Short Communication

A potential substitution of noble metal Pt by perovskite $LaCoO_3$ in $ZrTiO_4$ supported lean-burn NOx trap catalysts

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ABSTRACT

The support $ZrTiO_4$ and the lean-burn NOx trap (LNT) catalyst $K/LaCoO_3/ZrTiO_4$ were prepared by co-precipitation and successive impregnation, respectively. This catalyst exhibits much better NOx storage performance than the conventional Pt-containing catalyst $K/Pt/ZrTiO_4$. Compared with Pt, the perovskite $LaCoO_3$ possesses higher capability for NO to NO_2 oxidation, giving a higher NOx storage capacity. NOx is mainly stored as nitrate at 350 °C over $K/LaCoO_3/ZrTiO_4$. Mild sulfation shows little effect on the structure and performance of this catalyst. Total substitution of Pt by perovskite $LaCoO_3$ to lower the cost of LNT catalysts is feasible.

1. Introduction

Lean-burn NOx trap LNT technique is a feasible solution to solving lean-burn NOx pollution [1]. Conventional LNT catalysts consist of three components: (1) noble metals (e.g. Pt or Pt-Rh) which catalyze NO oxidation in lean-burn stage and NOx reduction in rich-burn stage; (2) storage component (e.g. Ba, K or Li) which can store NOx as nitrates or nitrites; (3) the supports (e.g. Al_2O_3 or TiO_2-ZrO_2) which can provide large surface to disperse noble metals and storage medium.

In the last several years, the catalytic system $K/Pt/TiO_2$-ZrO_2 [2–4] has received more attention due to its excellent performance for NOx storage and sulfur resistance. However, these LNT catalysts contain a considerable amount of Pt (e.g. 1–2 wt.%), increasing the catalyst cost. To save noble metal resources and lower catalyst cost, base metal oxides such as Co have been tried to replace noble metals [5,6]. Perovskites normally possess better redox property and higher thermal stability than single oxides [7,8], so, they are often used for CO, VOC and soot oxidation [9–12], and NO reduction by CO or C_3H_6 [13–15]. Sometimes, perovskites display similar or higher activity than supported Pt catalysts [16]. However, perovskites usually have low surface area and exhibit serious sintering tendency. A potential solution to this problem is to disperse perovskites on the supports with relatively large surface area and high thermal stability.

In present work, a series of $ZrTiO_4$ supported LNT catalysts $K/LaCoO_3/ZrTiO_4$ were successfully prepared by co-impregnation, using $LaCoO_3$ to replace the noble metal Pt. Such catalysts show much better NOx trap performance than the conventional LNT catalysts $K/Pt/ZrTiO_4$.

2. Experimental

2.1. Support and catalyst preparation

Support $ZrTiO_4$ (ZT) was prepared by co-precipitation at room temperature. An aqueous solution containing 0.1 mol/L titanium tetrachloride and 0.1 mol/L zirconium oxychloride was added into aqueous ammonia until the pH decreases from 13.0 to 9.0. After the precipitate was dried at 120 °C for 24 h and calcined at 700 °C for 5 h in air, the support $ZrTiO_4$ was obtained.

Catalyst $K/LaCoO_3/ZrTiO_4$ (K/L/ZT) was prepared by successive impregnation: the support was first impregnated by a mixed solution of $La(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and citric acid monohydrate (atomic ratio: citric acid/La/Co = 2.2/1/1). The weight of the solution was twice of that for the support powder. The obtained slurry was stirred for 1 h and then slowly evaporated at 40 °C in a rotary evaporator. After being dried at 120 °C and calcined at 700 °C for 8 h in air, $LaCoO_3/ZrTiO_4$ (L/ZT) was obtained ($LaCoO_3$ content: 20 wt.%). Then L/ZT was impregnated by K_2CO_3 solution. After drying at 120 °C and calcined at 500 °C in air for 2 h, the catalyst $K/LaCoO_3/ZrTiO_4$ was obtained. The K_2CO_3 content is 5 wt.% in the catalyst. The bulk perovskite $LaCoO_3$ was prepared by a sol-gel method [10].

For comparison, Pt-based catalyst (K/Pt/ZT) was also prepared at the same conditions, using $H_2PtCl_6 \cdot 6H_2O$ as precursor. The K content is the same as that in K/L/ZT, the Pt content is 1 wt.% in the catalyst.

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Before experiments, the catalysts were reduced in 5 vol.% H_2/N_2 at 500 °C for 1 h.

2.2. Catalyst characterization

See Supporting material S1.1.

2.3. NOx storage capacity (NSC) measurement and sulfur-aging treatment

See Supporting material S1.2.

3. Results and discussion

3.1. Structural properties

The specific surface area and the pore structure data of the catalysts are listed in Supporting material S2. It is found that the support ZT possesses a larger specific surface area of 62 m^2/g as compared with that loaded with Pt and K (51 m^2/g); if Pt is replaced by perovskite $LaCoO_3$, it is further lowered to 45 m^2/g. However, the average pore diameter of ZT is increased after loaded with the perovskite (or Pt) and the potassium component. The decrease in the specific surface area and the increase in the average pore diameter should be induced by pore blocking and/or the disappearance of micro-pores, which is consistent with the decrease of total pore volume. Since the amount of perovskite $LaCoO_3$ in the supported catalysts is much larger than that of Pt, more obvious decrease in S_{BET} for K/L/ZT is natural. Even so, it is still much higher than that for bulk perovskites and other supported perovskites [8–14].

Fig. 1 shows the XRD pattern of the support ZT. $ZrTiO_4$ phase is identified, but no other Zr and Ti oxides are detected. The XRD pattern of K/Pt/ZT is similar to that of ZT. No phases of Pt and K are found, suggesting their small size or high dispersion. For K/L/ZT, some diffraction peaks of $LaCoO_3$ at 2θ=23.29º, 47.54º, 33.18º and 59.18º can be clearly identified [11,15]. After used for NOx storage, no obvious difference in XRD pattern is found, indicating a high stability of the supported perovskite.

The Co K-edge radial structure functions (RSFs) of the reference compounds (Co_3O_4 and $LaCoO_3$) and the catalyst K/L/ZT are presented in Fig. 2. According to literature [17], the first three peaks at about 0.15, 0.24, 0.31 nm (not corrected by phase scattering shift) in the RSF
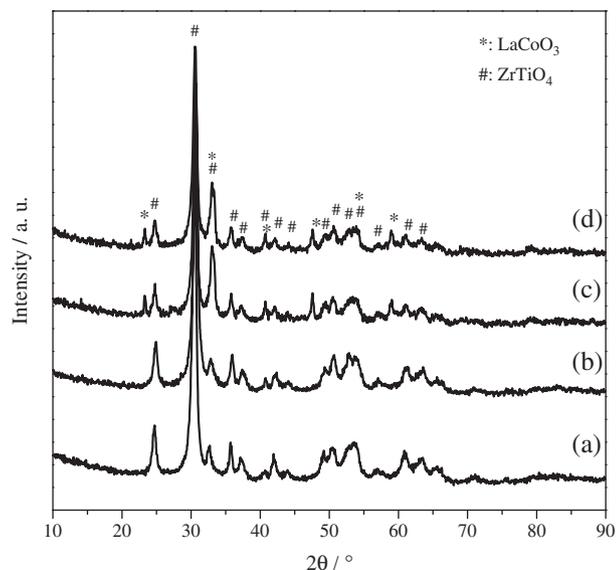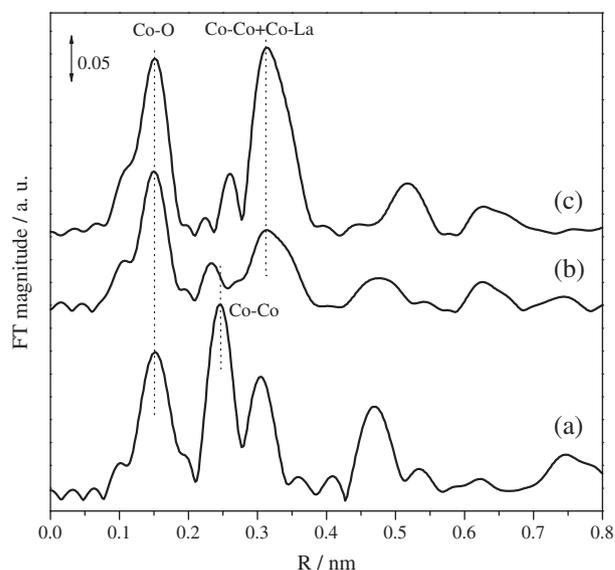

Fig. 2. Co K-edge radial structure functions of the catalyst and reference compounds: (a) Co_3O_4, (b) K/L/ZT, (c) $LaCoO_3$.

of Co_3O_4 can be assigned to Co–O shell at 0.191 nm, Co–Co shell at 0.285 nm, and Co–Co shell at 0.336 nm, respectively. The fourth peak at 0.47 nm corresponds to higher Co–Co shell. The RSF of $LaCoO_3$ presents two coordination peaks at 0.15 nm (Co–O shell) and 0.31 nm (both Co–Co and Co–La shells) [18,19]. In comparison, the RSF of K/L/ZT is more similar to that of $LaCoO_3$. However, the broad and weak peaks at 0.23 and 0.47 nm suggest the presence of a very small amount of Co_3O_4, which is hard to detect by XRD.

3.2. NOx trap performance and mechanistic investigation

The NOx storage curves over the K/Pt/ZT and K/L/ZT catalysts at 350 °C are shown in the Supporting material S3. Based on this, the conversion of NO to NO_2 over the catalysts is calculated. Fig. 3(a) shows the conversion of NO to NO_2 over K/Pt/ZT, K/L/ZT and L/ZT. As the temperature increasing within the kinetically limited regime this conversion increases and reaches the maximum when the equilibrium limit is achieved. The $LaCoO_3$-based catalysts K/L/ZT and L/ZT show a much higher NO conversion (38–39%) at 350 °C than the Pt-containing catalyst. Fig. 3(b) indicates that the NSC of K/L/ZT is also much higher than that of K/Pt/ZT, but the sample L/ZT shows the lowest NSC at all temperatures due to the lack of K, which mainly acts as base component to store the acidic nitrogen oxides. Since NO to NO_2 oxidation is a crucial step for NO storage [1], the higher NSC of K/L/ZT should be mainly determined by the higher oxidation ability of $LaCoO_3$. As compared with the Co with lower valence, Co atoms (Co^{3+}) in $LaCoO_3$ possess lower electron density in the d-orbit, which makes them more capable in accepting the lone-pair electrons of N atom in NO molecule. The defects such as oxygen vacancies on the supported $LaCoO_3$ are also favorable to oxygen activation and NO oxidation. Moreover, the much larger amount of $LaCoO_3$ in K/L/ZT may provide more sites for NO adsorption/oxidation, and increases the contacting efficiency between $LaCoO_3$ and the storage medium. Therefore, the perovskite-based catalyst K/L/ZT shows better NOx storage performance than Pt-based catalyst K/Pt/ZT.

Fig. 4 displays the in-situ DRIFT spectra of K/L/ZT after exposed to NO/O_2. When the temperature is as low as 200 °C, a band at 1230 cm^{-1} appears, indicating the formation of bidentate nitrite [6]. The negative band at 1520–1530 cm^{-1} is caused by the decomposition of surface carbonates or their transformation to nitrates and/or nitrites [20]. The 1640 cm^{-1} band corresponds to surface absorbed water [4]. When the temperature increases to 250 °C, the 1230 cm^{-1} band decreases, while the symmetric vibration mode of nitrate species at 1400 cm^{-1} [6] gets

Fig. 1. X-ray diffraction patterns of the support and catalysts: (a) ZT, (b) K/Pt/ZT, (c) K/L/ZT after NOx storage, (d) K/L/ZT.
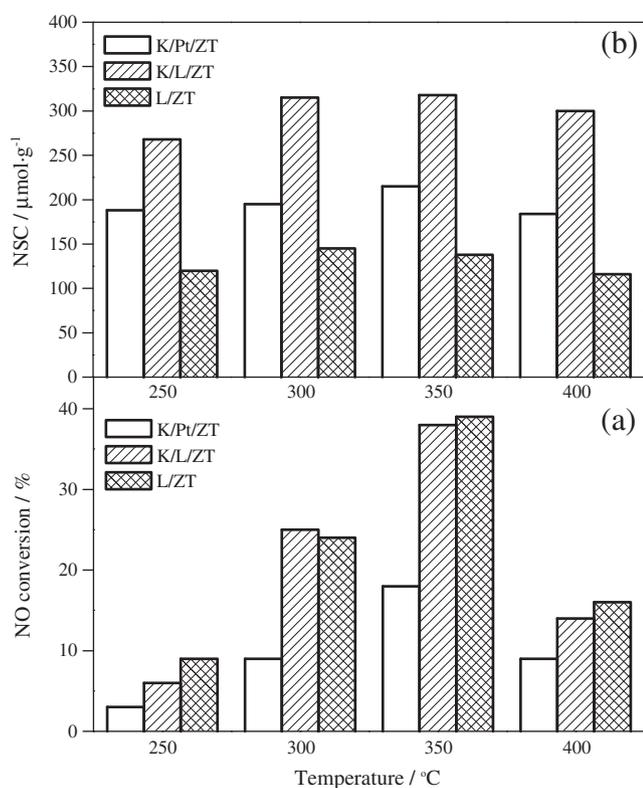
Fig. 3. NO conversion (a) and NOx storage capacity (NSC) (b) of the samples K/Pt/ZT K/L/ZT and L/ZT.

stronger. At higher temperature of 300 °C several new peaks of free nitrate ions (1438 cm^{-1}) [15,20], bidentate (1280 cm^{-1}) and monodentate nitrates (1340 cm^{-1}) [6] appear, suggesting the transformation of nitrites to nitrates. The peak at 1750 cm^{-1} is the combination band ($v_1 + v_4$) of free nitrate ions. These nitrates peaks reach the maximum upon heating to 300 °C. Up to 350 °C, the nitrite species totally disappear. Higher temperature remarkably decreases these bands, due to the decomposition of nitrate species. In a summary, over K/L/ZT, NOx is mainly stored as nitrite species below 300 °C, which can transform into nitrates at higher temperatures.
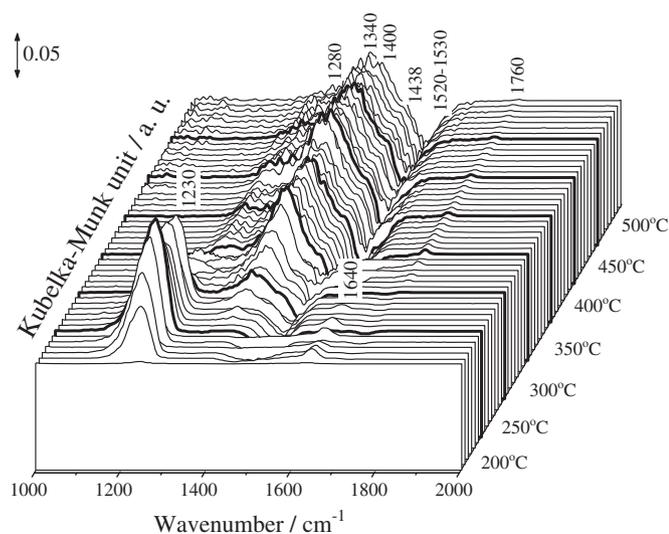
3.3. Desulfation

H$_2$-TPR results of the catalysts are presented in Fig. 5. For fresh K/L/ZT, as seen in Fig. 5(c), there are two reduction regions, located in 300–490 °C and 490–800 °C, respectively. As reported, the bulk LaCoO$_3$ can be reduced to oxygen-deficient perovskite La$_2$CoO$_4$ and CoO below 490 °C, then to discrete La$_2$O$_3$ and Co from 490 °C to 800 °C, accompanied by the collapse of perovskite structure [21]. The H$_2$ consumption ratio for the second step to the first step is 2. However, in this work, the ratio is approaching 10, implying a different reduction behavior of supported LaCoO$_3$ from the bulk LaCoO$_3$. In EXAFS section (Fig. 2), it is indicated that the presence of a small amount of Co$_3$O$_4$ is potential which is evidenced by the broad and weak coordination peaks at 0.23 and 0.47 nm in the Co K-edge RSF of K/L/ZT. So, the peak below 490 °C is probably related to the reduction of Co$_3$O$_4$, while the other above 490 °C may correspond to the one-step reduction of LaCoO$_3$.

After sulfation, as shown in Fig. 5(d), the reduction behavior of K/L/ZT changes not much, and the H$_2$ consumption is not increased, indicating that little sulfur deposits on the catalyst. The peaks at 395 and 489 °C may correspond to the reduction of sulfates, while the big peak above 500 °C is still attributed to the reduction of LaCoO$_3$. For comparison, the H$_2$-TPR profiles of fresh and sulfated K/Pt/ZT are also presented in Fig. 5(a) and (b). The peak around 156 °C is assigned to the reduction of platinum oxide; another one at 430 °C in Fig. 5(b) should correspond to the reduction of potassium sulfate; the broad peak above 500 °C is possibly related to the reduction of Ti^{4+} to Ti^{3+} in the support. It seems that Pt is catalytically more active than LaCoO$_3$ for SO$_2$ oxidation, making more sulfates formed on Pt-containing catalyst.

4. Conclusion

The replacement of Pt by perovskite LaCoO$_3$ in the LNT catalyst K/Pt/ZT is feasible, which remarkably improves the NOx storage performance of the catalyst. Compared with Pt-based catalyst, the supported perovskite catalyst possesses higher oxidation ability for NO to NO$_2$ conversion, which is crucial for NOx storage. On perovskite-based catalyst, NOx is mainly stored as nitrite species below 300 °C, which can transform into nitrate species at higher temperatures. Mild sulfation shows little effect on the structure and performance of the perovskite-based catalyst. The supported
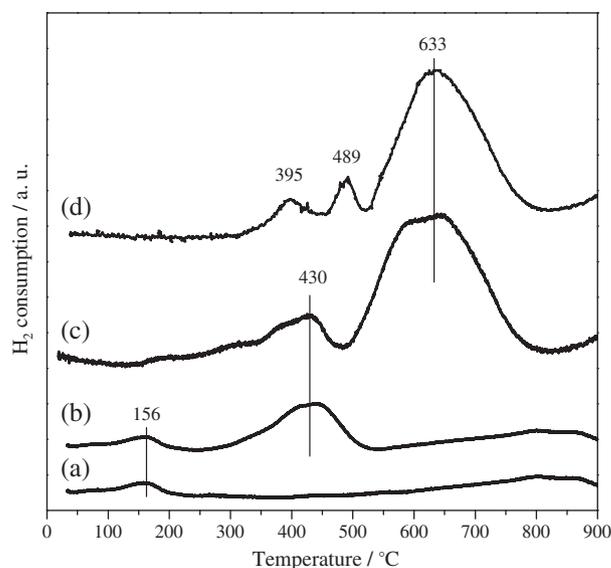

Fig. 4. In-situ DRIFT spectra of K/L/ZT after 40 min exposure to the atmosphere containing 400 ppm NO and 5 vol.% O$_2$ (balanced by N$_2$) at different temperatures.

Fig. 5. H$_2$-TPR profiles of the catalysts: (a) K/Pt/ZT without sulfation, (b) K/Pt/ZT sulfated by 40 ppm SO$_2$ for 50 min, (c) K/L/ZT without sulfation, (d) K/L/ZT sulfated by 40 ppm SO$_2$ for 50 min.

perovskite LNT catalyst is promising for the replacement of Pt-based ones.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.09.016.

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