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Catalytic oxidation of toluene over LaNi$_{x}$B$_{1-x}$O$_3$ (B=Co, Cu) perovskite catalysts

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Abstract: A series of LaNi$_{1-x}$B$_{1-x}$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 LaNi$_{1-x}$Co$_{1-x}$O$_3$ perovskite was 3:1, LaNi$_{0.75}$Co$_{0.25}$O$_3$ catalyst exhibited the best activity, and it showed relatively short time and low temperature for toluene conversion of 100%. Therefore, LaNi$_{0.75}$Co$_{0.25}$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, ABO₃ perovskite has been extensively studied in the field of photocatalysis, such as photoreduction of CO₂ (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 LaNiO₃ 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 ABO₃ 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 CO₂ 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 (La(NO$_3$)$_3$·xH$_2$O), nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O), cobalt
acetate (C$_4$H$_6$CoO$_4$·4(H$_2$O)), and polyethylene glycol (PEG) were purchased from
Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Copper acetate
(Cu(CH$_3$COO)$_2$·H$_2$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=Ni, Co, Cu)

1.0 mmol of Ni(CH$_3$COO)$_2$·4H$_2$O, 1.0 mmol of La(NO$_3$)$_2$·xH$_2$O, and 2.0 mmol of
C$_6$H$_8$O$_7$·H$_2$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 ℃) for different
time (7, 6, 5, 4, and 3 h) to obtain a series of LaNiO$_3$. The preparation of LaCoO$_3$ and
LaCuO$_3$ was same as LaNiO$_3$, just replacing nickel acetate with cobalt acetate and copper acetate.

2.2.2. Preparation of LaNi$_x$(Co,Cu)$_{1-x}$O$_3$

0.25 mmol of C$_4$H$_6$CoO$_4$·4(H$_2$O), 0.75 mmol of Ni(CH$_3$COO)$_2$·4H$_2$O, 1.0 mmol of La(NO$_3$)$_2$·xH$_2$O and 2.0 mmol of C$_6$H$_8$O$_7$·H$_2$O as a complexing agent was first mixed evenly, the remaining preparation steps are the same as that of LaNiO$_3$. The obtained pre-treated solution was calcined at 700 °C for 7 h to obtain LaNi$_{0.75}$Co$_{0.25}$O$_3$ (the molar ratio of Ni:Co is 3:1). LaNi$_{0.5}$Co$_{0.5}$O$_3$ and LaNi$_{0.25}$Co$_{0.75}$O$_3$ were obtained only adding different molar ratios of Ni to Co. Likewise, the preparation of LaNi$_x$Cu$_{1-x}$O$_3$ is in accordance with LaNi$_x$Co$_{1-x}$O$_3$ 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% BaSO$_4$ 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 C$_7$H$_8$ and N$_2$ is 280 SCCM (mL min$^{-1}$), where the concentration of C$_7$H$_8$ is 1000 ppm. Toluene concentration is recorded every five minutes from 50 °C, and the CO$_2$ concentration is recorded from the initial CO$_2$ concentration of 0 ppm. The recording is stopped after the temperature reaches the specified temperature.

The toluene conversion rate and CO$_2$ yield can be calculated as follows:

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

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

Where, [Toluene]$_\text{in}$ and [Toluene]$_\text{out}$ represent the inlet and outlet concentration of C$_7$H$_8$, respectively. [CO$_2$]$_\text{out}$ stands for outlet concentration of CO$_2$. The toluene conversion rate and CO$_2$ yield are used to indicate catalyst activity and CO$_2$ 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 LaNiO$_3$

Different calcination temperatures will affect the types of catalysts and the strength of crystal shapes. In Fig. 1A, the XRD patterns of LaNiO$_3$ 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 $\theta = 23.32^\circ$, 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$_2$O$_3$, 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 LaNiO$_3$ with different calcination temperatures and time.

(2) LaBO$_3$ (B = Ni, Co, Cu)

Fig. 2 shows the contrast of the structure and composition of LaBO$_3$ (B = Ni, Co, Cu) perovskite. Still, the diffraction peak at $2\theta = 32.91^\circ$ (curve a) is indexed to (110) crystal plane of LaNiO$_3$ (JCPDS # 34-1181). The obvious peak corresponded to (104) crystal plane of LaCoO$_3$ 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 La$_2$CuO$_4$ (JCPDS # 30-0487), and the relatively weak peak near $2\theta = 32.95^\circ$ is attributed to (104) crystal plane of LaCuO$_3$ (JCPDS # 25-0291). It is evident that Ni and Co as substitution elements at the B-site of LaBO$_3$ perovskites are more reasonable relative to Cu element.
Fig. 2 XRD spectra of LaBO$_3$ (B = Ni, Co, Cu).

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

The structure of LaNi$_x$Co$_{1-x}$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 LaNi$_x$Co$_{1-x}$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 LaNi$_x$Co$_{1-x}$O$_3$ (x = 0.25, 0.5, 0.75). Therefore, it is proved that LaNi$_x$Co$_{1-x}$O$_3$ (x = 0, 0.25, 0.5, 0.75, 1) perovskites can be successfully prepared. Likewise, the structure of LaNi$_x$Cu$_{1-x}$O$_3$ (x = 0, 0.25, 0.5, 0.75, 1) perovskites are also compared in Fig. 3B. LaNi$_x$Cu$_{1-x}$O$_3$ (x = 1, 0.75) perovskites only has one obvious diffraction peak, which is attributed to (110) crystal plane of LaNiO$_3$. While LaNi$_x$Cu$_{1-x}$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° and 32.91° are attributed to (113) crystal plane of La$_2$CuO$_4$ (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 \( 32.95^\circ \) are due to (113) crystal plane of \( \text{La}_2\text{CuO}_4 \) (ICDD PDF # 30-0487) and (104) crystal plane of \( \text{LaCuO}_3 \) (JCPDS # 25-0291). This may be because the radius of \( \text{Cu}^{2+} \) is larger than that of \( \text{Ni}^{2+} \). It is difficult for a large number of \( \text{Cu}^{2+} \) to enter the lattice of \( \text{LaNiO}_3 \).

![XRD spectra](image)

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 \( \text{LaNiO}_3 \), and \( \text{LaCoO}_3 \) has the weakest absorption within the wavelength range from 200 to 400 nm. While in the range of 400 ~ 650 nm, the absorption of \( \text{LaNiO}_3 \) 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 \( \text{LaNiO}_3 \) 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 \( \text{LaNiO}_3 \) 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.](image)

### 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.
38.29%, 35.07%, 12.44%, 8.53%, and 5.67% respectively, suggesting the presence of LaNi\textsubscript{0.75}Co\textsubscript{0.25}O\textsubscript{3} and LaNi\textsubscript{0.75}Cu\textsubscript{0.25}O\textsubscript{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) LaNi\textsubscript{0.75}Co\textsubscript{0.25}O\textsubscript{3} and (D), (E) LaNi\textsubscript{0.75}Cu\textsubscript{0.25}O\textsubscript{3} with different scales and EDS of (C) LaNi\textsubscript{0.75}Co\textsubscript{0.25}O\textsubscript{3} and (F) LaNi\textsubscript{0.75}Cu\textsubscript{0.25}O\textsubscript{3}.

3.1.4 XPS analysis

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

3.2. Toluene conversion over LaNi_{x}Co_{1-x}O_{3} and LaNi_{x}Cu_{1-x}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 LaNi$_{x}$Co$_{1-x}$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 LaNi$_x$Co$_{1-x}$O$_3$ perovskite is uneven, which is related to the molar ratio of the two groups of elements. It is obvious that all LaNi$_x$Co$_{1-x}$O$_3$ catalysts have shown good catalytic effects on the toluene degradation. Among them, the activity of LaNi$_{0.75}$Co$_{0.25}$O$_3$ (Ni/Co= 3:1) has the best catalytic effect. When the temperature rises to a certain value, the degradation rates of all LaNi$_x$Co$_{1-x}$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 LaNi$_x$Cu$_{1-x}$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 LaNi$_{0.75}$Cu$_{0.25}$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$_2$CuO$_4$. 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 LaNi$_{0.75}$Co$_{0.25}$O$_3$.

**Fig. 8** Catalytic activity of LaNi$_x$Cu$_{1-x}$O$_3$ perovskite.
3.3. CO₂ selective test of LaNiₓCo₁₋ₓO₃ and LaNiₓCu₁₋ₓO₃

Another important indicator of the catalytic degradation of toluene by the catalyst is the selectivity of CO₂. Fig. 9A is CO₂ selectivity of LaNiₓCo₁₋ₓO₃ catalyst. Still the CO₂ selectivity of LaNiₓCo₁₋ₓO₃ gradually increases from 0% to 100% as the reaction temperature increases. Among which, the CO₂ selectivity of LaNi₀.₇₅Co₀.₂₅O₃ is the best, and the CO₂ selectivity of other LaNiₓCo₁₋ₓO₃ 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 LaNiₓCo₁₋ₓO₃, the CO₂ selectivity of LaNiₓCu₁₋ₓO₃ corresponds to its activity. As shown in Fig. 9B, the CO₂ selectivity of LaNiO₃ is the best, followed by LaNi₀.₇₅Cu₀.₂₅O₃ and La₂CuO₄ again, the worst is LaNi₀.₅Cu₀.₅O₃. From what has been discussed above, LaNi₀.₇₅Co₀.₂₅O₃ exhibited the best CO₂ selectivity.

![Fig. 9](image_url) CO₂ selectivity of (A) LaNiₓCo₁₋ₓO₃ and (B) LaNiₓCu₁₋ₓO₃.

4. Stability of LaNi₀.₇₅Co₀.₂₅O₃

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, LaNi$_{0.75}$Co$_{0.25}$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$_7$H$_8$ mixture of 280 sccm (where the content of C$_7$H$_8$ 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, LaNi$_{0.75}$Co$_{0.25}$O$_3$ always maintains a high activity, and the degradation rate has barely changed, remaining at 100%. Therefore, LaNi$_{0.75}$Co$_{0.25}$O$_3$ perovskite is very effective for catalytic degradation of toluene.

![Figure 10](image_url) **Fig.10** Stability of LaNi$_{0.75}$Co$_{0.25}$O$_3$ catalyst.

5. The mechanism of toluene catalytic oxidation
Scheme 1 Catalytic degradation mechanism of toluene on LaNi$_{0.75}$Co$_{0.25}$O$_3$ catalyst.

The catalytic oxidation of toluene on LaNi$_{0.75}$Co$_{0.25}$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 (CO$_2$ + H$_2$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$_{\text{ads}}$ and O$_{\text{latt}}$ were proposed as active oxygen to react with toluene to generate oxygen vacancies, thereby reducing the aggregation of O$_{\text{ads}}$ and O$_{\text{latt}}$. 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$_{\text{ads}}$ and O$_{\text{latt}}$ 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 = 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 LaNi$_{0.75}$Co$_{0.25}$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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Figure 1

XRD comparison of LaNiO3 with different calcination temperatures and time.
Figure 2

XRD spectra of LaBO$_3$ (B = Ni, Co, Cu).
Figure 3

XRD spectra of (A) LaNixCo1-xO3 and (B) LaNixCu1-xO3.

Figure 4

UV-Vis analysis of (A) LaNixCo1-xO3 and (B) LaNixCu1-xO3 perovskite.
Figure 5

SEM images of (A), (B) LaNi0.75Co0.25O3 and (D), (E) LaNi0.75Cu0.25O3 with different scales and EDS of (C) LaNi0.75Co0.25O3 and (F) LaNi0.75Cu0.25O3.
Figure 6

XPS analysis of LaNi0.75Co0.25O3.
Figure 7
Catalytic activity of LaNiO$_3$ (A) at different calcination temperatures and (B) at different calcination times.

Figure 8
Catalytic activity of LaNi$_x$Cu$_{1-x}$O$_3$ perovskite.
Figure 9

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

Figure 10

Toluene Conversion (%) vs Time (h)
Stability of LaNi0.75Co0.25O3 catalyst.

**Supplementary Files**

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