Catalytic Oxidation of Toluene Over LaNixB1-xO3 (B=Co, Cu) Perovskite Catalysts

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Abstract: A series of $\text{LaNi}_x\text{B}_{1-x}\text{O}_3$ (B=Co, Cu) perovskite catalysts were prepared by sol-gel method and employed in toluene degradation. The catalysts were characterized by XRD, UV-Vis, SEM and XPS to investigate crystal structure, morphology and composition of the catalyst. The effect of different calcination temperatures and time on the performance of perovskite catalysts for toluene degradation were investigated. And the CO_2 selectivity was also carried out on as-prepared catalysts. The results showed that a small amount of Co-doping in B site of LaNiO_3 could significantly improve its toluene degradation, while the substitution of Ni with Cu could not effectively enhance its activity. When the Ni/Co molar ratio in $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ perovskite was 3:1, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ catalyst exhibited the best activity, and it showed relatively short time and low temperature for toluene conversion of 100%. Therefore, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ catalyst has a broad prospect in the degradation of volatile organic pollutants.

Key words: Perovskite; Toluene; Volatile organic pollutants

1. Introduction

VOCs are those organic compounds with a Reid vapor pressure of over 10.3 Pa at normal temperature (293.15 K) and pressure (101.325 kPa) (Kamal et al. 2016). As a carbon-based chemical, VOCs evaporate easily at room temperature. The harm of VOCs is mainly manifested in two aspects: evaporation and its own volatilization (Garcia et al. 2009). In which, evaporation is the main cause of serious air pollution, which produces ozone, smog and other pollutants and pollutes the environment, thus affecting seriously human health (Mikulova et al. 2007; Rumchev et al. 2007). The most volatile pollutants in industry are benzene series, such as styrene, toluene, ethylbenzene, xylene and many organic compounds of alkane (Pan et al. 2018). In view of the increasing VOCs emissions to the environment caused by rapid urbanization and industrialization (Roberts et al. 1990; Ivanova et al. 2013; Kamal et al. 2016), many countries around the world have formulated strict laws and regulations to limit the VOCs content in the environment (Kamal et al. 2016). Under such circumstances, it is urgent to explore effective ways to degrade VOCs. Thermal catalysis or biological oxidation can destroy the structure of VOCs and degrade it into carbon dioxide and water (Moretti et al. 2002; Blasin-Aube et al. 2003). While in catalytic reaction, catalysts play a decisive role in pollutant removal efficiency (Ojala et al. 2015). And numerous studies have shown that the perovskite-type metal oxides with the general molecular formula ABO_3 have both photocatalytic and thermocatalytic activities (Alifanti et al. 2007; Huang et al. 2008; Zhang et al. 2015), and are an effective catalyst for the removal of VOCs. Some perovskites (ABO_3) have

a narrow band gap and good photo-responsiveness to visible light (Kanhere et al. 2014), resulting in excellent photocatalytic performance. In the ideal rare earth perovskite, the octahedral coordination is 12 anions when type A cation is large, and 6 anions when type B cation is small. Due to the flexible transformation of A or B sites by band-gap engineering, ABO_3 perovskite has been extensively studied in the field of photocatalysis, such as photoreduction of CO_2 (Jia et al. 2009; Vereshchagin et al. 2015), photocatalytic decomposition of water (Yuan et al. 2008; Sang et al. 2009), and photocatalytic degradation of dyes (Torres-Martínez et al. 2009; Abou-Gamra et al. 2016). The main characteristics of its catalytic application include the stability of inclusion and abnormal valence states of transition metal ions, the presence of defect sites and the high oxygen mobility. Among all perovskites, La- series perovskite especially $LaNiO_3$ shows high thermal stability and oxygen mobility, and good activity in the catalytic oxidation of VOCs (Lu et al. 2014). The A- and B-sites ion substitution cations can change the composition and symmetry of metal cations and directly act on the valence state of metal cations without changing the structure (Ebbinghaus et al. 2009; Yoon et al. 2013; Chen et al. 2017; Chen et al. 2017). Therefore, in this work, a series of ABO_3 perovskites ($A = La$) with the B site (Cu, Co and Ni) were prepared by sol-gel method. The structure, morphology, element valence, and oxidation properties of as-prepared La-series perovskites were first investigated. And then, their catalytic activity and CO_2 selectivity were compared by toluene degradation. On this basis of the experimental results, the possible formation mechanism was also put forward finally. The purpose is to explore the preparation

conditions of the appropriate ABO_3 perovskite, and to select the LaBO_3 perovskite with the best degradation rate of toluene, which is of great significance for the degradation of volatile pollutants in daily life.

2. Experimental

2.1. Reagents and apparatus

Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), cobalt acetate ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4(\text{H}_2\text{O})$), and polyethylene glycol (PEG) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) was obtained from Shanghai Xinbao Fine Chemical Factory (Shanghai, China). All gases used were of high grade pure and purchased from Changzhou Wujin Huayang Gas Co., Ltd (Jiangsu province, China). All other reagents not mentioned were of analytical grade.

2.2. Preparation of catalyst

2.2.1. Preparation of LaBO_3 ($B=\text{Ni}, \text{Co}, \text{Cu}$)

1.0 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 1.0 mmol of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, and 2.0 mmol of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ as a complexing agent was first mixed evenly, 6 g of PEG as a dispersant was also added dropwise into above mixture, then about 150 mL of anhydrous as a solvent was poured into it, followed by stirring to dissolve completely. The resulting solution was heated at a constant temperature of 85 °C to obtain gel, which was transferred into a crucible for preheating to remove the citric acid, and then it was calcined at different temperatures (700, 600, 500, 400, and 300 °C) for different time (7, 6, 5, 4, and 3 h) to obtain a series of LaNiO_3 . The preparation of LaCoO_3 and

LaCuO₃ was same as LaNiO₃, just replacing nickel acetate with cobalt acetate and copper acetate.

2.2.2. Preparation of LaNi_x(Co,Cu)_{1-x}O₃

0.25 mmol of C₄H₆CoO₄·4(H₂O), 0.75 mmol of Ni(CH₃COO)₂·4H₂O, 1.0 mmol of La(NO₃)₂·xH₂O and 2.0 mmol of C₆H₈O₇·H₂O as a complexing agent was first mixed evenly, the remaining preparation steps are the same as that of LaNiO₃. The obtained pre-treated solution was calcined at 700 °C for 7 h to obtain LaNi_{0.75}Co_{0.25}O₃ (the molar ratio of Ni:Co is 3:1). LaNi_{0.5}Co_{0.5}O₃ and LaNi_{0.25}Co_{0.75}O₃ were obtained only adding different molar ratios of Ni to Co. Likewise, the preparation of LaNi_xCu_{1-x}O₃ is in accordance with LaNi_xCo_{1-x}O₃ only with different precursors.

2.3. Catalyst characterization

The crystal structure of the catalysts was analyzed by the X-ray diffraction (XRD), which using an X-ray diffractometer equipped with a Cu anode (D/Max 2500 PC, Rigaku Corporation, Japan); scanning angle was 2-80°, sweep rate was 3°/min, CuKα (40 KV, 40 mA). Scanning electron microscope (SEM) images and EDS were obtained via a scanning electron microscope (SUPRA55, Zeiss, Germany). The UV-vis diffuse reflectance spectra of the photocatalysts were collected with a UV-vis spectrometer (Thermo Nicolet Evolution 500) which used 100% BaSO₄ as a reflectance sample. X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, USA) by Al Kα radiation was used to evaluate surface composition and oxidation state of metal species on the surface of the catalysts. The binding energy was corrected using the C 1s spectrum at 284.8 eV.

2.4. Activity test of catalyst

Toluene degradation by perovskite catalysts is simulated in a fixed-bed quartz reactor in the laboratory. The initial flow rate of C₇H₈ and N₂ is 280 SCCM (mL min⁻¹), where the concentration of C₇H₈ is 1000 ppm. Toluene concentration is recorded every five minutes from 50 °C, and the CO₂ concentration is recorded from the initial CO₂ concentration of 0 ppm. The recording is stopped after the temperature reaches the specified temperature.

The toluene conversion rate and CO₂ yield can be calculated as follows:

$$\text{Toluene Conversion (\%)} = \frac{[\text{Toluene}]_{\text{in}} - [\text{Toluene}]_{\text{out}}}{[\text{Toluene}]_{\text{in}}} \times 100\% \quad (\text{I})$$

$$\text{CO}_2 \text{ Yield} = \frac{[\text{CO}_2]_{\text{out}}}{[\text{VOC}]_{\text{out}} + [\text{CO}_2]_{\text{out}}} \times 100\% \quad (\text{II})$$

Where, [Toluene]_{in} and [Toluene]_{out} represent the inlet and outlet concentration of C₇H₈, respectively. [CO₂]_{out} stands for outlet concentration of CO₂. The toluene conversion rate and CO₂ yield are used to indicate catalyst activity and CO₂ selectivity, respectively.

3. Results and discussion.

3.1 Characterization analysis of catalyst

3.1.1 XRD analysis

(1) Effect of calcination temperature and time on formation of perovskite-type LaNiO₃

Different calcination temperatures will affect the types of catalysts and the strength of crystal shapes. In Fig. 1A, the XRD patterns of LaNiO₃ calcined at temperatures of 700, 600, 500, 400, and 300 °C for 7 h are compared. Among which, when calcination

temperatures are 700 and 600 °C, the main peaks at $2\theta=23.32^\circ$, 32.91° , 47.36° are ascribed to (101), (110), and (202) crystal plane of LaNiO_3 (JCPDS #34-1181). While for calcination temperatures of 500, 400, and 300 °C, the peaks at $2\theta = 29.68^\circ$ correspond to (004) of La (JCPDS #51-1165), and there is almost no LaNiO_3 . At the same time, it can be noticed that the diffraction peak of LaNiO_3 at 700 °C is distinctly sharper than that at 600 °C. On basis of XRD comparison, the calcination temperature of 700 °C is appropriate for the preparation of LaBO_3 perovskite. In addition, the calcination time will also affect the crystal form of catalysts. Hence, the XRD patterns of LaNiO_3 with calcination time of 7, 6, 5, 4 and 3 h at the calcination temperature of 700 °C were compared in Fig. 1B. There is a prominent diffraction peak $2\theta = 32.91^\circ$ when the calcination time is 7, 6 and 5 h, which is indexed to (110) crystal plane of LaNiO_3 (JCPDS # 34-1181). When the calcination time is 4 and 3 h, they also have a more prominent diffraction peak derived from LaNiO_3 at the same position, namely $2\theta = 32.914^\circ$ (JCPDS # 34-1181), but the peak intensity at this position is relatively smaller, and more other impurities are produced, such as NiO , La_2O_3 , LaNi_5 . Therefore, the LaNiO_3 crystal form is relatively good and there are few impurities within calcination time of 5 h. In summary, in order to obtain better crystal shape, ABO_3 -type perovskites in this work was prepared by calcining at 700 °C for 7 h.

Fig. 1 XRD comparison of LaNiO₃ with different calcination temperatures and time.

(2) LaBO₃ (B = Ni, Co, Cu)

Fig. 2 shows the contrast of the structure and composition of LaBO₃ (B = Ni, Co, Cu) perovskite. Still, the diffraction peak at $2\theta = 32.91^\circ$ (curve a) is indexed to (110) crystal plane of LaNiO₃ (JCPDS # 34-1181). The obvious peak corresponded to (104) crystal plane of LaCoO₃ appears at $2\theta = 33.30^\circ$ (curve b) (JCPDS # 48 -0123). As for curve c, the strong diffraction peak at $2\theta = 31.07^\circ$ is ascribed to (113) crystal plane of La₂CuO₄ (JCPDS # 30-0487), and the relatively weak peak near $2\theta = 32.95^\circ$ is attributed to (104) crystal plane of LaCuO₃ (JCPDS # 25-0291). It is evident that Ni and Co as substitution elements at the B-site of LaBO₃ perovskites are more reasonable relative to Cu element.

Fig. 2 XRD spectra of LaBO_3 ($\text{B} = \text{Ni, Co, Cu}$).

(3) $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ perovskites

The structure of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) perovskites are also compared in Fig. 3A. It can be clearly noticed that the peak position and peak shape of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.25, 0.5, 0.75, 1$) are basically the same. All curves present the (110) crystal plane derived from LaNiO_3 , and a few diffraction peaks of LaNiO_3 or LaCoO_3 is covered by the strong peak of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.25, 0.5, 0.75$). Therefore, it is proved that $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) perovskites can be successfully prepared. Likewise, the structure of $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) perovskites are also compared in Fig. 3B. $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ ($x = 1, 0.75$) perovskites only has one obvious diffraction peak, which is attributed to (110) crystal plane of LaNiO_3 . While $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ ($x = 0, 0.25, 0.5$) has two distinct peaks, when $x = 0.5$ or 0.25 , the two peaks at $2\theta = 31.07^\circ$ and 32.91° are attributed to (113) crystal plane of La_2CuO_4 (JCPDS # 30-0487) and (110) crystal plane of LaNiO_3 (JCPDS #

34-1181), respectively; when $x = 0$, the two peaks at $2\theta = 31.07^\circ$ and 32.95° are due to (113) crystal plane of La_2CuO_4 (ICDD PDF # 30-0487) and (104) crystal plane of LaCuO_3 (JCPDS # 25-0291). This may be because the radius of Cu^{2+} is larger than that of Ni^{2+} . It is difficult for a large number of Cu^{2+} to enter the lattice of LaNiO_3 .

Fig. 3 XRD spectra of (A) $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and (B) $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$.

3.1.2 UV-Vis analysis of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$

Fig. 4 shows the UV-Vis absorption spectra of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$. As shown in the Fig. 4, all catalysts display strong absorption in the entire region of the wavelength from 200 to 650 nm, and the absorption become stronger as the wavelength increases. In Fig. 4A, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ has the strongest absorption, followed by $\text{LaNi}_{0.25}\text{Co}_{0.75}\text{O}_3$ and LaNiO_3 , and LaCoO_3 has the weakest absorption within the wavelength range from 200 to 400 nm. While in the range of 400 ~ 650 nm, the absorption of LaNiO_3 will be stronger than $\text{LaNi}_{0.25}\text{Co}_{0.75}\text{O}_3$, but still weaker than $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$. It can be noticed that a small amount of Co doping at the B site of LaNiO_3 can enhance its absorbance. In Fig. 4B, when the wavelength is about 310 and 360 nm, absorbance drops briefly, then continues to rise. In the same wavelength

range, the UV-Vis absorption intensity follows the order: $\text{LaNiO}_3 > \text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3 >$
 $\text{La}_2\text{CuO}_4 > \text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$. It is further proved that Cu-doping at B-site of LaNiO_3
cannot improve its absorbance.

Fig. 4 UV-Vis analysis of (A) $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and (B) $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ perovskite.

3.1.3 SEM analysis of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$

The microstructure and morphology of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$ were characterized by SEM and analyzed with EDS. As shown in Fig. 5A that the as-prepared $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ are uniformly dispersed in the form of irregular crystal particles, and the combination of crystal particles relatively loose, resulting in a better pore structure, which allows the active material to be in good contact with the volatile gas. This morphology can be observed more clearly in Fig. 5B. Such phenomenon helps the catalyst to exert the best catalytic effect. In Fig. 5D $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$ has local agglomeration, which can be intuitively observed in Fig. 5E. Fig. 5 C and F are the EDS spectra of the sample, there are four elements of C, O, La, Ni, and Co in Fig. 5 C and C, O, La, Ni, and Cu in Fig. 5 F. The corresponding weight percentage of each element in Fig.5 C is 13.58%, 37.64%, 19.99%, 21.36%, and 7.43% in Fig.5 F is

38.29%, 35.07%, 12.44%, 8.53%, and 5.67% respectively, suggesting the presence of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$ perovskite nanoparticles. Further observations indicate that these particles are stacked tightly to form pore structure, which will promote the transfer of organic matter and provide a larger reaction surface and more active sites (Chen et al. 2011).

Fig. 5 SEM images of (A), (B) $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and (D), (E) $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$ with different scales and EDS of (C) $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and (F) $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$.

3.1.4 XPS analysis

Fig. 6 shows the XPS analysis pattern of optimal $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$, which can determine the elemental composition and valence of the catalyst. The full spectrum of

233 Fig. 6A shows the presence of the elements La, Ni, Co and O, which is consistent with
 234 the results of EDS and indirectly verified the successful preparation of
 235 $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ perovskite. The XPS spectrum of La 3d is shown in Fig. 6B. The
 236 peaks at 833.62 and 837.05 eV are ascribed to La $3d_{5/2}$, and the peaks at 850.25 and
 237 854.17 eV are belonged to La $3d_{3/2}$, indicating that La is in form of La^{3+} in
 238 $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ (Li et al. 2015). Fig. 6C is the XPS spectrum of Co 2p. The two
 239 strong peaks near 782.1 and 795.6 eV are attributed to Co $2p_{3/2}$ and Co $2p_{1/2}$,
 240 respectively, which illustrates that Co is also mainly in the form of +3 valence (Chen
 241 et al. 2018). In Fig. 6D, the peaks near 850.2 and 854.3 eV corresponds to Ni $2p_{3/2}$,
 242 and the peaks at around 862.25 and 872.05 eV are due to Ni $2p_{1/2}$, suggesting that the
 243 existence of Ni^{3+} in $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ (Olszewska et al. 2012). Furthermore, there are
 244 two types of oxygen on the surface of the catalyst, namely lattice oxygen (O_{latt}) and
 245 adsorbed oxygen (O_{ads}) of the catalyst ($\text{O}_{\text{latt}}/\text{O}_{\text{ads}} = 0.45$) in Fig. 6 E, among which the
 246 lattice oxygen is mainly responsible for oxidation, but the absorbed oxygen can
 247 continuously supplement the consumption of lattice oxygen (Zhong et al. 2012) .

Fig. 6 XPS analysis of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$.

3.2. Toluene conversion over $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ catalysts

It can be known from the XRD results in Fig. 1A that the lower calcination temperature cannot form good crystal form, and there are more La in the product instead of LaNiO_3 , which does not catalyze the degradation of toluene. In order to further verify this conclusion, the toluene degradation of LaNiO_3 prepared at different calcination temperatures and time was investigated and the test temperature was set within the 50 ~ 350 °C. As shown in Fig. 7A, the overall trend of the five curves is basically the same. The degradation rate of toluene gradually increases from 0% with the increase of reaction temperature, and then stabilizes after reaching the highest degradation rate of 100%. Although the degradation rate at 700 °C is higher than 600 °C, the reaction temperature required to reach the conversion rate of 100% is not

much different. On the contrary, when the calcination temperature is 500, 400, and 300 °C, the degradation rate of toluene at the same reaction temperature is significantly reduced due to non-catalytic effect of La on the toluene degradation. Obviously, the reaction temperature required to reach the highest conversion rate for LaNiO_3 catalysts with calcination temperatures of 500, 400 and 300 °C is much higher. In addition, according to XRD pattern in Fig. 1B, the shorter the calcination time at the calcination temperature of 700 °C, the more impurities will be produced, and the yield of LaNiO_3 will undoubtedly decrease, which will also affect the catalytic performance of the as-prepared catalysts. In order to verify the above deduction, the activity of LaNiO_3 prepared at different time is compared in Fig. 7B. It is obvious that LaNiO_3 prepared at 5, 6, and 7 h has similar catalytic effect on toluene degradation, while the degradation rate of toluene over the catalyst prepared at 3 and 4 h is slower. Combining the catalytic activity and XRD results. The calcination temperature of 700 °C and calcination time of 7 h were selected in this work so as to pursue a higher toluene conversion rate at the same temperature.

Fig. 7 Catalytic activity of LaNiO_3 (A) at different calcination temperatures and (B) at different calcination times.

The catalytic activity of $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ with different molar ratios ($x = 0, 0.25, 0.5, 0.75$) were investigated. As shown in Fig. 8A, the catalytic activity of each $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ perovskite is uneven, which is related to the molar ratio of the two groups of elements. It is obvious that all $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ catalysts have shown good catalytic effects on the toluene degradation. Among them, the activity of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ (Ni/Co= 3:1) has the best catalytic effect. When the temperature rises to a certain value, the degradation rates of all $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ catalysts reach the maximum of 100%. The results are well agreement with previous conclusion and show that a small amount of Co doping at the B site of LaNiO_3 can improve its catalytic activity. Similar to Co, the activity tests of $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) are presented in Fig. 8B. Where the activity of LaNiO_3 is the best, and $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$ is second. When the content of Cu is high, the activity of the catalyst will decrease obviously. Additionally, it should be noted that when the molar ratio of Ni/Cu is 1:1 or 1:3, the activity of the catalyst is even worse than that of pure La_2CuO_4 . The results illustrate that Cu doping at B-site of LaNiO_3 cannot improve its activity. In summary, the perovskite with the best activity in this work is $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$.

Fig. 8 Catalytic activity of $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ perovskite.

3.3. CO₂ selective test of LaNi_xCo_{1-x}O₃ and LaNi_xCu_{1-x}O₃

Another important indicator of the catalytic degradation of toluene by the catalyst is the selectivity of CO₂. Fig. 9A is CO₂ selectivity of LaNi_xCo_{1-x}O₃ catalyst. Still the CO₂ selectivity of LaNi_xCo_{1-x}O₃ gradually increases from 0% to 100% as the reaction temperature increases. Among which, the CO₂ selectivity of LaNi_{0.75}Co_{0.25}O₃ is the best, and the CO₂ selectivity of other LaNi_xCo_{1-x}O₃ also corresponds to its activity. However, it is worth noting that the initial reaction temperature of the CO₂ selectivity of each catalyst from 0% is higher than that of degradation rate of toluene. This is because toluene degradation has intermediate products instead of being converted to CO₂ at the beginning of degradation. Similar as LaNi_xCo_{1-x}O₃, the CO₂ selectivity of LaNi_xCu_{1-x}O₃ corresponds to its activity. As shown in Fig. 9B, the CO₂ selectivity of LaNiO₃ is the best, followed by LaNi_{0.75}Cu_{0.25}O₃ and La₂CuO₄ again, the worst is LaNi_{0.5}Cu_{0.5}O₃. From what has been discussed above, LaNi_{0.75}Co_{0.25}O₃ exhibited the best CO₂ selectivity.

Fig. 9 CO₂ selectivity of (A) LaNi_xCo_{1-x}O₃ and (B) LaNi_xCu_{1-x}O₃.

4. Stability of LaNi_{0.75}Co_{0.25}O₃

Stability is another important factor of the catalyst. The test method of stability is

the same as the activity test. Among all the as-prepared catalysts, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ has the best degradation rate of toluene and CO_2 selective, and so it was selected to do stability test. The simulated air conditions are as follows: O_2 of 70 sccm and N_2 and C_7H_8 mixture of 280 sccm (where the content of C_7H_8 is 1000 ppm) were fed. The catalyst was used to catalyze the degradation of toluene at 350 °C for 10 h. The results in Fig. 10 show that during the continuous reaction, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ always maintains a high activity, and the degradation rate has barely changed, remaining at 100%. Therefore, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ perovskite is very effective for catalytic degradation of toluene.

Fig.10 Stability of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ catalyst.

5. The mechanism of toluene catalytic oxidation

Scheme 1 Catalytic degradation mechanism of toluene on $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ catalyst.

The catalytic oxidation of toluene on $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ perovskite follows the Mars-van Krevelen redox cycle. On the one hand, toluene molecules are adsorbed on the active site of the catalyst to form an adsorbed species, which reacts with the lattice oxygen to produce oxidation products ($\text{CO}_2 + \text{H}_2\text{O}$) (Aguero et al. 2009; Li et al. 2010; Zhang et al. 2011; Zhang et al. 2014); on the other hand, gaseous oxygen are converted into active oxygen, so that the redox reaction can be repeated (Merino et al. 2006; Paulis et al. 2000; Zhu et al. 2010). At the same time, increasing the temperature will increase the mobility of lattice oxygen ions (Liu et al. 2009). Considering the relationship between gaseous oxygen (O_2) and adsorbed oxygen on the surface, O_{ads} and O_{latt} were proposed as active oxygen to react with toluene to generate oxygen vacancies, thereby reducing the aggregation of O_{ads} and O_{latt} . At the same time, gaseous O_2 molecules are preferentially adsorbed on oxygen vacancies in an oxygen-rich environment to form active oxygen species, supplementing the consumed O_{ads} and O_{latt} species (Wang et al. 2018). In other words, it indicates that the presence of surface oxygen species, surface oxygen content and low-temperature

reduction degree have a clear correlation with toluene oxidation activity.

6. Conclusion

A series of La series perovskites were prepared by sol-gel method and employed in Toluene degradation. XRD results show that the optimal preparation condition of LaBO_3 ($B = \text{Ni, Co, Cu}$) perovskite were calcination temperature of 700 °C and calcination time of 7 h. Toluene conversion, CO_2 selectivity, and catalyst stability of as-prepared La series catalysts were explored to further verify their catalytic performance. The results show that the B-site in LaNiO_3 with a small amount of Co-doped can improve its activity, while Cu-doped La series perovskite has little effect on toluene degradation. The catalyst with the best toluene degradation activity prepared in this experiment is $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$, which has potential prospects for toluene degradation.

Author contributions This manuscript was contributed by all the authors. Songya Qi and Wanqi Zhang devised experimental methods, collected the data, and wrote the initial draft; Xiang Li, Qing Wang, and Zerui Zhu performed experiment work; Ting Zhou and Gaoxiang Wang verified the availability of the data and information; Aijuan Xie and Shiping Luo compiled, wrote, and reviewed the manuscript and provided sources of funding. All authors read and approved the final manuscript.

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Data availability The data and materials are true and reliable.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Reference

Aguero FN, Alberto S, Barbero BP, Cadu's LE (2009) Influence of the support treatment on the behavior of MnOx/Al₂O₃ catalysts used in VOC combustion.

Catal Lett 128(3-4):268-280

Alifanti M, Florea M, Pârvulescu VI (2007) Ceria-based oxides as supports for

LaCoO₃ perovskite; catalysts for total oxidation of VOC. Appl Catal B-Environ

70(1-4):400-405

Abou-Gamra ZM, Ahmed MA (2016) Synthesis of mesoporous TiO₂-curcumin

nanoparticles for photocatalytic degradation of methylene blue dye. J Photoch

Photobio B 160:134-141

Blasin-Aube V, Belkouch J, Monceaux L (2003) General study of catalytic oxidation

of various VOCs over La_{0.8}Sr_{0.2}MnO_{3+x} perovskite catalyst-influence of mixture.

Appl Catal B-Environ 43:175-186

Chen DL, Pan KL, Chang MB (2017) Catalytic removal of phenol from gas streams

by perovskite-type catalysts. J Environ Sci 56:131-139

Chen JY, He ZG, Li GY, An TC, Shi HX (2017) Visible-light-enhanced

photothermocatalytic activity of ABO₃-type perovskites for the decontamination

389 of gaseous styrene. Appl Catal B-Environmental 209:146-154

390 Chen JY, Liu XL, Li GY, Nie X, An TC, Zhang SQ, Zhao HJ (2011) Synthesis and
 391 characterization of novel SiO₂ and TiO₂ co-pillared montmorillonite composite
 392 for adsorption and photocatalytic degradation of hydrophobic organic pollutants
 393 in water. Catal Today 164:364-369

394 Chen X, Li JJ, Chen X, Cai SC, Yu EQ, Chen J, Jia HP (2018) MOF-templated
 395 ap-proach for hollow NiO_x/Co₃O₄ catalysts: enhanced light-driven
 396 thermocatalytic degradation of toluene. ACS Appl Nano Mater 1:2971–2981

397 Ebbinghaus SG, Abicht HP, Dronskowski R, Müller T, Reller A, Weidenkaff A (2009)
 398 Perovskite-related oxynitrides-recent developments in synthesis, characterisation
 399 and investigations of physical properties. Prog Solid State Chem
 400 37(2-3):173-205

401 García V, Pongrácz E, Muurinen E, RL Keiski (2009) Pervaporation of
 402 dichloromethane from multicomponent aqueous systems containing n-butanol
 403 and sodium chloride. J Membrane Sci 326(1):92-102

404 Huang H, Liu Y, Tang W, Chen Y (2008) Catalytic activity of nanometer
 405 La_{1-x}Sr_xCoO₃ (x=0, 0.2) perovskites towards VOC scombustion. Catal Commun
 406 9(1):55-59

407 Ivanova S, Pérez A, Centeno MA, Odriozola JA (2013) Structured Catalysts for
 408 Volatile Organic Compound Removal. Elsevier BV 233-256

409 Jia LS, Li JJ, Fang WP, Song H, Li QB, Tang Y (2009) Visible-light-induced
 410 photocatalyst based on C-doped LaCoO₃ synthesized by novel microorganism

411 chelate method. Catal Commun 10:1230-1234

412 Kamal MS, Razzak SA, Hossain MM (2016) Catalytic oxidation of volatile organic
 413 compounds (VOCs)-a review. Atmos Environ 140:117-134

414 Kanhere P, Chen Z (2014) A review on visible light active perovskite-based
 415 photocatalysts. Molecules 19:19995-20022

416 Li S, Li Y, Yang F, Liu Z, Gao R, Zhao J (2015) Photocatalytic oxidation
 417 desulfurization of model diesel over phthalocyanine/La_{0.8}Ce_{0.2}NiO₃. J Colloid
 418 Interf Sci 460:8-17

419 Li Y, Huang J, Peng T, Xu J, Zhao X (2010) Photothermocatalytic Synergetic Effect
 420 Leads to High Efficient Detoxification of Benzene on TiO₂ and Pt/TiO₂
 421 Nanocomposite. Chemcatchem 2(9):1082-1087

422 Liu XW, Zhou KB, Wang L, Wang BY, Li YD (2009) Oxygen Vacancy Clusters
 423 Promoting Reducibility and Activity of Ceria Nanorods. Am J Chem Soc
 424 131:3140-3141.

425 Lu YJ, Dai QG, Wang XY (2014) Catalytic combustion of chlorobenzene on modified
 426 LaMnO₃ catalysts. Catal Commun 54:114-117

427 Merino NA, Barbero BP, Eloy P, Cadus LE (2006) La_{1-x}Ca_xCoO₃ perovskite-type
 428 oxides:identification of the surface oxygen species by XPS. Appl Surf Sci 253
 429 (3):1489-1493

430 Mikulova J, Rossignol S, Barbier J, Duprez D, Kappenstein C (2007)
 431 Characterizations of platinum catalysts supported on Ce,Zr,Pr-oxides and

432 formation of carbonate species in catalytic wet air oxidation of acetic acid. *Catal*
433 *Today* 124:185-190

434 Moretti EC (2002) Reduce VOC and HAP emissions. *Chem Eng Prog* 98:30-40

435 Olszewska D (2012) Application of XPS method in the research into Ni ion-modified
436 montmorillonite as a SO₂ sorbent. *Fuel Process Technol* 95:90-95

437 Pan KL, Pan GT, Chong S, Chang MB (2018) Removal of VOCs from gas streams
438 with double perovskite-type catalysts. *J Environ Sci* 69:205-216

439 Paulis M, Gandía LM, Gil A, Sambeth J, Odriozola JA, Montes M (2000) Influence of
440 the surface adsorption-desorption processes on the ignition curves of volatile
441 organic compounds (VOCs) complete oxidation over supported catalysts. *Appl*
442 *Catal B-Environ* 26(1):37-46

443 Roberts JM (1990) The atmospheric chemistry of organic nitrates. *Atmos Environ*
444 24(2):243-287

445 Rumchev K, Brown H, Spickett J (2007) Volatile organic compounds: do they present
446 a risk to our health. *Rev Environ Health* 22(1):39-55

447 Sang WB, Ji SM, Hong SJ, Ji WJ, Lee JS (2009) Photocatalytic overall water splitting
448 with dual-bed system under visible light irradiation. *Int J Hydrogen Energ*
449 34:3243-3249

450 Satu O, Niina K, Tiina L, Anass M, Prem S, Said L, Kaisu A, Rachid B, Riitta K
451 (2015) Utilization of volatile organic compounds as an alternative for
452 destructive abatement. *Catalysts* 5(3):1092-1151

453 Torres MLM, Cruz LA, Juárez RI, Rosa MEM (2009) Methylene blue degradation by

454 NaTaO₃ sol-gel doped with Sm and La. J Hazard Mater 165:774-779
 455 Vereshchagin SN, Solov'ev LA, Rabchevskii EV, Dudnikov VA, Ovchinnikov SG,
 456 Anshits AG (2015) New method for regulating the activity of ABO₃ perovskite
 457 catalysts. Kinet Catal 56:640-645
 458 Wang Y, Deng W, Wang YF, Guo LM, Ishihara T (2018) A comparative study of the
 459 catalytic oxidation of chlorobenzene and toluene over Ce-Mn oxides. Mol Catal
 460 459:61-70
 461 Yoon S, Maegli AE, Karvonen L, Matam SK, Shkabko A, Riegg S (2013) Bandgap
 462 tning in SrTi(N,O,F)₃ by aionic-lattice variation. J Solid State Chem 206:226-232
 463 Yuan YP, Zheng J, Zhang XL, Li ZS, Yu T, Ye JH, Zou ZG (2008) BaCeO₃ as a novel
 464 photocatalyst with 4f electronic configuration for water splitting. Solid State
 465 Ionics 178:1711-1713
 466 Zhang C, Guo Y, Guo Y, Lu G, Boreave A, Retailleau L, Baylet A, Giroir-Fendler A
 467 (2014) LaMnO₃ perovskite oxides prepared by different methods for catalytic
 468 oxidation of toluene. Appl Catal B-Environ 148-149:490-498
 469 Zhang J, Tan D, Meng Q, Weng X, Wu Z (2015) Structural modification of LaCoO₃
 470 perovskite for oxidation reactions: the synergistic effect of Ca²⁺ and Mg²⁺
 471 Co-substitution on phase formation and catalytic performance. Appl Catal
 472 B-Environ 172-173:18-26
 473 Zhang L, Dong L, Yu W, Liu L, Deng Y, Liu B, Wan H, Gao F, Sun K, Lin K (2011)
 474 Effect of cobalt precursors on the dispersion, reduction, and CO oxidation of
 475 CoO_x/γ-Al₂O₃ catalysts calcined in N₂. J Colloid Interface Sci 355(2):464-471

476 Zhong JH, Wang AL, Li GR, Wang JW, Ou YN, Tong YX (2012) $\text{Co}_3\text{O}_4/\text{Ni}(\text{OH})_2$
477 composite mesoporous nanosheet networks as a promising electrode for
478 super-capacitor applications. *J Mater Chem* 22:5656-5665

479 Zhu Y, Sun Y, Niu X, Yuan F, Fu H (2010) Preparation of La-Mn-O perovskite
480 catalyst by microwave irradiation method and its application to methane
481 combustion. *Catal Lett* 135(1-2):152-158

Figures

Figure 1

XRD comparison of LaNiO3 with different calcination temperatures and time.

Figure 2

XRD spectra of LaBO_3 ($B = \text{Ni, Co, Cu}$).

Figure 3

XRD spectra of (A) $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and (B) $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$.

Figure 4

UV-Vis analysis of (A) $\text{LaNi}_x\text{Co}_{1-x}\text{O}_3$ and (B) $\text{LaNi}_x\text{Cu}_{1-x}\text{O}_3$ perovskite.

Figure 5

SEM images of (A), (B) $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and (D), (E) $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$ with different scales and EDS of (C) $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ and (F) $\text{LaNi}_{0.75}\text{Cu}_{0.25}\text{O}_3$.

Figure 6

XPS analysis of LaNi_{0.75}Co_{0.25}O₃.

Figure 7

Catalytic activity of LaNiO_3 (A) at different calcination temperatures and (B) at different calcination times.

Figure 8

Catalytic activity of $\text{LaNixCu}_{1-x}\text{O}_3$ perovskite.

Figure 9

CO₂ selectivity of (A) LaNixCo1-xO₃ and (B) LaNixCu1-xO₃.

Figure 10

Stability of $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ catalyst.

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