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High Performance Catalysts BaCoO₃-CeO₂ Prepared by the One-Pot Method for NO Direct Decomposition

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Abstract: NO direct decomposition is the most promising but also the most challenging approach for nitrogen oxides abatement. Developing high performance catalysts is greatly desirable to promote the application of this technology. The present catalysts BaCoO₃-CeO₂ prepared by the one-pot method show superior activity towards NO direct decomposition, robust oxygen resistance and decent durability. The NO conversion to N₂ of 5%BaCoO₃-CeO₂ catalyst is 57.2%, 70.1% and 75.6% at 700, 750 and 800 °C, respectively. It still maintains at 54.3% even in the presence of 10 vol% O₂ at 800 °C and is stable in 1 vol% O₂ at least for 24 h at 750 °C. Such impressive performance is ascribed to the unique properties of CeO₂, strong interaction between perovskite and CeO₂, and microstructure of the catalysts rendered by the citric acid-nitrate one-pot method.

Introduction

Reducing the emission of nitrogen oxide (NO_x) especially NO is greatly desirable due to its harmful impact on both the mankind and the environment. Among the various technologies for NO removal^[1] such as selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR), NO_x storage-reduction (NSR), the NO direct decomposition (2NO = N₂ + O₂) stands out because no reductants such as ammonia or hydrocarbons are required and the products are eco-friendly N₂ and O₂.^[2] Nevertheless, it is far from commercialization with the core problem lying in the catalysts. The noble metals such as Pt and Pd are the earliest studied catalysts for NO direct decomposition. However, the formidable cost and the poor resistance to sintering and oxidation impede their wide application.^[3] The molecular sieves such as Cu-ZSM-5 are alternatively studied and they show high activity at intermediate temperatures.^[4] However, the high sensitivity to H₂O and SO₂ poses serious challenges for their practical application.^[5] The simple metal oxides show decent activity at moderate temperatures.^[6] The NO conversion of 52% at 550 °C was reported for Na-Co₃O₄ but it deactivates quickly at higher temperatures.^[7] In contrast, the perovskite-type metal oxides (ABO₃) have gained increasing attention in recent years owing to their attractive activity, thermal stability, reasonably well resistance to sulfur poisoning at

elevated temperatures (> 500 °C), and composition versatility with strong elemental accommodation at both A- and B-sites.^[8]

Various ABO₃ oxides have been investigated as catalysts for NO direct decomposition such as LaCo/Fe/MnO₃-based^[8b, 9] and BaCo/Fe/MnO₃-based^[10] materials. Different catalytic mechanisms have been proposed for the ABO₃ catalysts. Shin and Hatakeyama^[11] proposed that the disordered oxygen vacancies are extremely important for NO decomposition based on their study on Sr₂Fe₂O₅. Later, Shin et al.^[12] reported that the active sites contains two adjacent oxygen vacancies and two NO molecules attack them simultaneously. However, Teraoka et al.^[9e] suggested that the attack of NO on oxygen vacancy occurs stepwise, and the attack of the second NO molecule is the rate-determining step (RDS) based on the unity of the reaction order of NO in the reaction. N₂O intermediate mechanism^[9d] and recycle mechanism^[13] were also reported. Although no consensus has been reached in terms of the reaction mechanism on the perovskite catalysts, the importance and involvement of oxygen vacancy have all been highlighted. The oxygen vacancy is needed for NO adsorption in the first step. The release of oxygen will regenerate the oxygen vacancy for further redox cycles.

Compared with other catalysts, the main problems with the ABO₃ oxides are their low activity and poor resistance to O₂. It should be noted that the concentration of oxygen in the exhaust gases of diesel engines and lean-burn gasoline engines is 1–15%.^[14] The N₂ yield of La_{0.8}Sr_{0.2}CoO₃ decreased from 55% and 40% to ~26% and ~15% when 2 vol% O₂ was present at 800 and 700 °C, respectively.^[9e] The N₂ yield of La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃ decreased monotonically with increasing O₂ concentration, from 63% to 12% when 10 vol% O₂ was introduced.^[9d] It is owing to the competitive adsorption of O₂ and NO on the oxygen vacancies. Furthermore, the oxygen vacancies can be compensated by O₂ in the feed, which reduces the active site and thus lower activity. Accordingly, it is necessary to develop catalysts of high activity and robust oxygen-resistance.

CeO₂, which is characterized by high oxygen storage capacity and feasible conversion between Ce³⁺ and Ce⁴⁺, has been widely applied in catalysis.^[15] The Ce and MgO addition substantially enhanced the NO direct decomposition activity of La-Sr-Ni-O.^[16] The NO conversion to N₂ of La_{0.6}Ce_{0.4}CoO₃ was ~61% at 500 °C in the presence of 8% O₂.^[14] Most work focuses

on the substitution of A- and/or B-sites with Ce and the influence on the catalytic performance for NO direct decomposition.^[17] Less attention has been paid to the effect of the secondary component CeO₂ although it facilitates the regeneration of oxygen vacancy.

Besides the composition, the preparation method has a significant influence on the catalytic performance. Recently, the one-pot method emerges as a promising approach to fabricate multi-component materials for oxygen separation,^[18] solid oxide fuel cells,^[19] etc. The resultant materials show much smaller grains and higher homogenization of the components and thus better performance.^[18]

Herein, the catalysts BaCoO₃-CeO₂, synthesized by the one-pot method, show high activity towards NO direct decomposition and excellent resistance to O₂ deactivation. The underlying reasons were explored with various characterization techniques.

Results and Discussion

Catalytic activity

The NO direct decomposition activity of BaCoO₃-CeO₂ catalysts was evaluated by NO conversion to N₂, which is calculated by $(2 \times \text{outlet concentration of N}_2) / (\text{inlet concentration of NO}) \times 100\%$. The results are shown in Figure 1 along with those of BaCoO₃ and CeO₂. The pure CeO₂ is almost inactive towards NO decomposition to N₂, similar with those reported.^[20] The pure BaCoO₃ also shows poor activity with the highest NO conversion of 27.2% at 750 °C. However, the addition of CeO₂ substantially enhances the activity. The NO conversion to N₂ of 81%BaCoO₃-CeO₂ is 53.6% at 750 °C, two times of that of pure BaCoO₃. The activity increases with decreased BaCoO₃ content until 5%. Further decrease in the BaCoO₃ amount (3%) results in declined activity. The sample 5%BaCoO₃-CeO₂ shows the highest activity among all the samples; the NO conversion to N₂ is 57.2%, 70.1% and 75.6% at 700, 750 and 800 °C, respectively, which is higher than most reported catalysts for NO direct decomposition, including perovskite-type, perovskite-related complex metal

Figure 1. Catalytic activity of $x\text{BaCoO}_3\text{-CeO}_2$ catalysts ($x = 3, 5, 11, 22, 32, 59$, and 81%) along with pure BaCoO₃ and CeO₂ samples as a function of the reaction temperature. Reaction conditions: 2 vol% NO, He balance, 1.5 g s/cm³, 500–850 °C.

oxides, and simple metal oxides (Table S1). Such performance is attractive considering the fairly low content of the BaCoO₃ component (5%) in 5%BaCoO₃-CeO₂ compared with the bulk catalysts (100%) in the literature (Table S1).

The activity decreases at elevated temperatures. It reduces sharply when the reaction temperature is beyond 750 °C for pure BaCoO₃, from 27.2% at 750 °C to 15.6% at 800 °C and further to 5.2% at 850 °C. Such decline is due to sintering. Since all the samples were calcined at 700 °C, which is found to be the optimum temperature to achieve high activity (Figure S1), sintering will inevitably happen when the reaction temperature is higher than the calcination temperature. However, the sintering issue is significantly alleviated with the addition of CeO₂. For example, the conversion of catalyst 59%BaCoO₃-CeO₂ decreases from 56.8% at 750 °C only to 54.9% at 800 °C. When the CeO₂ content further increases, the activity even increases when the testing temperature ascends from 750 to 800 °C, followed by slight decrease at 850 °C for 5%BaCoO₃-CeO₂. Accordingly, CeO₂ serves as a sintering inhibitor, which is highly desirable for the high temperature operation.

Oxygen resistance and durability

Figure 2. (a) Catalytic activity of 5%BaCoO₃-CeO₂ catalyst at different O₂ concentration as a function of the reaction temperature; (b) Catalytic activity of 5%BaCoO₃-CeO₂ with the presence of different concentration of O₂ compared with (Gd_{0.70}Y_{0.26}Ba_{0.04})₂O_{2.96}, La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃ (3.0 g s/m³), La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ (4.0 g s/m³) and La_{0.8}Sr_{0.2}CoO₃ (4.0 g s/m³) at 800 °C. Reaction conditions: 2 vol% NO, 1–10 vol% O₂, He balance, 1.5 g s/cm³.

As aforementioned, the competitive adsorption of O_2 and NO molecules on the oxygen vacancies^[21] and the regeneration of oxygen vacancies are the great concerns for the activity, the O_2 resistance of the catalysts is thus investigated. After adding 1-10 vol% O_2 into the feed gas (NO balanced with helium), the activity of 5%BaCoO₃-CeO₂ at 800 °C indeed decreases (Figure 2a). However, such decrease is very gradual. The NO conversion to N₂ declines from 75.6% to 71.1% when 1 vol% O_2 is added, and then to 67.1, 61.6 and 54.3% in 2, 5 and 10 vol% O_2 -containing atmosphere. In sharp contrast, the pure BaCoO₃ is deactivated with introduction of only 1 vol% O_2 . Such O_2 -resistance of 5%BaCoO₃-CeO₂ catalysts is outstanding compared with that reported. As shown in Figure 2b, at 800 °C, the activity declines quickly with O_2 concentration, from 73% and 63% to 22% and 12% for (Gd_{0.70}Y_{0.26}Ba_{0.04})₂O_{2.96}^[22] and La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃^[9d] respectively, when 10 vol% O_2 is present; from 63% and 43% to ~31% and ~18% for La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ and La_{0.8}Sr_{0.2}CoO₃^[9e] respectively, when 5 vol% O_2 is present. It is noted that all the samples^[9d, 9e, 22] were operated at higher contact time compared with the present catalysts. Furthermore, the resistance of 5%BaCoO₃-CeO₂ to deactivation in O_2 atmosphere is superior to that of Cu-ZSM-5, K-doped Co₃O₄, and 5%Pd/Al₂O₃.^[7b] The O_2 -resistance is influenced by temperature, which is better at higher temperatures (Figure S2) due to the easier desorption and diffusion of O_2 .^[9c, 9d]

As long-term stability is necessary for practical application, the durability of 5%BaCoO₃-CeO₂ under the simulated condition of 2 vol% NO/He containing 1 vol% O_2 at 750 °C was investigated. As shown in Figure 3, high and stable NO conversion of ~60% was achieved over 24 h. Although the result is insufficient to verify stability for the practical application, it confirms the high stability during continuous flow operation and no deactivation in the presence of O_2 .

Phase composition and surface oxidation state

In order to explore the underlying reasons for the significantly improved performance, various characterization techniques were employed. The crystal structure of xBaCoO₃-CeO₂ catalyst was first examined by X-ray diffraction (XRD). The characteristic diffraction peaks of BaCoO₃ and CeO₂ can be clearly distinguished in the XRD pattern of xBaCoO₃-CeO₂ ($x > 5\%$, Figure 4a). No diffraction peaks of BaCoO₃ can be found in the

Figure 3. Durability of 5%BaCoO₃-CeO₂ in O_2 -containing atmosphere. Reaction conditions: 2 vol% NO, 1 vol% O_2 , He balance, 1.5 g s/cm³, 750 °C.

Figure 4. (a) XRD patterns of xBaCoO₃-CeO₂ samples ($x = 0, 3, 5, 11, 22, 32, 59, 81$ and 100%). (b) Enlargement of the XRD patterns in the 2θ range of $24\text{--}34^\circ$.

3-5%BaCoO₃-CeO₂ samples probably due to the detection limit of the XRD instrument. It indicates that the BaCoO₃-CeO₂ catalysts are successfully synthesized by the simple and scalable one-pot method. No shift of the diffraction peaks with the composition (Figure 4b) is found, implying very low inter-diffusion of the two components at the calcination temperature of 700 °C based on the XRD results.

The X-ray photoelectron spectroscopy (XPS) results indicate slight reaction between BaCoO₃ and CeO₂ components. For the Co 2p spectra (Figure 5a), the peaks at ~779.8 and ~795.1 eV are assigned to Co³⁺ whilst those at ~782.0 and ~796.9 eV to Co²⁺.^[23] The Co species mainly exist as Co³⁺. For the Ce 3d spectra (Figure 5b), there are eight peaks labeled as v, v', v'', v''', u, u', u'' and u''', respectively. The v' and u' peaks are assigned to Ce³⁺ whilst others to Ce⁴⁺.^[24] The Co peaks clearly shift to

Figure 5. XPS spectra of (a) Co 2p and (b) Ce 3d for xBaCoO₃-CeO₂ catalysts ($x = 5, 22$, and 59%) along with pure BaCoO₃ and CeO₂.

higher binding energy with increasing CeO₂. However, the peak positions of Ce species remain unchanged according to the Ce 3d spectra. It suggests the partial replacement of Co³⁺ in BaCoO₃ by Ce⁴⁺ (BaCo_{1-y}Ce_yO_{3-δ}), resulting in more Co²⁺, which is consistent with the high solubility of Ce species in the BaCoO₃-based materials.^[25] Such substitution is easier to take place for the one-pot prepared materials,^[18] but it happens only at the very surface, which is difficult to observe from the XRD results. Nevertheless, the BaCo_{1-y}Ce_yO_{3-δ} phase at the interface between BaCoO₃ and CeO₂ probably plays an important role in the activity as Co²⁺ has been reported to be more beneficial for NO direct decomposition.^[7a] Both the main phase BaCoO₃ and the interface phase BaCo_{1-y}Ce_yO_{3-δ} are assumed to be active for NO direct decomposition, which will be further studied in our future work.

Surface area and microstructure

The specific surface area of BaCoO₃-CeO₂ samples was measured by N₂ sorption and the BET surface area (S_{BET}) results are listed in Table 1. S_{BET} of pure BaCoO₃ is rather low (7.3 m²/g) due to the high calcination temperature of the perovskite-type oxides.^[9e, 14] However, the addition of CeO₂ increases S_{BET} of the catalysts, which increases with incremental CeO₂ content. It is 35.9 and 42.0 m²/g for 5% and 3%BaCoO₃-CeO₂ samples, respectively, even higher than that of pure CeO₂ (32.2 m²/g). It suggests that CeO₂ significantly impedes the sintering of BaCoO₃, resulting in more fine particles and thus higher catalytic activity (Figure 1). Such assertion can be further proved by the scanning electron microscopy (SEM) results (Figure 6).

CeO₂ are uniformly distributed sphere particles with the size of ~25 nm whereas BaCoO₃ particles are irregular with large

pallet shape. For the BaCoO₃-CeO₂ samples prepared by the one-pot method, large amounts of CeO₂ spherical particles are located on the external surface of BaCoO₃ pallets, which can prevent the sintering of BaCoO₃ at elevated temperatures, in consistent with the S_{BET} results (Table 1). Furthermore, the O₂ molecules are expected to adsorb preferentially on the CeO₂ surface, which can improve the O₂-resistance of BaCoO₃ in the O₂-containing atmosphere. However, superabundant CeO₂ may be harmful for the activity if too many active sites on the surface of BaCoO₃ are covered, i.e., the BaCoO₃ particles are wrapped by CeO₂, which should be responsible for the declined activity of 3%BaCoO₃-CeO₂ although it shows the maximum sintering resistance. The elemental mapping results (Figure S3) show that Ba, Co and Ce distribute homogeneously throughout the powders, which is an advantage of the one-pot method.^[26]

Specific activity

Considering the differences in S_{BET} , the intrinsic activity of BaCoO₃-CeO₂ is evaluated by the N₂ formation rate per surface area (specific activity).^[7b] The cases at the temperatures of 500–650 °C are considered owing to the lower NO conversion to N₂ of less than 30%. As shown in Figure 7, the specific activity increases quickly with BaCoO₃ content until 11% and then maintains almost constant. Such trend is different from the activity in Figure 1, which implies that besides the geometric factor (S_{BET}), the electronic factors also play an important role.^[7b] The resultant apparent activation energy (E_a), calculated by the linear fitting N₂ formation rate at different temperatures based on the Arrhenius equation^[9e], is listed in Table 1. The E_a values are 100–140 kJ/mol, which are similar with those reported.^[8b, 9b] The 5%BaCoO₃-CeO₂ catalyst gives the lowest E_a , leading to the highest activity (Figure 1).

Redox activity and oxygen sorption behavior

To further reveal the electronic factors and also the interaction of the two components in the BaCoO₃-CeO₂ catalysts, the chemisorption tests were performed. The hydrogen temperature-programmed reduction (H₂-TPR) results are shown in Figure 8a. For pure BaCoO₃, the peaks at ~365, ~585 and ~900 °C are

Table 1. S_{BET} and E_a of xBaCoO₃-CeO₂ catalysts along with pure BaCoO₃ and CeO₂.

x (wt%)	0	3	5	11	22	32	59	81	100
S_{BET} (m ² /g)	32.2	42.0	35.9	20.8	18.1	15.9	14.3	12.2	7.3
E_a (kJ/mol)	-	126	101	112	122	126	137	131	125

Figure 6. SEM images of xBaCoO₃-CeO₂ samples. From (a) to (i), x is 0, 3, 5, 11, 22, 32, 59, 81 and 100% respectively.

Figure 7. Specific activity of xBaCoO₃-CeO₂ catalysts as a function of x at 500, 550, 600 and 650 °C.

Figure 8. (a) H_2 -TPR and (b) O_2 -TPD profiles of $x\text{BaCoO}_3\text{-CeO}_2$ catalysts ($x = 3, 5, 11, 22, 32, 59$, and 81%) along with pure BaCoO_3 and CeO_2 .

probably originated from the stepped reduction of Co species, $\text{Co}^{4+} \rightarrow \text{Co}^{3+} \rightarrow \text{Co}^{2+} \rightarrow \text{Co}^0$. The small shoulder peak at $\sim 310^\circ\text{C}$ is due to the reduction of Co^{4+} at the surface. For the catalysts $\text{BaCoO}_3\text{-CeO}_2$, the reduction temperatures of Co species decrease with increasing CeO_2 content. The reduction temperatures for Co^{4+} and Co^{3+} decrease by ~ 34 and $\sim 188^\circ\text{C}$ for $11\%\text{BaCoO}_3\text{-CeO}_2$ compared with the pure BaCoO_3 . It indicates that the redox activity of BaCoO_3 is promoted in the $\text{BaCoO}_3\text{-CeO}_2$ catalysts, which results in higher activity. For pure CeO_2 , the two obvious peaks at ~ 515 and $\sim 820^\circ\text{C}$ are assigned to the reduction of Ce species at the surface and in the bulk, respectively.^[27] The bulk reduction peak of Ce species shifts to lower temperature with increasing BaCoO_3 content, which suggests that the addition of BaCoO_3 also improves the reducibility of the bulk Ce species, leading to the increased mobility of the lattice oxygen and thus higher activity.^[28]

Figure 8b shows the oxygen temperature-programmed desorption (O_2 -TPD) profiles. There are two kinds of oxygen desorbed for ABO_3 oxides, α -type accommodated in the oxygen vacancies and β -type ascribed to the lattice oxygen.^[29] For pure BaCoO_3 , the peak at $\sim 660^\circ\text{C}$ is associated with the desorption of α -type oxygen whereas the peaks at ~ 835 and $\sim 890^\circ\text{C}$ are related with β -type oxygen, i.e., the reduction of Co^{4+} to Co^{3+} and Co^{3+} to Co^{2+} , respectively.^[30] The desorption of lattice oxygen due to the reduction of Co^{2+} to Co^0 is invisible probably it is beyond the testing temperature. In the catalysts $x\text{BaCoO}_3\text{-CeO}_2$, both types of oxygen desorption peaks move to lower temperature as x decreases. Furthermore, the desorption peak associated with the reduction of Co^{2+} to Co^0 gradually emerges in the testing temperature scale; it also shifts to lower temperatures with reduced x . All those results show that CeO_2 weakens the Co-O bond strength and accelerates the desorption of O_2 from BaCoO_3 , which is beneficial for the activity and O_2 -resistance.

At the present stage, although it is still unclear the catalytic mechanism for the present one-pot $\text{BaCoO}_3\text{-CeO}_2$ catalyst, the high activity and robust oxygen resistance are probably closely

associated with the CeO_2 component. Both NO adsorption on the oxygen vacancies and the desorption of O_2 from the oxygen vacancies have been proposed to be the RDS for ABO_3 catalysts.^[8c] The CeO_2 component serves as a sintering inhibitor, which increases the surface area and exposes more active sites. It is also an oxygen vacancy provider due to the easy transition between Ce^{3+} and Ce^{4+} . The CeO_2 particles cover on the surface of BaCoO_3 , which can help the adsorption of O_2 in the feed and thus alleviate the oxygen poisoning. The strong interaction caused by the diffusion of Ce species into the BaCoO_3 lattice at the interface enhances the reducibility of BaCoO_3 and the mobility of lattice oxygen, contributing to the high activity. Furthermore, the interface phase $\text{BaCo}_{1-y}\text{Ce}_y\text{O}_{3-\delta}$ probably plays an important role in the activity, which needs further study.

Conclusion

In summary, the catalysts $\text{BaCoO}_3\text{-CeO}_2$ prepared by the one-pot method show high activity towards NO direct decomposition, robust oxygen resistance in O_2 -containing atmosphere and decent durability. Compared with the pure BaCoO_3 , such high performance of the catalysts is mainly attributed to the homogeneous distribution of both components, higher surface area, and enhanced redox activity due to the interaction between the two components. Furthermore, the sintering-resistance and O_2 -resistance are substantially improved with CeO_2 addition. $5.0\%\text{BaCoO}_3\text{-CeO}_2$ shows superior activity, with NO conversion to N_2 of 57.2, 70.1 and 75.6% at 700, 750 and 800°C , respectively. It still sustains higher than 50% conversion when 10 vol% O_2 is present at 800°C . The CeO_2 component plays multiple roles in the catalysis process for $\text{BaCoO}_3\text{-CeO}_2$ catalysts, as a BaCoO_3 sintering inhibitor and an oxygen vacancy provider; the strong interaction with BaCoO_3 renders it a reducibility improver and oxygen mobility promoter. Both the main phase BaCoO_3 and the interface phase $\text{BaCo}_{1-y}\text{Ce}_y\text{O}_{3-\delta}$ probably play important roles in the activity. Such outstanding performance and scalable fabrication make $\text{BaCoO}_3\text{-CeO}_2$ a promising catalyst candidate for practical application in NO direct decomposition before the activity and stability in the real exhaust conditions are explored.

Experimental Section

Catalyst preparation

The catalysts $x\text{BaCoO}_3\text{-CeO}_2$ were synthesized by the citric acid-nitrate one-pot method, x was the weight percent of BaCoO_3 which varied from 3 to 81 wt% while the total weight of the catalyst remained unchanged.

Appropriate amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in de-ionized water, while ethylene diamine tetraacetic acid (EDTA) was dissolved in ammonia water and continuously added to the former nitrate solution. After adding the citric acid under vigorous stirring, the pH of the solution was adjusted by ammonia (28%) to ~ 8 . The molar ratio of total metal ions:EDTA: citric acid was 1:1:2. The resultant solution was heated with a water bath at 80°C to form a sol and then a gel. The sticky gel was heated at $\sim 400^\circ\text{C}$ on a hot plate and then calcined at 700°C for 6 h to obtain the catalyst powders. The powders were pelleted, crushed and finally sieved to particles of 40-60 meshes. The pure BaCoO_3 and CeO_2 were prepared by the same procedure.

Catalyst characterization

The crystal structure was examined by XRD (Rigaku D/Max-2500) with monochromatic Cu K α radiation in 20–70 ° at a scan rate of 2 °/min. The microstructures of the catalysts were observed by SEM (Hitachi S-4800) equipped with an energy dispersive spectroscopy (EDS) unit. The particle sizes are counted by the Image J software. The specific surface area was measured with the nitrogen sorption at -196 °C and analyzed by multipoint BET method (Quantachrome Autosorb-1). The samples were pre-treated at 250 °C for 4 h under vacuum before sorption test. The oxidation states of the elements were analyzed by XPS (K-Alpha+) with Al K α as X-ray source (1486.6 eV) under a vacuum pressure of 5×10⁻⁸ Pa. The binding energy was calibrated with adventitious carbon 1s at 284.8 eV. The reducibility of the catalysts was tested by H₂-TPR (Xianquan TP-5076). 0.05 g samples were loaded in the quartz reactor and purged under pure Ar with a flow rate of 30 mL/min at 200 °C for 0.5 h, then cooled to room temperature (RT). The H₂-TPR profiles were recorded from RT to 1000 °C at a heating rate of 10 °C/min under 5% H₂/N₂ (30 mL/min). The oxygen desorption property of the sample was analyzed using O₂-TPD on the same instrument as H₂-TPR. 0.2 g samples were pretreated in pure O₂ at 500 °C for 0.5 h and then cooled to RT. The O₂-TPD profiles were recorded at the atmosphere of pure He from RT to 1000 °C at a ramping rate of 10 °C/min.

Activity test

The activity of the catalysts towards NO direct decomposition was evaluated with a quartz fixed-bed reactor. 0.5 g catalysts were loaded in the reactor and tested at 500–850 °C with the interval of 50 °C. The reaction was held at each temperature for 0.5 h before the gas sample was taken. The reaction gas (2 vol% NO/He) was fed at the flow rate of 20 mL/min (W/F = 1.5 g s/cm³). The oxygen resistance was tested by introducing 1–10 vol% O₂ into the feed gas balanced with pure He to keep the total flow rate of reactant at 20 mL/min constant. The N₂ produced was monitored by the network gas chromatography system (GC, Agilent 6890N). The NO conversion to N₂ was calculated by eq. 1.

$$NO \text{ conversion to } N_2 = \frac{2[N_2]_{out}}{[NO]_{in}} \times 100\% \quad (1)$$

where [NO]_{in} and [N₂]_{out} are the inlet and outlet concentration of NO and N₂, respectively. It is noted that almost no N₂O was produced in the reaction. Based on the nitrogen mass balance, there might be a certain amount of by-product NO₂, which is easily generated from NO and O₂ at lower temperature in the cool zone after the reaction.

In addition, the specific activity of the catalyst was calculated by the N₂ formation rate per surface area, and the reaction rate was determined by eq. 2. when the NO conversion to N₂ was lower than 30%.^[7b]

$$r_{N_2} = \frac{F \cdot c \cdot \alpha}{W \cdot S \cdot t} \quad (2)$$

where F, c, α , W, S and t are the feed flow (mol/min), NO inlet concentration (vol%), NO conversion to N₂ (%), the weight of the catalyst (g), the specific surface area (m²/g) and the unit time (1 min), respectively.

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Keywords: Cerium • Nitrogen oxide • NO direct decomposition • Perovskite

- [1] S. Roy, M. Hegde, G. Madras, *Appl. Energy* **2009**, *86*, 2283–2297.
- [2] a) Q. Sun, Z. Wang, D. Wang, Z. Hong, M. Zhou, X. Li, *Catal. Sci. Technol.* **2018**, *8*, 4563–4575; b) M. Haneda, H. Hamada, *C. R. Chim.* **2016**, *19*, 1254–1265.

- [3] X. Wang, S. M. Sigmon, J. J. Spivey, H. H. Lamb, *Catal. Today* **2004**, *96*, 11–20.
- [4] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya, S. Kagawa, *J. Chem. Soc., Chem. Commun.* **1986**, *16*, 1272–1273.
- [5] a) J. Pérez-Ramírez, F. Kapteijn, G. Mul, J. Moulijn, *Appl. Catal. B* **2002**, *35*, 227–234; b) M. V. Konduru, S. S. Chuang, *J. Catal.* **1999**, *187*, 436–452.
- [6] a) E. Winter, *J. Catal.* **1971**, *22*, 158–170; b) S. Xie, G. Mestl, M. P. Rosynek, J. H. Lunsford, *J. Am. Chem. Soc.* **1997**, *119*, 10186–10191.
- [7] a) P. Park, J. Kil, H. H. Kung, M. Kung, *Catal. Today* **1998**, *42*, 51–60; b) M. Haneda, Y. Kintaichi, N. Bion, H. Hamada, *Appl. Catal. B* **2003**, *46*, 473–482.
- [8] a) W. Libby, *Science* **1971**, *171*, 499–500; b) D. Klvana, J. Kirchnerová, C. Tofan, *Korean J. Chem. Eng.* **1999**, *16*, 470–477; c) J. Zhu, A. Thomas, *Appl. Catal. B* **2009**, *92*, 225–233; d) S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari, *Chem. Rev.* **2014**, *114*, 10292–10368; e) J. Zhu, H. Li, L. Zhong, P. Xiao, X. Xu, X. Yang, Z. Zhao, J. Li, *ACS Catal.* **2014**, *4*, 2917–2940.
- [9] a) Y. Yokoi, H. Uchida, *Catal. Today* **1998**, *42*, 167–174; b) C. Tofan, D. Klvana, J. Kirchnerová, *Appl. Catal. A* **2002**, *223*, 275–286; c) C. Tofan, D. Klvana, J. Kirchnerová, *Appl. Catal. A* **2002**, *226*, 225–240; d) T. Ishihara, M. Ando, K. Sada, K. Takiishi, K. Yamada, H. Nishiguchi, Y. Takita, *J. Catal.* **2003**, *220*, 104–114; e) Y. Teraoka, T. Harada, S. Kagawa, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1887–1891.
- [10] a) W. Xu, J. Cai, J. Zhou, Y. Ou, W. Long, Z. You, Y. Luo, *ChemCatChem* **2016**, *8*, 417–425; b) H. Iwakuni, Y. Shinmyou, H. Yano, H. Matsumoto, T. Ishihara, *Appl. Catal. B* **2007**, *74*, 299–306; c) H. Iwakuni, Y. Shinmyou, H. Yano, K. Goto, H. Matsumoto, T. Ishihara, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1175–1182; d) W. Xu, N. Shi, Z. You, J. Cai, K. Peng, Z. Su, J. Zhou, *Fuel Process. Technol.* **2017**, *167*, 205–214.
- [11] S. Shin, Y. Hatakeyama, K. Ogawa, K. Shimomura, *Mater. Res. Bull.* **1979**, *14*, 133–136.
- [12] S. Shin, H. Arakawa, Y. Hatakeyama, K. Ogawa, K. Shimomura, *Mater. Res. Bull.* **1979**, *14*, 633–639.
- [13] J. Zhu, D. Xiao, J. Li, X. Xie, X. Yang, Y. Wu, *J. Mol. Catal. A: Chem.* **2005**, *233*, 29–34.
- [14] Z. Liu, J. Hao, L. Fu, T. Zhu, *Appl. Catal. B* **2003**, *44*, 355–370.
- [15] W. Yang, X. Wang, S. Song, H. Zhang, *Chem* **2019**, *5*, 1743–1774.
- [16] J. Zhu, D. Xiao, J. Li, X. Yang, K. Wei, *Catal. Commun.* **2006**, *7*, 432–435.
- [17] X. Li, H. Gao, *RSC Adv.* **2018**, *8*, 11778–11784.
- [18] a) X. Zhu, H. Wang, W. Yang, *J. Membr. Sci.* **2008**, *309*, 120–127; b) H. Luo, K. Efimov, H. Jiang, A. Feldhoff, H. Wang, J. Caro, *Angew. Chem. Int. Ed.* **2011**, *50*, 759–763.
- [19] W. Fang, T. Yang, K. Huang, *Chem. Commun.* **2019**, *55*, 2801–2804.
- [20] a) G. K. Reddy, T. C. Peck, C. A. Roberts, *J. Phys. Chem. C* **2019**, *123*, 28695–28706. b) W. Hong, S. Iwamoto, S. Hosokawa, K. Wada, H. Kanai, M. Inoue, *J. Catal.* **2011**, *277*, 208–216.
- [21] a) J. Zhou, G. Chen, K. Wu, Y. Cheng, *J. Phys. Chem. C* **2013**, *117*, 12991–12999; b) A. Staykov, H. Téllez, T. Akbay, J. Druce, T. Ishihara, J. Kilner, *Chem. Mater.* **2015**, *27*, 8273–8281.
- [22] N. Imanaka, T. Masui, H. Masaki, *Adv. Mater.* **2007**, *19*, 3660–3663.
- [23] X. Zhu, S. Zhang, Y. Yang, C. Zheng, J. Zhou, X. Gao, X. Tu, *Appl. Catal. B* **2017**, *213*, 97–105.
- [24] H. Ding, Y. Xu, C. Luo, Q. Wang, C. Shen, J. Xu, L. Zhang, *Energy Convers. Manage.* **2018**, *171*, 12–19.
- [25] C. Zhang, H. Zhao, *Electrochem. Commun.* **2011**, *13*, 1070–1073.
- [26] H. Luo, H. Jiang, K. Efimov, J. Caro, H. Wang, *AIChE J.* **2011**, *57*, 2738–2745.
- [27] A. Bueno-López, *Appl. Catal. B* **2014**, *146*, 1–11.
- [28] L. Chen, X. Niu, Z. Li, Y. Dong, D. Wang, F. Yuan, Y. Zhu, *J. Mol. Catal. A: Chem.* **2016**, *423*, 277–284.
- [29] Y. Teraoka, H. Zhang, N. Yamazoe, *Chem. Lett.* **1985**, *14*, 1367–1370.
- [30] Y. Teraoka, M. Yoshimatsu, N. Yamazoe, T. Seiyama, *Chem. Lett.* **1984**, *13*, 893–896.

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The catalysts 5%BaCoO₃-CeO₂ prepared by the one-pot method show high activity with 75.6% NO conversion to N₂ at 800 °C and superior O₂-resistance with the conversion sustaining at 54.3% in the presence of 10 vol% O₂, making it a promising catalyst candidate for practical application in NO direct decomposition.