



The effects of BaO on the catalytic activity of $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ in direct decomposition of NO



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ABSTRACT

The $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_{4-x}\text{BaO}$ ($x=0, 5, 10, 15, 20, 25, 30$) catalysts were prepared by heating the mixture of $\text{Ba}(\text{NO}_3)_2$ and $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ in situ, and their catalytic performances were evaluated for NO direct decomposition. The results showed that the activities of the $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_{4-x}\text{BaO}$ catalysts had been improved with the increasing of BaO amount. Among these catalysts, the $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_{4-20}\text{BaO}$ exhibited the best catalytic performance for NO direct decomposition, and the yield of N_2 kept 57% during 500 h at 923 K in the absence of O_2 , even the concentration of O_2 was 0.2% in the feed, the N_2 yield still up to 57% at 923 K. So much higher activity for the perovskite(-like) oxides catalysts at such reaction temperature was first observed. In order to understand the role of BaO, a serial of experiments and characterizations were carried out on the $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_{4-x}\text{BaO}$ catalysts. The results revealed that the number of chemical adsorption oxygen adsorbed on the oxygen vacancies increased and the mobility of the lattice oxygen could be improved due to the BaO addition. Moreover, BaO may play an important role in NO_x transportation and storage, which is favorable for the regeneration of the active sites.

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1. Introduction

Nitrogen oxides (NO_x), emitted from coal and fossil combustion, are extremely toxic to human health and also harmful to the environment, which can result in acid rain, photochemical smog, ozone depletion and atmospheric visibility degradation [1]. In order to minimize the NO_x emission, several techniques have been developed in the past years, such as three-way catalyst (TWC) [2], NO_x storage reduction catalysts (NSR) [3] and selective catalytic reduction (SCR) by NH_3 [4]. TWC and SCR have been applied in the automobile engine exhaust and stationary source emission, respectively. However, the direct decomposition of nitric oxide (NO) into harmless N_2 and O_2 is regarded as one of the most attractive methods for NO removal based on its negative Gibbs free energy and thermodynamically favorable [5–7]. Moreover, this reaction is simple, economical and does not require any other reductants like NH_3 , H_2 , CO, or hydrocarbons.

Since the early work carried out by Winter [8], a number of catalysts have been examined for the direct decomposition of NO, such as precious metals [9,10], metal oxides [8,11], ion exchanged zeolites [12,13] and perovskites [14,15]. However, activities of the proposed catalysts up to now are not high enough for the use in a practical application and it is also known that these catalysts are easily deactivated by adsorption of oxygen formed by direct decomposition of NO.

Perovskite(-like) oxides, ABO_3 and A_2BO_4 structures, have high structural stability, and the A- and/or B-site cations can be substituted by a foreign cation having different oxidation states or radius [16,17]. Thus, the oxidation state of B-site cation and the content of oxygen vacancy can be controlled when desired foreign cation is used, offering a convenient and feasible way of correlating physicochemical properties with catalytic performance of the materials. Many perovskite-like oxide catalysts have been investigated on NO direct decomposition based on their structural properties. Teraoka et al. reported that $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ was highly active in NO decomposition, the yield of N_2 and O_2 reached to 72% and 40% at 1073 K, respectively [15]. They found that the yield of N_2 was much higher than that of O_2 , which suggested that the surface of the catalyst was covered by strongly adsorbed oxygen, and the removal of surface oxygen followed by adsorption of NO might be the most important

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steps for the NO decomposition reaction. $\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_{0.8}\text{In}_{0.2}\text{O}_3$ perovskite oxides exhibited much higher activity to NO direct decomposition over 1073 K, which was reported by Ishihara et al. [18]. Zhao et al. also found that LaSrNiO_4 showed far much higher activity than La_2NiO_4 in the reaction, with NO conversion of 94% and 20%, respectively. The reason was that LaSrNiO_4 with an oxygen vacancy could show good NO adsorption capacity even at room temperature, but La_2NiO_4 with excess oxygen showed no adsorption capacity for NO at low temperature [19]. Zhu et al. thought the perovskite oxides with an oxygen defect were beneficial to NO removal. On the one hand, oxygen vacancy could provide space for NO adsorption, and on the other hand, electrons could be generated in the structure to activate NO, in the form of $\text{B}^{4+}-(\text{NO}^-)-\text{B}^{3+}$, as a result of the oscillation between $\text{B}^{3+}-\text{B}^{3+}$, and $\text{B}^{4+}-(\text{e}^-)-\text{B}^{3+}$ [16]. Many other works also have shown that the presence of oxygen vacancy and the redox ability of B-site cation were two major factors influencing NO adsorption and activation [7,15,17,18,20–24]. But, the reaction temperature for the NO direct decomposition is high over the perovskite(-like) oxides (>1023 K), and how to improve the regeneration ability of active sites to obtain the high activity of NO decomposition at low temperature is still a challenge over the perovskite(-like) oxide catalysts.

In our previous study [20], NO direct decomposition over the $\text{La}_{2-x}\text{Ba}_x\text{NiO}_4$ ($x \leq 1.2$) catalysts had been investigated. It was found that the highest N_2 yield was achieved with $\text{La}_{1.2}\text{Ba}_{0.8}\text{NiO}_4$ composed of perovskite-like structure phase and BaCO_3 in the absence/presence of oxygen. It is suggested that the BaCO_3 phase, NO_x storage component, contributes to the increase in activity, and plays an important role in quickening up the run of catalytic NO decomposition recycle. Therefore, in this study, the effect of BaO on the NO decomposition over the $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ was studied in details in the absence/presence of oxygen because the alkaline of BaO is stronger than BaCO_3 . The $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ -20%BaO exhibits an excellent catalytic performance for the NO decomposition at 923 K, BaO plays a key role in NO_x transportation and storage, which is favorable for the regeneration of the active sites and the promotion of the catalytic activity of $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ -20%BaO sample. The possible reaction routes are brought out for the NO decomposition over the $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ -20%BaO catalyst.

2. Experimental

2.1. Preparation of catalysts

$\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ was prepared by citrate combustion method as described elsewhere [6,20]. 16 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 10 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4 mmol of $\text{Ba}(\text{NO}_3)_2$ were dissolved in 100 mL of deionized water under stirring for 30 min. At the same time, 45 mmol $\text{C}_6\text{H}_8\text{O}_7$ was dissolved in 225 mL of deionized water under stirring for 30 min. Subsequently, the above citric acid solution was dripped into the nitrate solution dropwisely and stirred for 30 min. The resulting solution was evaporated to dryness, and then the precursor was calcined at 573 and 873 K for 1 h, respectively. Finally, the precursors were palletized and calcined at 1123 K in air for 6 h, and then the synthesized pellets were pulverized to 40–60 mesh size.

Because BaO reacts easily with CO_2 and generates BaCO_3 , $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ -x%BaO ($x = 5, 10, 15, 20, 25, 30$) was prepared by mixing $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ with $\text{Ba}(\text{NO}_3)_2$ and heated them to obtain in situ. A certain amount of the mixture (40–60 meshes) without dilution was set into the quartz reactor (containing $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ 0.500 ± 0.001 g), which was firstly treated by 1% O_2 from 293 K to 1023 K at 10 K/min, and kept at 1023 K for 1 h, then cooled to 423 K in 1% O_2 , finally switched to 1% NO.

2.2. Characterizations

X-ray diffraction patterns (XRD) were obtained with a BrukerD8 Advance from 30 to 900 °C, using Cu $\text{K}\alpha$ radiation combined with Ni-filter, wavelength of 0.15406 nm, voltage of 40 kV, current at 40 mA, scan range 2θ of 10–65°, scan speed of 10°/min, and sampling interval of 0.02°. Temperature programmed reduction with hydrogen (H_2 -TPR) was carried out in a conventional self-made apparatus equipped with TCD as a detector. 30 mg of catalyst was pretreated by 1% O_2 with a total flow rate of 25 mL/min from 323 K to 1023 K at 10 K/min, and kept at 1023 K for 1.5 h, then cooled to 323 K in the same atmosphere, then switched to 5% (volume) H_2/N_2 for 2 h in order to remove the residual O_2 . Finally, the sample was reduced with a 5% (volume) H_2/N_2 mixture (25 mL/min) by heating from 323 K to 1023 K at a rate of 10 K/min

Temperature programmed desorption of O_2 (O_2 -TPD) was performed on a conventional self-made apparatus equipped with mass spectrometry (MS Hiden-Qic-20) as a detector. 100 mg of sample was first treated in 10% O_2 (50 mL/min) by heating from 323 K to 1023 K at a rate of 10 K/min and hold for 1 h at 1023 K. After cooled to 323 K in the same atmosphere, then, the sample was swept with Ar at a rate of 50 mL/min for 30 min in order to remove the residual O_2 . Finally, the sample was heated to 1023 K at a rate of 10 K/min in Ar to record the TPD spectra with MS. Temperature programmed desorption of NO (NO -TPD) was performed on a conventional self-made apparatus equipped with mass spectrometry (MS Hiden-Qic-20) as a detector. 100 mg of sample was first treated in 2000 ppm NO (50 mL/min) by heating from 323 K to 1023 K at a rate of 10 K/min and for 1 h at 1023 K. After cooled to 323 K in the same atmosphere, then, the sample was swept with Ar at a rate of 50 mL/min for 30 min in order to remove the residual O_2 . Finally, the sample was heated to 1023 K at a rate of 10 K/min in Ar to record the TPD spectra with MS.

2.3. Catalytic activity tests

Direct decomposition of NO was performed in a fixed-bed quartz reactor with an inner diameter of 6 mm under 1% NO diluted with He. A certain of $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ -x%BaO ($x = 0, 5, 10, 15, 20, 25, 30$) (containing $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ 0.500 ± 0.001 g) prepared in situ without dilution was always set in the reactor by using quartz wool. The feed rate of the reactant was fixed at $W/F = 1.2 \text{ g}_{\text{cat}} \text{ s mL}^{-1}$, where W and F were the catalyst weight ($\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$) and the gas flow rate. Produced N_2 , O_2 , and the fed NO were analyzed by gas chromatography online, which had a molecular sieve 5A column and a thermal conductivity detector (TCD). In the coexistence of O_2 experiment, a certain of $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ -20%BaO (containing $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ 0.500 ± 0.001 g) was adopted and the gas reactant of the 1% NO, balance He and the concentration of O_2 varied from 0.2% to 1.0% at constant W/F of 1.2 $\text{g}_{\text{cat}} \text{ s mL}^{-1}$.

In any particular run, the data was recorded after temperature change every time to ensure that the equilibrium of catalytic reaction was reached. The activity of NO decomposition was evaluated by the following equations:

$$\text{N}_2\text{yield}\% = 2[\text{N}_2]_{\text{out}}/[\text{NO}]_{\text{in}} \times 100\% \quad (1)$$

$$\text{O}_2\text{yield}\% = 2[\text{O}_2]_{\text{out}}/[\text{NO}]_{\text{in}} \times 100\% \quad (2)$$

$$\text{NOconversion}\% = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}} \times 100\% \quad (3)$$

Where $[\text{NO}]_{\text{in}}$ was the concentration of NO measured before the reaction, $[\text{NO}]_{\text{out}}$, $[\text{N}_2]_{\text{out}}$ and $[\text{O}_2]_{\text{out}}$ was the concentration of NO, N_2 and O_2 measured after the reaction, respectively.

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