Enhanced catalytic activity for NO oxidation over Ba-doped LaCoO3 catalyst (Postprint)

Authors: Zhou, C, Feng, ZJ, Zhang, YX, Hu, LJ, Chen, R, Shan, B, Yin, HF, Wang, WG, Huang, AS

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Abstract

A series of La1-xBaxCoO3(x = 0, 0.1, 0.2, 0.3) perovskites were synthesized by the modified sol-gel method, and their activities for NO oxidation were investigated as well. The relevant structural characterizations of the prepared catalysts were conducted

Full Text

Enhanced Catalytic Activity for NO Oxidation over Ba-Doped LaCoO Catalyst

Chen Zhou,a Zijian Feng,b Yexin Zhang,a Lingjun Hu,a Rong Chen,c Bin Shan,*b Hongfeng Yin,*a Wei Guo Wang,a and Aisheng Huanga

aNingbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, Zhejiang, People' s Republic of China. E-mail: yinhf@nimte.ac.cn
bState Key Laboratory of Digital Manufacturing Equipment and Technology and School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, People' s Republic of China. E-mail: bshan@hust.edu.cn
cState Key Laboratory of Material Processing and Die and Mould Technology and School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, People' s Republic of China

A series of La Ba CoO (x = 0, 0.1, 0.2, 0.3) perovskites were synthesized by a modified sol-gel method, and their catalytic activities for NO oxidation were systematically investigated. The prepared catalysts were characterized using XRD, ICP, BET, FTIR, TEM, H -TPR, and NO-TPD techniques. Performance evaluation revealed that introduction of Ba at the A-site of LaCoO greatly improved the activity for NO oxidation, with the best performance achieving 93% NO

conversion at 265 °C on La . Ba . CoO . Additionally, the Ba-doped LaCoO catalysts exhibited superior performance compared to the classical Pt/Al O catalyst, implying that these non-noble materials could be considered as potential substitutes for noble metal-based catalysts.

Introduction

Lean-burn engines have attracted increasing attention compared to conventional engines due to their better fuel economy and power output. However, the elimination of NO under lean-burn conditions is difficult because of the lack of reductants. Consequently, the abatement of NO has become critical due to increasingly stringent emission regulations and the harmful effects of NO on human health and the environment. Currently, selective catalytic reduction (SCR) and lean NO trap (LNT) represent the two main technologies for NO removal. For SCR technology, the presence of NO can promote NO removal, while for LNT technology (also known as NO Storage-Reduction, NSR), NO is more readily absorbed on catalysts as nitrates than NO. Therefore, the conversion of NO to NO is of great importance for NO removal. Conventional noble metal-based catalysts are typically employed for this reaction, but their lower stability and high cost necessitate the development of alternative catalysts.

In recent decades, much attention has been paid to catalysts derived from perovskite structures with the general formula ABO , where A is a rare earth cation and B is a transition metal (Co, Ni, Fe, or Mn). During the NO removal process, the ability to oxidize NO to NO is significant. LaMO (M = Co, Mn, Fe) perovskites have been studied as NO oxidation catalysts, with Co-based catalysts exhibiting superior catalytic activity. Kim et al. investigated a mixture of La . Sr . MO (M = Mn, Co) and Pd-Rh/BaO/CeO -ZrO to compete with a commercial Pt-containing LNT catalyst, and notably found that La . Sr . MO (M = Mn, Co) showed much higher NO oxidation activity than Pt-based catalysts. Thus, studying perovskite-based catalysts is significant because they are much less expensive and more active toward NO oxidation than Pt-based catalysts.

Barium has been reported to be beneficial for the adsorption of NO as nitrate. Moreover, Liang et al. evaluated Ba-doped La-Ba-Ni mixed oxide catalysts for the total oxidation of chlorinated hydrocarbons and found that Ba doping promoted the catalytic activity, with La . Ba . NiO exhibiting the best performance. Bhavani et al. studied CO reforming of methane using Ba-substituted LaMnO perovskite and found that the optimal Ba substitution level was 0.1-0.15 (Ba/Mn), which showed the highest CH and CO conversion, syngas selectivity, and robust performance maintenance with minimal coke formation. These investigations imply that introducing Ba into the perovskite structure might promote catalytic performance. Co-based perovskite oxides are the most promising candidates as NO oxidation catalysts due to their superior performance, yet the application of Ba-doped LaCoO in NO oxidation for emission control has not been studied. Hence, in the present study, Ba-doped LaCoO catalysts with different substitution levels were investigated for NO oxidation. We found that Ba introduction dramatically improved the activity for NO oxidation, with a maximum NO conversion of 93% at 265 °C for La . Ba . CoO , which exhibited much better performance than Pt-based catalysts (maximum conversion of 62% at 320 °C). Our results indicate that Ba-doped LaCoO could serve as a low-cost, high-performance candidate material for NO oxidation catalysts.

2.1 Catalyst Synthesis

The Ba-doped LaCoO perovskite oxides were synthesized by a modified sol-gel method using citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) as complexing agents, with aqueous solutions of nitrate precursors (La, Ba, Co, Sr). The obtained gel was dried at 150 °C overnight and calcined at 700 °C for 5 hours in air after preliminary calcination at 550 °C for 2 hours. A 2% Pt/Al O catalyst was also prepared via wet impregnation as a reference. In this paper, perovskite-type oxides with the formula La Ba CoO (x = 0, 0.1, 0.2, 0.3) are hereafter designated as LBC10*x. For example, La . Ba . CoO is abbreviated as LBC1.

2.2 Characterizations

X-ray diffraction (XRD) was performed to determine the phase structure of the synthesized catalysts using a Bruker D8 Advance diffractometer with a copper anode (K Cu = 1.54056 Å), operated at an accelerating voltage of 40 kV and current of 40 mA with a step size of 0.02° in the Bragg angle (2) range from 10° to 90°. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was conducted to measure the elemental chemical composition using a Perkin-Elmer Optima 2100 spectrometer. The Brunauer-Emmett-Teller (BET) specific surface areas were determined via nitrogen adsorption at 77 K using a Micromeritics ASAP 2020M physisorption analyzer. Prior to measurements, the catalysts were degassed at 200 °C for 5 hours. Fourier transform infrared (FT-IR) spectra of the oxides were collected on a Bruker Tensor 27 spectrometer in the range of 300–4000 cm ^{1} with a resolution of 4 cm ^{1}, averaging 32 scans. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM 2100 microscope operated at 200 kV.

For temperature-programmed desorption of NO (NO-TPD) experiments, 50 mg of catalyst was pretreated in 10% O /N at 500 °C for 1 hour and then cooled to room temperature. After purging with N for 30 minutes, the gas flow was switched to 500 ppm NO with N as the balance gas. Following adsorption, N was introduced again, and the catalyst was heated to 600 °C at a rate of 10 °C min ^{1} under pure N (200 mL min ^{1}). Desorbed species were detected using an ECO Physics chemiluminescent NO analyzer (CLD822Mh), which can detect NO and NO with a detection limit of 0.25 ppm.

H temperature-programmed reduction (H -TPR) of the catalysts was carried out in a stream of 10% H -Ar mixture at a flow rate of 50 mL min ^{1} using a FINESORB3010E instrument (Zhejiang Finetec Co.). For each H -TPR test, 30 mg of catalyst placed in a U-type quartz tube reactor was pretreated at 300 °C for 1 hour under a 21% O /N stream and then cooled to room temperature. During the H -TPR process, the sample was heated at a rate of 5 °C min ^{1}. The H concentration in the effluent gas was determined by a thermal conductivity detector (TCD) with Ar as the reference gas.

2.3 Activity Testing

Catalytic evaluation for NO oxidation was carried out under lean conditions using the same reactor as for temperature-programmed experiments, with a reactor tube inner diameter of 3 mm. For each test, 50 mg of catalyst was used, with temperature measured by a K-type thermocouple placed in direct contact with the upper quartz wool near the powder. The gas mixture consisting of 400 ppm NO, 10% O , and N as the balance gas (150 mL min ^{1}) passed through the loaded catalyst. The space velocity was approximately 180,000 mL g ^{1} h ^{1}. The furnace was ramped at 2 °C min ^{1} from room temperature to 400 °C. NO conversion was defined by the following formula:

$$\text{NO conversion (\%)} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100$$

where NO in is the NO concentration in the inlet gas and NO out is the NO concentration in the outlet gas.

3.1 Structural Characterizations

XRD patterns of the obtained LBC catalysts are shown in Fig. 1 [Figure 1: see original paper]. LaCoO exhibited the typical hexagonal perovskite structure (JCPDS 25-1060). Note that the main (110) peaks around 2 = 33° were split into two sub-peaks, indicating rhombohedral distortion of the perovskite structure. For Ba-doped catalysts, the two sub-peaks of the main (110) peak merged into one and shifted to lower 2 angles. This demonstrates that Ba was successfully doped into the lattice structure and improved the symmetry of the perovskite structure. A similar phenomenon was also observed for Ca- and Sr-doped LaCoO elsewhere. The shift of the main peak to lower 2 angles suggests lattice volume expansion resulting from the larger ionic radius of Ba^{2} (1.35 Å) compared to that of La^{3} (1.06 Å), which agrees with the results of Bhavani et al. Meanwhile, the corresponding lattice parameters, shown in Table 1 and calculated from the XRD results, increased with increasing Ba doping content. Additionally, only the perovskite structure was observed in LaCoO , while a very weak diffraction peak of BaCO was detected in LBC1. However, diffraction peaks of BaCoO (JCPDS 70-0363) and BaCO (JCPDS 05-0378) were also observed for LBC2 and LBC3, implying some degree of phase segregation.

The detailed phase composition based on XRD patterns is shown in Table 2 . With increasing Ba addition, the content of BaCO increased while the phase content of perovskite oxides (including LBC and BaCoO) decreased. ICP measurements, displayed in Table 3 , demonstrated that the intended compositions were nearly obtained.

The BET specific surface areas of the as-synthesized catalysts are also shown in Table 1. The BET surface area for LBC0 was 7.48 m^{2} g ^{1}, while those of Ba-doped catalysts ranged between 5.16 and 9.81 m^{2} g ^{1}. This demonstrates that introduction of Ba into the perovskite structure improved the BET surface area of the catalysts.

Fig. 2 [Figure 2: see original paper] displays the FT-IR results of the as-prepared La Ba CoO perovskite oxides. For LaCoO , spectral bands were observed at 598 cm ^{1} (strong), 558 cm ^{1} (strong), 423 cm ^{1} (strong), and 343 cm ^{1} (weak). These bands are consistent with vibrational frequencies corresponding to three normal modes reported by Merino et al., where the doublet bands at 598–558 cm ^{1} correspond to the v mode, the band at 423 cm ^{1} to the v mode, and the band at 329 cm ^{1} to the v mode. With Ba introduction into the A-site, the v mode with a shoulder became broader and weaker. Especially for LBC3 with the maximum Ba content, the v mode became a single band compared with the Ba-free LaCoO sample. Moreover, the intensity of the v and v modes decreased as Ba doping increased. The v mode band at 329 cm ^{1} represents O–Co–O angle deformation, which is usually IR-inactive for a cubic structure but active in a distorted structure. The vibrations of the v , v , and v modes suggest that La substitution by Ba favored improved symmetry of the perovskite structure by transforming some Co^{3} into Co . The interaction of Co with O is stronger than that of Co^{3} with O, thus the Co -O stretching vibration peak shifts to higher wavenumbers. The decreased intensity of Ba-doped samples shows that La substitution by Ba favored improved symmetry of the perovskite structure.

For LBC1, bands at 857 cm ^{1} and 1432 cm ^{1} were detected. These bands correspond to the out-of-plane bending and the v mode of carbonates, respectively, which could originate from incomplete combustion of CA and EDTA. Additionally, two new bands at 668 cm ^{1} and 693 cm ^{1} were observed on LBC2 and LBC3. The band at 668 cm ^{1} was assigned to Co O (the ABO vibrations, where A denotes Co^{2} in a tetrahedral position), indicating that Co O was generated when the Ba doping content reached 20%. The other band at 693 cm ^{1} was attributed to the in-plane bending mode of CO ^{2} .

TEM and HRTEM images of LBC0 and LBC3 are displayed in Fig. 3 [Figure 3: see original paper]. The particle sizes of the as-prepared catalysts ranged between 40 and 60 nm. From the HRTEM image of LBC0 (Fig. 3c), the observed lattice spacing of 0.38 nm corresponded to the (110) crystallite orientation of LaCoO . For LBC3 (Fig. 3d), two additional crystal planes with lattice spacings of 0.34 nm and 0.25 nm were observed, corresponding to the (311) and (101) crystallite orientations of BaCoO and Co O , respectively. This confirms that BaCO and Co O existed on LBC3, coinciding with the FT-IR results. The failure to observe the Co O phase by XRD could be ascribed to its small quantity.

3.2 XPS Analysis

The surface compositions of the catalysts obtained from XPS analysis are listed in Table 4 . The reactivity of perovskites has been attributed to the active transition B ions, as reported by Voorhoeve et al., thus the surface content of B ions can be considered an index correlating with catalytic activity. As shown in Table 4, the surface Co content in LBC0 was 11.60 at%, while higher values of 17.85, 20.72, and 21.95 at% were obtained for LBC1, LBC2, and LBC3, respectively. This indicates that Ba substitution significantly increased the surface Co content, demonstrating surface segregation of Co. The content of Co on the surface improved by 53.8% with 10% Ba doping, implying that Ba doping increased Co content on the surface, which could provide more active sites. With further increase in Ba content, the surface Co content continued to increase. The extra amounts of Co and Ba existed as BaCO , Co O , and BaCoO on the surface and/or in the bulk of the catalysts.

3.3 H -TPR

The H -TPR results are shown in Fig. 4 [Figure 4: see original paper], with the reductions of Co O (358 °C) and BaCO (800 °C) provided as references. For LBC0, three reduction peaks were observed at 335 °C, 378 °C, and 525 °C, respectively. The first two peaks were attributed to the reduction of Co^{3} to Co^{2} , while the last peak at 525 °C was ascribed to the reduction of Co^{2} to Co in the LaCoO perovskite structure. For all Ba-doped samples, the reduction peaks shifted to lower temperatures. The three reduction peaks of LBC1 shifted to 283 °C, 324 °C, and 496 °C, respectively, and much lower reduction temperatures were observed for LBC2 and LBC3. This might be attributed to surface segregation of Co due to Ba substitution, which could facilitate reduction by H . Especially, the reduction temperatures of Co^{3} and Co^{2} gradually approached the reduction temperature of Co O (358 °C) with increasing Ba doping amount, suggesting that severe surface segregation of Co favored the formation of Co O observed in the HRTEM image (Fig. 3d) and FT-IR spectra (Fig. 2). Meanwhile, after Ba substitution, the starting reduction temperature began around 220 °C, which was much lower than that of LaCoO (290 °C). For each Ba-doped sample, an additional reduction peak above 700 °C was observed. With increasing Ba amount, this peak intensified and shifted to higher temperature, approaching the reduction temperature of BaCO (800 °C). This coincided with the observation of the BaCO phase in the XRD results for LBC2 and LBC3 (Fig. 1).

3.4 NO-TPD

NO-TPD experiments were conducted to investigate the NO adsorption/desorption behavior over the La Ba CoO catalysts. For LBC0, two desorption peaks were observed in Fig. 5 [Figure 5: see original paper]: one below 250 °C and another at higher temperatures. Wen et al. demonstrated that three species existed on LaCoO : bridging nitrates, hyponitrite species, and monodentate nitrates. The former two species disappeared by 250 °C, which might be responsible for the desorption peak below 250 °C in Fig. 5, while the most stable monodentate nitrate corresponded to the desorption peak at higher temperatures. For all Ba-doped catalysts, the intensities of the two desorption peaks both increased significantly, indicating their higher capacities for NO adsorption. As listed in Table 5 , the amount of NO desorption over Ba-doped samples was above 110 mol g^{1}, much larger than that over LBC0 (35.3 mol g^{1}). Furthermore, the desorption temperatures of Ba-doped samples were also higher, as shown in Fig. 5, implying higher stabilities of adsorbed species. The higher NO adsorption capacity of Ba-doped samples might be ascribed to the stronger basicity of Ba.

As a reference, the desorption behavior of NO on BaCO and Co O was also examined. From Fig. 5, NO desorption was observed for BaCO (peak temperature at 480 °C) and Co O (peak temperatures at 185 °C and 334 °C), indicating that both materials could adsorb NO. This explains why the desorption peaks of Ba-doped catalysts became broader due to the formation of BaCO , Co O , and BaCoO on the catalyst surfaces.

3.5 Activity Evaluation

The catalytic activity of the as-prepared catalysts toward NO oxidation is shown in Fig. 6 [Figure 6: see original paper], with the thermodynamic equilibrium of NO to NO provided as a reference curve. The equilibrium conversion decreased with increasing reaction temperature because NO oxidation is an exothermic and reversible reaction. For LaCoO , NO conversion began to increase at 200 °C, reaching a maximum of 77% in the range of 310–320 °C. After that, the conversion dropped due to thermodynamic limitations. For all Ba-doped samples, introduction of Ba into the perovskite structure dramatically promoted NO conversion, with the light-off temperatures shifted to approximately 150 °C and the maximum conversions achieved at lower temperatures. Among these catalysts, LBC1 exhibited the best performance with a maximum NO conversion of 93% at 265 °C. With further increase in Ba doping amount, the reactivity decreased slightly but remained much higher than that of LaCoO . It is worth mentioning that all Ba-doped samples showed significantly higher activity than 2% Pt/Al O , and thus could be used as potential substitutes for noble metal-based catalysts. For comparison, the activities of Co O and BaCoO are also shown in Fig. 6, and the reactivity of different Co oxides toward NO oxidation followed the sequence: LaCoO > Co O > BaCoO . Note that with increasing Ba doping content, the content of the perovskite oxide LBC decreased (Table

2) while the Co content on the catalyst surface increased (Table 4), yet LBC1, LBC2, and LBC3 showed similar catalytic performance. This might indicate that composite interfaces such as LBC/Co O existed on the catalyst surfaces, and the interaction between the perovskite oxides and Co O contributed more significantly to the performance than the pure LBC catalyst alone.

4. Conclusions

Ba-doped LaCoO catalysts were readily prepared by a modified sol-gel method. XRD, FT-IR, and H -TPR indicated that segregation phases such as BaCO , Co O , and BaCoO were produced with increasing Ba doping content. Ba substitution for La in the LaCoO perovskite greatly improved the activity for NO oxidation, with the best performance showing a maximum NO conversion of 93% at 265 °C on La . Ba . CoO . XPS demonstrated that Ba substitution led to surface segregation of Co, which could promote the activity for NO oxidation. Moreover, all Ba-doped LaCoO catalysts exhibited better NO oxidation performance than the classical Pt/Al O catalyst. This suggests that these materials could be considered as potential substitutes for noble metal-based catalysts and provides a viable direction for finding low-cost materials with good NO–NO conversion capability.

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