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Article

Engineering the Mechanically Mixed BaMnO₃-CeO₂ Catalyst for NO Direct Decomposition: Effect of Thermal Treatment on Catalytic Activity

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Abstract: A 5 wt% BaMnO₃-CeO₂ composite catalyst prepared by the one-pot method exhibits extraordinary catalytic performance for nitrogen monoxide (NO) direct decomposition into N₂ and O₂; however, the reasons for the high activity remain to be explored. Here, the catalyst was prepared by mechanical mixing and then subjected to thermal treatment at different temperatures (600–800 °C) to explore the underlying reasons. The thermal pre-treatment at temperatures higher than 600 °C can improve the catalytic activity of the mechanically mixed samples. The 700 °C-treated 5%BaMnO₃-CeO₂ sample shows the highest activity, with NO conversion to N₂ of 13.4%, 40.6% and 57.1% at 600, 700, and 800 °C, respectively. Comparative activity study with different supports (ZrO₂, TiO₂, SiO₂, Al₂O₃) reveals that CeO₂ is indispensable for the high performance of a BaMnO₃-CeO₂ composite catalyst. The Ce species (mainly Ce³⁺) in CeO₂ components diffuse into the lattice of BaMnO₃, generating oxide ion vacancy in both components as evidenced by X-ray photoelectron spectroscopy and Raman spectra, which accelerates the rate-determining step and thus higher activity. The chemisorption results show that the interaction between BaMnO₃ and CeO₂ leads to higher redox activity and mobility of lattice oxygen. This work demonstrates that engineering the oxide ion vacancy, e.g., by thermal treatment, is an effective strategy to enhance the catalytic activity towards NO direct decomposition, which is expected to be applicable to other heterogeneous catalysts involving oxide ion vacancy.

Keywords: NO direct decomposition; thermal treatment; perovskite; BaMnO₃; CeO₂



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1. Introduction

The nitrogen oxides (NO_x, including mainly NO and NO₂) can jeopardize human health and the natural environment by acid rain, photochemical smog, ozone layer depletion, etc. Selective catalytic reduction, selective non-catalytic reduction, and NO_x storage and reduction have been widely applied in the purification of NO_x emitted from mobile vehicles and industrial process [1]. Among the various technologies, NO direct decomposition (2NO → N₂ + O₂) is regarded as the most desirable NO_x abatement technology because this reaction is thermodynamically favorable, eco-friendly and requires no additional reductant. However, its application is hindered by the sluggish reaction rate due to the high activation energy (~335 kJ mol⁻¹) [2]. The core lies in the catalysts of high performance. Therefore, various catalysts have been developed for NO direct decomposition, including noble metals, simple metal oxides, rare-earth metal oxides, perovskite-type metal oxides, zeolites and other catalysts [3,4].

In recent years, the Co₃O₄-based simple metal oxide catalysts have been paid much attention based on early research [5]. The effect of elemental modification [6–10] and

combining with other oxides [11] has been extensively investigated. However, the biggest issues with the simple oxides are their moderate activity and high sensitivity to O₂. For example, the NO conversion to N₂ of K-promoted Co-Zn-Mn-Al mixed oxide is ~52% at 700 °C, which decreases sharply to only ~8% after introducing 2 mol% O₂ [8]. In such context, the perovskite-based complex oxides (ABO₃) can be an alternative to solve the issues above considering their powerful doping capability at both A- and B-sites [3]. The activity of LaMnO₃ and BaMnO₃ can be enhanced by doping at La/Ba- and Mn- sites via tuning the amount of oxide ion vacancy and the mobility of lattice oxygen [12]. The Ba₃Y_{3.6}Cu_{0.4}O₉ showed an N₂ yield of 81% at 700 °C and 3 g s m⁻³ and good stability in 1% O₂-containing atmosphere [13]. However, one issue with the perovskite-based oxides is their low specific surface area, which results from the high calcination temperature required to obtain the desirable phase. It limits the further improvement of catalytic performance. Loading the perovskite oxides on the supports by impregnation is a typical choice, but it is time-consuming.

Aiming to find high-performance catalysts for NO direct decomposition, our group focused on the perovskite–CeO₂ composite catalysts considering the appealing properties of both components [3]. The citric acid–nitrate method was employed to synthesize the catalysts to obtain a high surface area. Our recent work revealed that the obtained perovskite–CeO₂ composite oxides are very promising catalysts for NO direct decomposition in terms of catalytic activity, oxygen resistance and durability [14–16]. The 5%BaCoO₃–CeO₂ catalyst shows NO conversion to N₂ of 75.6% at 800 °C and 1.5 g s cm⁻³ [14,15], which increases to 85.9% when the perovskite component is changed to BaMnO₃ [16]. The 5% BaMnO₃–CeO₂ catalyst exhibits 66.5% activity even in the presence of 10 vol% O₂ and runs stable for more than 200 h in 5 vol% O₂ at 800 °C [16]. Such attractive performance was attributed to the strong interaction between the perovskite and CeO₂ components. It is further confirmed by the results of the influence of the preparation method. Among the samples prepared by the one-pot, impregnation, and mechanical mixing methods, the one-pot derived samples show the highest activity [15].

Although the one-pot method can produce catalysts of high performance, it is a great challenge to explore the exact interaction between the perovskite and CeO₂ components considering the complex composition. Herein, the catalysts prepared by the mechanical mixing method were employed to investigate the interaction. The influence of thermal treatment on the catalytic performance of 5% BaMnO₃–CeO₂ was explored.

2. Results and Discussion

2.1. Catalytic Performance

Figure 1a displays the NO conversion to N₂ over 5%BaMnO₃–CeO₂ prepared by mechanical mixing (BaMnO₃–CeO₂–M). Compared with pure BaMnO₃, the BaMnO₃–CeO₂–M catalyst exhibits similar NO conversion at 500–600 °C but enhanced activity at temperatures >600 °C. The NO conversion to N₂ over BaMnO₃–CeO₂–M is 61.8% at 850 °C, which is about four times that of pure BaMnO₃ (12.4%). Since the BaMnO₃ and CeO₂ powders were only mixed manually, their interaction must be very weak, which should be responsible for similar activity at medium temperatures. The testing temperature higher than 600 °C can be regarded as an in-situ thermal treatment process, which enhances the interaction and thus improved activity at higher temperatures. It is also noted that the one-pot derived sample (BaMnO₃–CeO₂–O) exhibits much higher activity than BaMnO₃–CeO₂–M, which infers stronger intimate interaction between the components in the former sample.

We also tested the activity of BaMnO₃ mixed with other classical supports such as ZrO₂, TiO₂, SiO₂ and Al₂O₃. The specific surface area of those supports (20–40 m² g⁻¹) was controlled to be similar with that of CeO₂ (26 m² g⁻¹) except for SiO₂ (172 m² g⁻¹) in order to minimize the influence of geometric factors on catalytic activity. It is interesting to find that only CeO₂ can substantially improve the catalytic activity whereas other supports all suppress the activity of BaMnO₃ (Figure 1b). The results clearly reveal that CeO₂ is critical for the high performance of the BaMnO₃–CeO₂ catalyst.

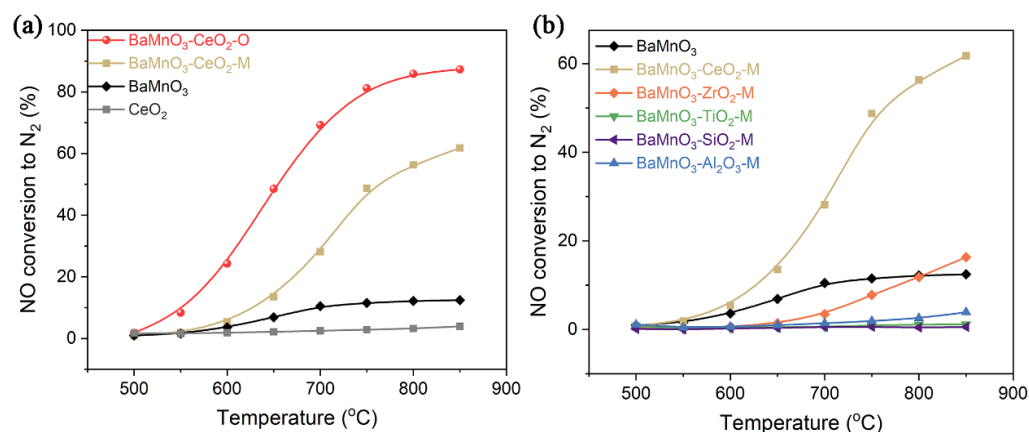


Figure 1. Catalytic activity of (a) BaMnO₃-CeO₂-M and (b) BaMnO₃-A_xO_y-M (A = Ce, Zr, Ti, Si and Al). The BaMnO₃-CeO₂-O, BaMnO₃ and CeO₂ samples were also included for comparison. Reaction conditions: 2 vol% NO/He, 1.5 g s cm⁻³, 500–850 °C.

Considering that the elevated temperature probably promotes the interaction between the components (Figure 1a), the BaMnO₃-CeO₂-M samples were pretreated at 600–800 °C before the catalytic activity test. The 600 °C-treated sample (BaMnO₃-CeO₂-M-600) shows almost similar activity with BaMnO₃-CeO₂-M over the whole temperature range (Figure 2a). In contrast, 700 and 800 °C calcination (BaMnO₃-CeO₂-M-700/800) enhances the activity clearly. The BaMnO₃-CeO₂-M-700 sample shows the highest activity, 26.5%, 40.6% and 50.5% at 650, 700 and 750 °C, respectively, which increases by ~17%, ~20% and ~15% compared with BaMnO₃-CeO₂-M. BaMnO₃-CeO₂-M-800 shows slightly lower activity than BaMnO₃-CeO₂-M-700, but still higher than BaMnO₃-CeO₂-M. Accordingly, the thermal treatment above 600 °C can improve the catalytic activity of BaMnO₃-CeO₂-M. Furthermore, BaMnO₃-CeO₂-M-700 shows a rather stable durability in the 5 vol% O₂-containing atmosphere at 800 °C, with only ~11% decrease over more than

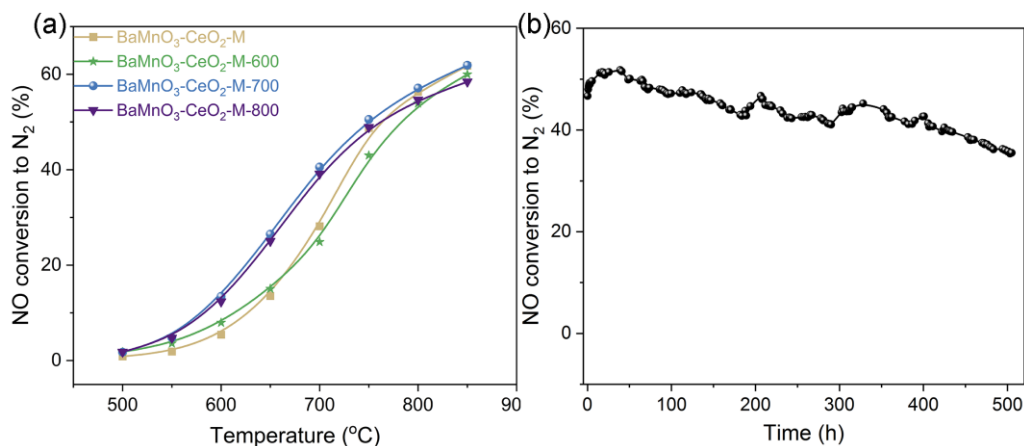


Figure 2. (a) Catalytic activity of BaMnO₃-CeO₂-M thermally pre-treated at different temperatures (600, 700 and 800 °C). Reaction conditions: 2 vol% NO/He, 1.5 g s cm⁻³, 500–850 °C. (b) Durability of BaMnO₃-CeO₂-M-700 in O₂-containing atmosphere. Reaction conditions: 2 vol% NO/He, 5 vol% O₂, 1.5 g s cm⁻³, 800 °C. 500 h.

(Figure 2b). As aforementioned, although the activity of BaMnO₃-CeO₂-M-700 is lower than that of BaMnO₃-CeO₂-O, it is still higher than or comparable with that of the reported finely designed perovskite-based catalysts, e.g., ~43% at 800 °C and 4 g s m⁻³ for La_{0.8}Sr_{0.2}CoO₃ [17], 63.7% at 800 °C and 3 g s m⁻³ for La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃ [12], 39% at 650 °C and 3 g s m⁻³ for La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O₃ [18].

2.2. XRD and SSA

To explore the reasons for the promoting effect of thermal treatment on BaMnO₃-CeO₂-M, various characterization was performed. The X-ray diffraction (XRD) pattern of 5%BaMnO₃-CeO₂-M (Figure 3) shows strong diffraction of CeO₂ but weak diffraction of BaMnO₃ due to their different contents, similar to our previous work [15]. The thermal pretreatment, even at 700 and 800 °C, shows no influence on the positions of the diffraction peaks, which indicates very limited, if not no, elemental diffusion between the two components. However, the diffraction peaks of CeO₂ in BaMnO₃-CeO₂-M-700 become weaker and wider, which is due to the reduced CeO₂ grain size (22.9 nm) compared with that in BaMnO₃-CeO₂-M (24.3 nm) and BaMnO₃-CeO₂-M-800 (26.6 nm) according to the Scherrer equation (Table 1). Therefore, the thermal treatment at 700 °C can suppress the CeO₂ grain growth, which is beneficial for NO direct decomposition. However, if temperature is too high (800 °C) treatment will again accelerate the grain growth, which may result in slightly decreased activity.

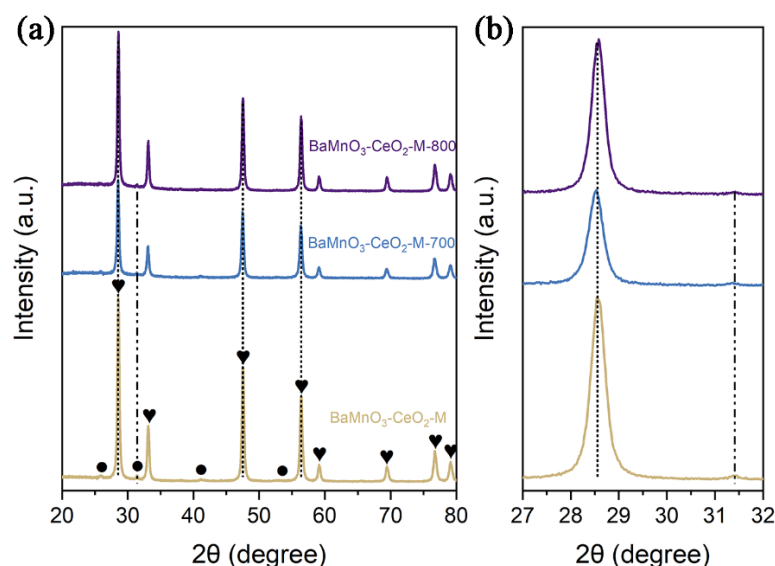


Figure 3. (a) XRD patterns of BaMnO₃-CeO₂-M and BaMnO₃-CeO₂-M-T (T = 700 and 800 °C) catalysts in the 2θ range of 20–80°. (b) Enlargement of the XRD patterns in the 2θ range of 27–32°.

Table 1. CeO₂ grain size, SSA, content of Mn, Ce and O species based on the XPS results, and I_D/I_{F2g} in Raman spectra.

Catalyst	CeO ₂ Grain Size (nm)	SSA (m ² g ⁻¹)	Mn ⁴⁺	Mn ³⁺	O _{II}	Ce ⁴⁺	I _D /I _{F2g}
CeO ₂	24.8	26	-	-	36.1%	67.1%	0.26
BaMnO ₃	-	8	53.5%	46.5%	60.7%	-	-
BaMnO ₃ -CeO ₂ -M	24.3	26	44.4%	55.6%	28.7%	65.3%	0.27
BaMnO ₃ -CeO ₂ -M-600	-	24	38.9%	61.1%	30.1%	74.1%	0.31
BaMnO ₃ -CeO ₂ -M-700	22.9	22	30.9%	69.1%	36.3%	74.8%	0.47
BaMnO ₃ -CeO ₂ -M-800	26.6	17	39.7%	60.3%	35.9%	78.9%	0.44
BaMnO ₃ -CeO ₂ -O	-	52	22.4%	77.6%	45.3%	88.7%	0.65

The scanning electron microscopy (SEM) results of the catalysts are shown in Figure 4. Rather serious agglomeration of BaMnO₃ and CeO₂ can be found for the BaMnO₃-CeO₂-M and BaMnO₃-CeO₂-M-600 samples; however, the thermal treatment at 700 and 800 °C weakens the agglomeration while increasing the particle size, which is in accordance with the reduced specific surface area (SSA) as discussed below.

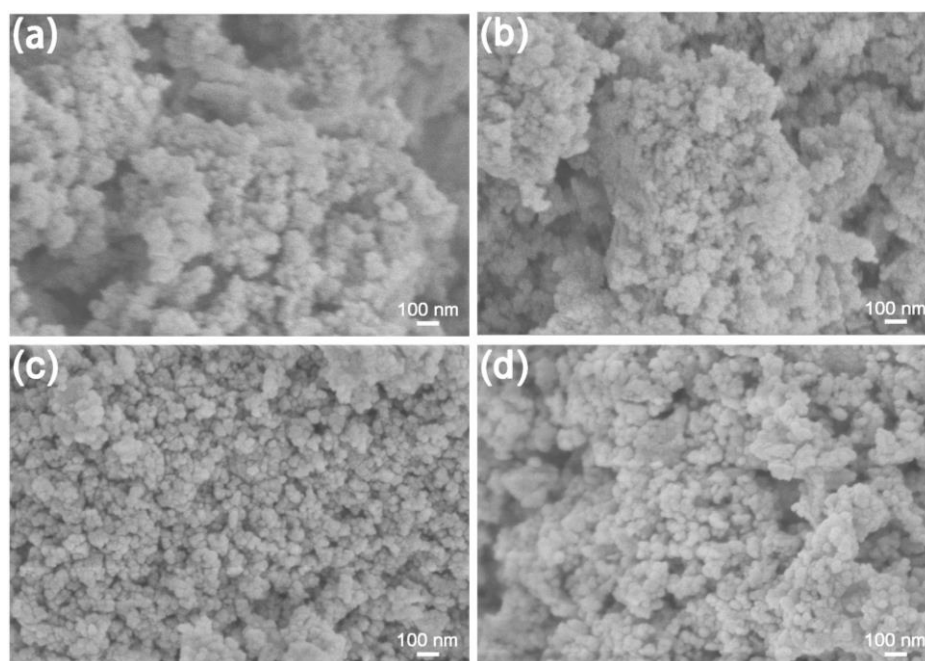


Figure 4. SEM microstructures of the (a) pristine mechanically mixed sample and treated at (b) 600 °C, (c) 700 °C, and (d) 800 °C.

As shown in Table 1, the SSA of BaMnO₃-CeO₂-M is 26 m² g⁻¹. The thermal treatment at 600–800 °C reduces SSA gradually, which is 24, 22 and 17 m² g⁻¹ for BaMnO₃-CeO₂-M-600, 700 and 800, respectively. Although high surface area is generally beneficial for the catalytic activity, the BaMnO₃-CeO₂-M-700 and 800 samples, with lower surface area, show higher activity compared with BaMnO₃-CeO₂-M, which suggests that the chemical interaction between the two components is the predominant activity.

2.3. XPS and UV Raman Spectra

In order to reveal the interaction between the two components of BaMnO₃ and CeO₂, X-ray photoelectron spectroscopy (XPS) was run and the results are shown in Figure 5. In the Ba 3d spectra (Figure 5a), the peaks at ~779.2/~794.5 eV are attributed to Ba²⁺ in BaMnO₃, and those at ~780.4/~795.7 eV to Ba²⁺ in BaCO₃ [19,20]. With increasing heat-treatment temperature, the Ba 3d spectra shift toward higher binding energy and the peak area of Ba²⁺ in BaCO₃ increases, i.e., the transformation of Ba²⁺ in BaMnO₃ to BaCO₃ due to the reaction of highly dispersed BaMnO₃ with the atmospheric CO₂.

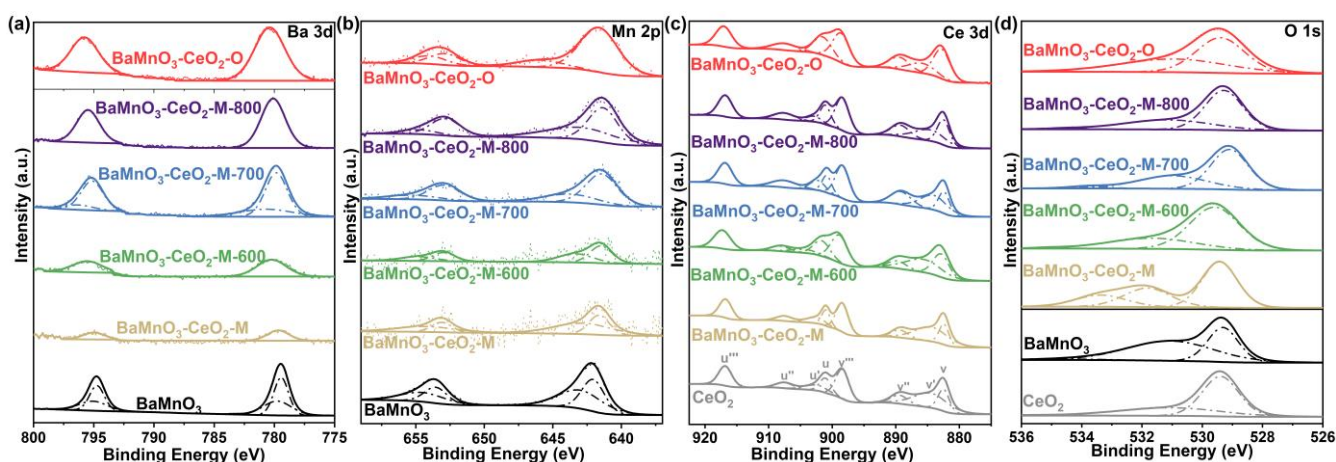


Figure 5. XPS spectra of (a) Ba 3d, (b) Mn 2p, (c) Ce 3d and (d) O 1s for BaMnO₃-CeO₂.

For the Mn 2p spectra (Figure 5b), the peaks at $\sim 641.7/\sim 653.2$ eV and $\sim 642.6/\sim 654.1$ eV are assigned to Mn^{3+} and Mn^{4+} , respectively [19,21,22]. The peaks gradually shift to lower binding energy with the heat-treatment temperature, which indicates partial transformation of Mn species to lower oxidation states ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$). According to Table 1, the Mn species exist mainly as Mn^{3+} at the surface of the catalysts. For the mechanically mixed samples, the Mn^{3+} content increases with the baking temperature, which reaches a maximum for the 700 °C-baked sample and then decreases for the 800 °C-baked one. It is also found that the one-pot prepared sample shows the highest content of Mn^{3+} . The trend of Mn^{3+} content is in agreement with the activity. The peak positions of both Ce^{3+} (v' and u') and Ce^{4+} (other peaks) [19,23] remain unchanged in the mixed samples (Figure 5c). However, the content of Ce^{4+} species increases with the treatment temperature (Table 1).

The O 1s spectra (Figure 5d) can be divided into lattice oxygen (O_I , 529.0–529.2 eV), surface-adsorbed oxygen (O_{II} , 530.9–531.3 eV) and adsorbed molecular water (O_{III} , 533.1–534.5 eV) [19,24]. The concentration of O_{II} , related to the oxide ion vacancy, increases with the heat-treatment temperature until 700 °C and then decreases slightly. Again, the one-pot sample shows the highest content of O_{II} . The increasing Mn^{3+} species in BaMnO_3 can be compensated by oxide ion vacancy to achieve charge balance. Expectedly, the content of Mn^{3+} and O_{II} show similar trend with the composition (Table 1).

To further determine the oxide ion vacancy, the ultraviolet (UV) Raman spectra were collected and the results are shown in Figure 6. The Raman characteristic bands at 462, 570 and 1179 cm^{-1} in pure CeO_2 can be assigned to the oxygen breathing frequency around the Ce^{4+} ions (F_{2g} mode) [25], defect sites (oxide ion vacancy, D) and second-order longitudinal optical (2LO) mode, respectively [26,27]. In the composite catalysts, the band at ~ 651 cm^{-1} is attributed to BaMnO_3 [28], indicating the simultaneous existence of two components. Based on the Raman spectra, there is no diffusion of Ba or Mn species to CeO_2 in BaMnO_3 - CeO_2 -M-T samples, as evidenced by the constant position of the F_{2g} and 2LO peaks. Since the content of surface oxide ion vacancy is closely related with the relative intensity of the D band to the F_{2g} band in the UV Raman spectra [27,29], $I_D/I_{\text{F}_{2g}}$ was calculated and the results are provided in Table 1. $I_D/I_{\text{F}_{2g}}$ increases with the thermal treatment temperature until 700 °C and then decreases slightly at 800 °C, indicating that increased oxide ion vacancies are created in the CeO_2 component during the thermal treatment. Furthermore, BaMnO_3 - CeO_2 -O delivers the largest $I_D/I_{\text{F}_{2g}}$, i.e., highest concentration of oxide ion vacancy.

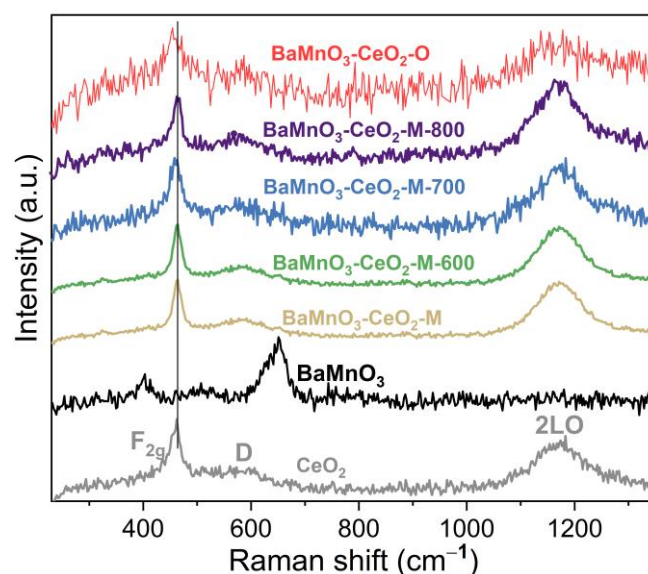


Figure 6. UV Raman spectra of various catalysts.

Based on the results above, we can propose that during the heat treatment, certain amounts of Ce species (probably Ce^{3+}) in CeO_2 diffuse into the lattice of BaMnO_3 , replacing

the Mn^{4+} species (Ce'_{Mn}) in $BaMnO_3$ and leaving Ce vacancy (V'''_{Ce}) in CeO_2 . Consequently, oxide ion vacancy (V) in $BaMnO_3$, Ce^{4+} (Ce_{Ce}) and V in CeO_2 are generated to achieve the charge balance. Our previous mechanistic study reveals that the oxide ion vacancy is involved in the rate-determining step (RDS) of $BaMnO_3$ - CeO_2 , where NO_2^{-*} reacts with NO^* and oxide ion vacancy to form N_2O^* , O^{2-} and O^* [16]. Higher concentration of oxide ion vacancy will accelerate the reaction of the RDS. Accordingly, the thermal pretreatment promotes the generation of oxide ion vacancy and thus higher activity.

2.4. Chemisorption Properties

To unearth the chemical interaction between the components during thermal treatment, the chemisorption was run. In the hydrogen temperature-programmed reduction (H_2 -TPR) profiles (Figure 7a), $BaMnO_3$ shows three main peaks at ~ 440 , ~ 700 , and ~ 875 °C, corresponding to the reduction of Mn^{4+} to Mn^{3+} , Mn^{3+} to Mn^{2+} species in the bulk, and decomposition of residual carbonate, respectively [30,31]. The shoulder peaks at ~ 410 and ~ 480 °C are due to the reduction of Mn^{4+} and Mn^{3+} species at the surface [30]. Pure CeO_2 exhibits two peaks at ~ 510 and ~ 780 °C due to the reduction of Ce^{4+} species at the surface and in the bulk, respectively [14,15]. The profile of $BaMnO_3$ - CeO_2 -M tends to be a simple combination of pure $BaMnO_3$ and CeO_2 , indicating constant reducibility due to limited interaction between the two components in the mechanically mixed catalyst. The thermal treatment at temperatures ≥ 600 °C can clearly increase the reduction activity of $BaMnO_3$ as evidenced by the shift to lower temperatures. In addition, $BaMnO_3$ - CeO_2 -O exhibits the lowest reduction temperature among all the samples, which is consistent with its highest reducibility. Since the NO direct decomposition is a redox reaction [32], the higher reducibility of the catalysts is beneficial for the reaction and thus higher activity.

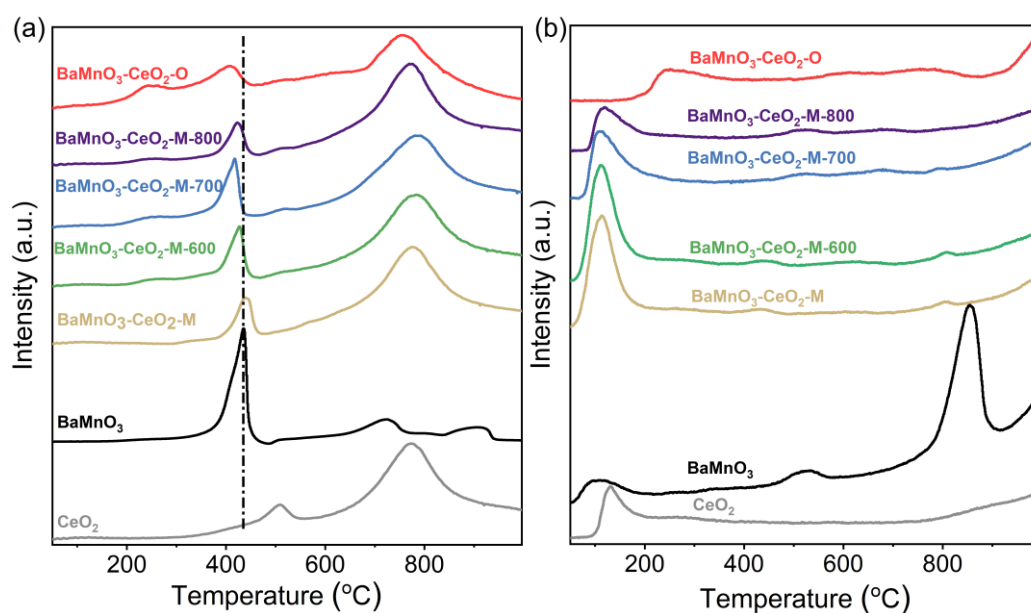


Figure 7. (a) H_2 -TPR and (b) O_2 -TPD profiles of various catalysts.

For oxygen temperature-programmed desorption (O_2 -TPD) profiles (Figure 7b), $BaMnO_3$ shows three desorption peaks assigned to chemically adsorbed oxygen species (α oxygen, O_2^- , < 200 °C), oxygen at the surface oxide ion vacancy (β oxygen, O^- , 400 – 600 °C) and lattice oxygen (γ oxygen, O^{2-} , > 700 °C), respectively [13–15]. Among them, the β and γ oxygen species are closely related to the catalytic activity and thus profiles within 400 – 1000 °C are focused. Compared with $BaMnO_3$, the desorption peaks of β oxygen shift to higher temperatures whereas γ oxygen shifts to lower temperatures for $BaMnO_3$ - CeO_2 composited oxides. The desorption peak area of β and γ oxygen decreases in the order of $BaMnO_3$ - CeO_2 -O $>$ $BaMnO_3$ - CeO_2 -M-700 $>$ $BaMnO_3$ - CeO_2 -M-800 $>$ $BaMnO_3$ - CeO_2 -M-600

> BaMnO₃-CeO₂-M, which is generally consistent with the catalytic activity trend. The higher thermal treatment temperature can efficiently enhance the sorption of oxygen species and mobility of lattice oxygen, which is conducive to the NO direct decomposition [13].

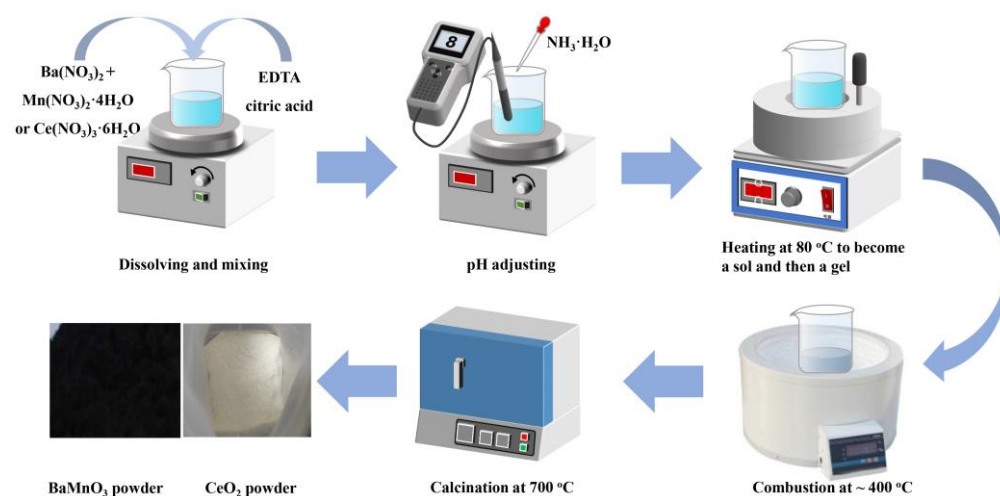
As a summary, the surface area, content of oxide ion vacancy, reducibility, and mobility of lattice oxygen contribute to the catalytic activity of the BaMnO₃-CeO₂ catalyst for NO direct decomposition. In particular, the amount of oxide ion vacancy is more important considering that it is involved in the RDS. Accordingly, the BaMnO₃-CeO₂-M-700 sample shows the highest activity among the mechanically mixed samples, although it is still lower than BaMnO₃-CeO₂-O prepared by a different method. This result suggests that simply heating the mechanically mixed BaMnO₃ and CeO₂ at elevated temperatures can effectively promote the NO direct decomposition activity. Such conclusion is supposed to be applicable to other heterogeneous catalysts involving oxide ion vacancy.

Finally, we would like to discuss the effect of support. As shown in Figure 1b, only CeO₂ can significantly enhance the catalytic activity of BaMnO₃ whereas others (ZrO₂, TiO₂, Al₂O₃, and SiO₂) cannot. As aforementioned, the Ce species in CeO₂ diffuse into BaMnO₃ and result in the formation of oxide ion vacancy in both components. BaCeO₃ is a typical proton-conducting material for various applications [33]. Although similar diffusion can happen for Zr and Ti, considering the well-known BaZrO₃ and BaTiO₃ materials, the less easy valence change compared with Ce species in CeO₂ probably limits their effect. The oxidation states of Al/Si species in Al₂O₃/SiO₂ can be deemed as unchanged, which makes the formation of an oxide ion vacancy in those components hard and thus low-activity since an oxide ion vacancy is deemed necessary for the active sites for NO direct decomposition [3]. In addition, in the mechanically mixed samples, the coverage of active sites in BaMnO₃ by those supports should be partly responsible for the lowered activity.

3. Experimental

3.1. Catalyst Preparation

The BaMnO₃ and CeO₂ catalysts were separately synthesized by the citric acid–nitrate method as reported previously [14–16], as schematically shown in Scheme 1. Briefly, stoichiometric amounts of Ba(NO₃)₂, Mn(NO₃)₂·4H₂O for BaMnO₃ and Ce(NO₃)₃·6H₂O for CeO₂, ethylene diamine tetraacetic acid (EDTA) in ammonia hydroxide and citric acid were mixed. The molar ratio of total metal ions:EDTA: citric acid was 1:1:2 and the pH was adjusted to ~8 by ammonia hydroxide. The solution was heated, which became a sol, then a gel, and finally combusted. The combusted powders were collected and calcined at 700 °C for 6 h, and BaMnO₃ and CeO₂ powders were obtained.



Scheme 1. Citric acid–nitrate route to synthesize the BaMnO₃ and CeO₂ powders.

The 5 wt% BaMnO₃-CeO₂ catalyst was prepared by mechanical mixing with a mortar and pestle by hand for 1 h, denoted by BaMnO₃-CeO₂-M, which was then subjected to

thermal treatment at 400, 600, 700 and 800 °C for 6 h, respectively. The resultant samples were named as BaMnO₃-CeO₂-M-T (T was thermal treatment temperature). In addition, 5%BaMnO₃-A_xO_y-M (A = Zr, Ti, Si and Al) catalysts were also prepared by a similar procedure except that the supports A_xO_y are commercial products, with specific surface areas (SSAs) of 21, 25, 172 and 37 m² g⁻¹ for ZrO₂, TiO₂, SiO₂ and Al₂O₃, respectively. The one-pot 5 wt% BaMnO₃-CeO₂ (BaMnO₃-CeO₂-O) sample [16] was also included for comparison.

3.2. Catalytic Performance Test

The as-prepared catalysts were pressed, crushed and sieved into particles of 40–60 mesh. NO direct decomposition was carried out in a fixed-bed quartz glass tube reactor of 10 mm internal diameter under 2 vol% NO/He (20 mL min⁻¹) with the contact time of 1.5 g s cm⁻³. 5 vol% O₂ was also introduced to examine the long-term stability under an O₂-containing atmosphere of the catalyst while keeping the total flow rate constant by adjusting He. The N₂ concentration in the reactor outlet was analyzed by an online gas chromatography system (Agilent 6890N) equipped with a thermal conductivity detector and molecular sieve 5A column. Steady-state results from GC were measured from 500 to 850 °C with an interval of 50 °C. The catalytic activity is evaluated by NO conversion to N₂.

3.3. Catalyst Characterization

The crystal structure was analyzed by XRD (Rigaku D/Max-2500) with monochromatic Cu K_α radiation in the 2θ range of 20–80° at a scan rate of 2° min⁻¹. The microstructures of the catalysts were observed by SEM (Hitachi S-4800, Hitachi, Japan) equipped with an energy-dispersive spectroscopy (EDS) unit. The SSA was determined on Quantachrome Autosorb-1 with nitrogen sorption at -196 °C after degassing at 250 °C for 4 h under vacuum. The UV Raman spectra were recorded at room temperature on a Renishaw laser Raman spectrometer (inVia reflex) with laser excitation at 325 nm. The reducibility and O₂ desorption properties were examined by H₂-TPR and O₂-TPD on a Xianquan TP-5076, respectively. The samples were pretreated at 200 °C for 30 min and then cooled to room temperature (RT) under pure N₂ before running an H₂-TPR test in 5 vol% H₂/N₂ (30 mL min⁻¹) from RT to 1000 °C. The catalysts were pretreated at 500 °C for 30 min and cooled to RT under pure O₂ (30 mL min⁻¹), followed by an O₂-TPD test in pure He from RT to 1000 °C. XPS (Thermo Scientific (Waltham, MA, USA) K-Alpha) was conducted on a SPECS system with Al K_α as X-ray source under a vacuum pressure of 5 × 10⁻⁸ Pa. The binding energy was calibrated with adventitious carbon 1 s at 284.8 eV.

4. Conclusions

We investigated the effect of thermal treatment on the catalytic performance over BaMnO₃-CeO₂ composite catalysts prepared by the mechanical mixing method. CeO₂ is crucial for the high performance of 5%BaMnO₃-CeO₂ compared with other conventional supports. The thermal treatment at >600 °C can improve catalytic performance. The 700 °C-treated samples show NO conversion to N₂ of 26.5%, 40.6% and 50.5% at 650, 700 and 750 °C, increased by ~17%, ~20% and 15%, respectively, compared with the pristine mechanically mixed sample. The promoting effect of higher-temperature thermal treatment is originated from the diffusion of Ce species into BaMnO₃, which can increase the content of oxide ion vacancy in both BaMnO₃ and CeO₂ components and thus is beneficial for the RDS. In addition, increased interaction between BaMnO₃ and CeO₂ can improve the redox activity and mobility of lattice oxygen. This work sheds light on the design of high-performance catalysts for NO direct decomposition by engineering the oxide ion vacancy.

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