11.8 mL/min until the base line on the recorder remained unchanged. Finally, the sample was heated at a rate of 20 K/min in helium to record the TPD profile.

2.3. Catalytic activity measurement

Steady-state activities of catalysts were evaluated using a single-pass flow micro-reactor made of quartz, with an internal diameter of 6 mm. The reactant gas was passed through 0.5 g catalysts (1%NO/He) at a rate of 25 mL/min or 0.8 g catalysts (1%NO + 1–6%O_2/He) at a rate of 40 mL/min (to keep $W/F = 1.2\ g\ s\ mL^{-1}$). The gas composition was analyzed before and after the reaction by an online gas chromatography, using molecular sieve 5 A column for separating NO, N_2 and O_2. N_2O was not analyzed here because it was difficult to form between 773 and 1123 K [18]. Before the data were obtained, reactions were maintained for a period of ~2 h at each temperature to ensure the steady-state conditions. The activity of NO decomposition was evaluated by the following equation:

$$N_2\ \text{yield (specific activity)} = \frac{1}{A_S}\frac{2[N_2]_{out}}{[NO]_{in}} \times 100$$

where A_S represented the specific surface areas of catalyst; $[NO]_{in}$ and $[N_2]_{out}$ were the concentration of NO and N_2 measured before and after the reaction, respectively.

3. Results and discussion

3.1. Study of powder X-ray diffraction

Fig. 1(a) shows the XRD patterns of $La_{1-x}Ce_xSrNiO_4$ with x from 0 to 0.7 (also see Table 1). All the samples have the perovskite-like structure with A_2BO_4 type. The peak at $2\theta = {\sim}28°$ (characteristic diffraction peak of CeO_2 phase) increased with the increase of Ce content, which might imply the appearance of CeO_2 phase, but this peak was also the reflection peak of $La_{1-x}Ce_xSrNiO_4$ (see XRD patterns of sample $x = 0$). Hence, in order to clarify whether this peak contains the contribution of CeO_2, the intensity ratio of CeO_2 ($2\theta = {\sim}28°$) to $La_{1-x}Ce_xSrNiO_4$ ($2\theta = {\sim}31.8°$) was plotted [9]. The results in Fig. 1(b) shows that this ratio (curve I) was almost unvaried at the beginning ($0 \leq x \leq 0.3$), then increased abruptly after $x > 0.3$, suggesting that the peak ($2\theta = {\sim}28°$) appeared in the sample $x \leq 0.3$ does not include the contribution of CeO_2. Namely, Ce occupied the La-site of $La_{1-x}Ce_xSrNiO_4$ completely at $x \leq 0.3$ without destroying the matrix structure. After $x > 0.3$, the abrupt increase of the ratio indicated that Ce cannot occupy the La-site of $LaSrNiO_4$ completely and CeO_2 phase appeared. Besides, a minor evidence obtained from XRD patterns also supported the result that Ce can occupy the La-site of $La_{1-x}Ce_xSrNiO_4$ completely at $x = 0.3$ (here, "minor" means that the peak analyzed is not the first strongest peak of CeO_2, but the fourth one). From Fig. 1(c), which

Table 1
Crystal structure and specific surface area (SSA) of the used catalysts

Catalysts	Crystal structure	BET surface area (m^2/g)
$LaSrNiO_4$	P-l	6.5
$La_{0.9}Ce_{0.1}SrNiO_4$	P-l	7.0
$La_{0.7}Ce_{0.3}SrNiO_4$	P-l	5.0
$La_{0.5}Ce_{0.5}SrNiO_4$	P-l + CeO_2	4.8
$La_{0.3}Ce_{0.7}SrNiO_4$	P-l + CeO_2 + P′	4.5

P-l: perovskite-like structure ($La_{1-x}Ce_xSrNiO_4$); P′: other perovskite phase(s).