NO\textsubscript{x} storage and reduction on Pt-supported BaTiO\textsubscript{3} with alkali washing

Zengyan Han, Dechao Zheng, Ying Xin, Qian Li, NaNa Zhang, Zhaoliang Zhang*

School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, University of Jinan, Shandong Province, 250022, P. R. China

*Corresponding author’s e-mail: chm_zhangzl@ujn.edu.cn

Abstract: In this paper, we prepared Pt/BaTiO\textsubscript{3}-\textsubscript{x} catalyst through modified the surface of BaTiO\textsubscript{3} perovskite by NaOH aqueous solution and loaded Pt by incipient wetness impregnation method. A series of characterization techniques including XRD, BET and in situ IR was conducted to investigate the physical and chemical properties. We found that NO\textsubscript{x} storage capacity of the catalyst was significantly improved as the sample was washed in alkali for 2 h, meanwhile NO\textsubscript{x} conversion was optimal. The surface of the catalyst was modified by alkali washing process, and then Pt was loaded. Further calcination could enhance the interaction between Pt and Ba, which facilitate the formation of a reactive nitrite species during the adsorption process, thus increasing NO\textsubscript{x} storage reduction (NSR) activity.

1. Introduction

NO\textsubscript{x} storage and reduction (NSR) catalysts are used primarily in light-duty diesel and lean-burn gasoline vehicles and considered as the most promising aftertreatment technology of NO\textsubscript{x} emissions. Traditional NSR catalysts are composed of Pt/BaO/Al\textsubscript{2}O\textsubscript{3}, in which Pt is the active component when NO was oxidized into NO\textsubscript{2} in the lean-burn period, and BaO is the storage component, where NO\textsubscript{2} and NO are stored in the form of nitrates. During a rich fuel atmosphere, nitrates are reduced to environmentally friendly N\textsubscript{2} by hydrogen. However, the possible calcination of Al\textsubscript{2}O\textsubscript{3} and BaO results in the decrease of NSR activity at high temperature.

Perovskites (ABO\textsubscript{3}) are widely used NSR catalysts due to their excellent thermal stability and ease of synthesis. Generally, the A site is an alkali metal or alkaline earth metal having a large ionic radius which can be used as a NO\textsubscript{x} storage component of the NSR catalyst, while the B site is a transition metal ion having a small radius. Various perovskite-based catalysts for NO\textsubscript{x} storage and reduction have been developed showing good NSR performance. For instance, Li et al.\textsuperscript{[1]} reported that the La\textsubscript{0.7}Sr\textsubscript{0.3}CoO\textsubscript{3} catalyst exhibits good NSR performance and could remove 71.4% NO\textsubscript{x} with 100% selectivity to N\textsubscript{2} at 300°C in successively alternative lean/rich atmospheres. In addition, Andonova et al.\textsuperscript{[2]} found that 20BaO/TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} can store, however, the reduction was not investigated.

In previous studies, the acid/base treatment for catalysts could improve their catalytic activities by surface modification and structure changes of perovskites catalysts\textsuperscript{[3, 4]}. Peng et al.\textsuperscript{[4]} modified the surface of La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3} using acetic acid treatment, selectively dissolving the A site and SrCO\textsubscript{3} species. The exposed Sr\textsuperscript{2+} ions exhibit good NSR performance. Furthermore, the NSR activity could be improved by adding the noble metals with excellent oxidized properties. Amongst, Pt is widely used in NSR catalysts.\textsuperscript{[5]}
Herein, we modified the surface of BaTiO$_3$ by alkali washing, and then loaded Pt to improve the interaction between Pt and Ba by calcination, finally obtained a highly active NSR catalyst. Types of surface intermediate nitrite/nitrate during the NO$_x$ adsorption process were identified using in situ Fourier transform Infrared (FTIR).

2. Experimental section

2.1. Catalyst Preparation and Tuning
Fresh BaTiO$_3$ was prepared by the citric acid complex method. Ba(NO$_3$)$_3$ and citric acid were dissolved into deionized water, which was recorded as solution A; C$_{16}$H$_{36}$O$_4$Ti and (CH$_2$OH)$_2$ were mixed evenly in a beaker, stirring for 10 min, which was denoted as solution B. Solution A was rapidly poured into B and continuous stirring at 60 °C for 3 h. The as-prepared mixture was evaporated at 80 °C under continued stirring until a gel was formed. The obtained sample was dried at 130 °C for 12 h, and then calcined at 750 °C for 5 h, The obtained samples were labelled as BaTiO$_3$ (BTO).

After the preparation of the BaTiO$_3$ sample, it was treated with 6M NaOH aqueous solution for different times at 70 °C. The sample was then centrifuged and washed by deionized water several times and dried at 100 °C overnight. The obtained samples were labelled as BTO-1, BTO-2, BTO-3, BTO-1 means washing with sodium hydroxide for 1h sample. 1 wt % Pt-only NSRs were prepared by wet impregnation and a similar procedure reported in the literature was used. The noble metal precursor solutions were prepared and then sample was slowly added to the aqueous solutions under the ultrasonic. The sample was placed in the drying vacuum oven at 60 °C overnight and calcined in air at 500 °C for 3 h before used for catalytic tests. The obtained samples were labelled as Pt/BTO, Pt/BTO-1, Pt/BTO-2, Pt/BTO-3.

2.2. Characterization
X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 PC diffractometer employing Cu Kα radiation ($\lambda$=1.5418 Å) operating at 50 kV and 200 mA. N$_2$ adsorption–desorption isotherms were measured on a Micromeritics ASAP2020 apparatus at 77 K. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method.

2.3. Performance Measurements
NO adsorption measurements were performed in a fixed-bed quartz reactor using 0.1 g of catalysts. The feed gas contained 300 ppm NO/ 7.5 vol.% O$_2$/He and were carried out at 250 °C. The total flow rate was 200 mL min$^{-1}$, and the gas hourly space velocity (GHSV) was 120 000 mL g$^{-1}$ h$^{-1}$. The temperature range of NSR reaction measurements was 200–450 °C under lean-burn (300 ppm of NO, 7.5% O$_2$ and He, 60 s) and fuel-rich (1% H$_2$/He, 10 s) flue gas. The concentrations of gas (NO, NO$_2$ and N$_2$O) were continually monitored using MKS MultiGas 2030. The NO$_x$ outlet concentration was calculated by integrating both the concentrations of NO and NO$_2$ after 20 lean-burn–fuel-rich cycles.

2.4. In situ IR study
In situ IR spectra were recorded using a Bruker Tensor 27 spectrometer over the range 4000-400 cm$^{-1}$, with 32 scans, at a resolution of 4 cm$^{-1}$. Self-supporting wafers were pretreated in the IR cell at 400 °C in a flow of He for 30 min. After the background spectrum was recorded, the IR spectra were recorded in the flow of 300 ppm NO + 7.5 vol % O$_2$ + He (100 mL/min) at 250 °C.

3. Results and Discussion

3.1. Characterizations
Figure 1. XRD patterns of the (a) BTO and (b) Pt/BTO samples treated with different alkaline washing time.

Figure 1 shows the XRD spectra of BTO and Pt/BTO series samples. All the diffraction peaks could be readily indexed to perovskite phases (BaTiO$_3$, JPCDS No. 74-1964) and no other phases were observed, indicating that the BaTiO$_3$ perovskite was successfully synthesized. After alkaline washing, the diffraction peaks did not change significantly, indicating that the perovskite structure was preserved after the alkaline washing process$^{[4]}$. After impregnation of 1 wt% Pt, the diffraction peaks did not change either, and the PtO phase (JCPDS, No. 85-0714) was not detected, suggesting that the loaded Pt species were well dispersed on the surface of catalyst.

Table 1 BET surface area, average pore size, and pore volume of BTO samples

| Catalyst | BET surface area (m$^2$/g) | average pore diameter (nm) | pore volume (cm$^3$/g) |
|----------|-----------------------------|-----------------------------|------------------------|
| BTO      | 8.7                         | 10.9                        | 0.024                  |
| BTO-1    | 11.4                        | 10.7                        | 0.030                  |
| BTO-2    | 8.3                         | 11.9                        | 0.025                  |
| BTO-3    | 5.7                         | 11.4                        | 0.016                  |

BET surface area, average pore size and pore volume of BTO samples are listed in Table 1. The surface areas of the catalysts initially increase and then decrease during the alkaline washing process. The surface area of fresh BTO was 8.7 m$^2$/g and further increases (11.4 m$^2$/g) after alkaline washing for 1h. However, as the alkaline washing time prolongs to 2 h, the surface area reduces to 8.3m$^2$/g. Combined with XRD results, the surface of the catalysts was modified, but the perovskite structure was not affected by alkaline washing.

3.2. NO$_x$ Storage capacity

Figure 2. (a) NO$_x$ concentration profiles during NO$_x$ adsorption at 250 °C with inlet 300 ppm of NO and 7.5% O$_2$ and (b) NO$_x$ storage capacity for Pt/BTO catalysts.
Figure 2(a) shows the NO\textsubscript{x} storage performance of Pt/BTO catalysts at 250 °C. When NO + O\textsubscript{2} was first introduced, NO\textsubscript{x} was stored in the catalyst. With the increase of adsorption time, NO\textsubscript{x} adsorption of the catalysts is saturated. NO\textsubscript{x} storage capacity (NSC) is showed in Figure 2(b). With the increase of alkali washing time, NSC increases gradually, and reaches the maximum at Pt/BTO-2. The order of NSC for the catalysts is: Pt/BTO-2 > Pt/BTO-3 ≈ Pt/BTO-1 > Pt/BTO.

3.3. NSR performance

Figure 3 shows the NO\textsubscript{x} conversion and N\textsubscript{2} selectivity of samples in lean (60 s)-rich (10 s) cycles as a function of the operating temperatures.

![Figure 3](image)

3.4. In situ IR of NO\textsubscript{x} Adsorption

In order to understand the NO storage mechanism, in-situ IR characterization for Pt/BTO and Pt/BTO-2 at 250 °C was carried out at 300 ppm NO + 7.5 vol.% O\textsubscript{2}/He (Figure 4). Figure 4 shows that the IR absorption peaks of different position appear at 1213-1223, 1300-1320, 1444, 1469, 1523, 1600 and 1630 cm\textsuperscript{-1}. According to relevant literatures\textsuperscript{[7-10]}, 1213-1223 cm\textsuperscript{-1} is classified as bridge nitrates, 1260-1300 cm\textsuperscript{-1} and 1523 cm\textsuperscript{-1} belong to bidentate nitrates, 1444 cm\textsuperscript{-1} belongs to ionic nitrates\textsuperscript{[8]}, 1469 cm\textsuperscript{-1} is assigned to monodentate nitrite\textsuperscript{[7]}, and 1600 and 1630 cm\textsuperscript{-1} are assigned to adsorbed NO\textsubscript{x}\textsuperscript{[4,9]}. While the inverted peaks at 1352(1353), 1415 and 1560 (1566) cm\textsuperscript{-1} are decomposition peaks of barium carbonate, belonging to the stretching vibration of C=O\textsuperscript{[10]}.

As observed on Pt/BTO (Figure 4a), the mainly stored NO\textsubscript{x} species are in the form of bridged nitrite (1223 cm\textsuperscript{-1}) and bidentate nitrate (1310 cm\textsuperscript{-1}) according to reactions (1)-(4). Negative bands at 1560 and 1415 cm\textsuperscript{-1} are caused by carbonates, which are gradually replaced by nitrate in the adsorption process. After the adsorption time increasing, the nitrite absorption peak gradually decreases. After 10 minutes, the nitrites completely disappear, while the nitrate absorption peaks near 1310 cm\textsuperscript{-1} and 1444 cm\textsuperscript{-1} gradually increase since the adsorbed nitrites were gradually oxidized to nitrates as expressed in equations (5) and (6)\textsuperscript{[11]}. Similar yet sharper peaks were observed for Pt/BTO-2, confirming the promoted effect of alkali washing.

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\begin{align*}
2\text{NO} + 1/2\text{O}_2 + \text{O}_2\text{^2}(s) & \rightarrow 2\text{NO}_2\text{(s)} \\
\text{NO} + \text{NO}_2 + \text{O}_2\text{^2}(s) & \rightarrow 2\text{NO}_2\text{(s)} \\
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_2 \\
2\text{NO}_2 + \text{O}_2\text{^2}(s) & \rightarrow \text{NO}_2\text{(s)} + \text{NO}_3\text{(s)} \\
2\text{NO}_2\text{(s)} + \text{O}_2 & \rightarrow 2\text{NO}_3\text{(s)} \\
\text{NO}_2\text{(s)} + \text{NO}_2 & \rightarrow \text{NO} + \text{NO}_3\text{(s)} 
\end{align*}
\]
4. Conclusion
In this paper, alkaline washing was found to be an effective way to improve NSR performance for Pt/BTO-x. The optimal catalyst was obtained at 2h washing time. Alkaline washing promotes the interaction between Pt and Ba, which facilitates the formation of a reactive nitrite/nitrate species during the adsorption process and subsequent reduction during the reduction process.

![In situ IR spectra of (a) Pt/BTO and (b) Pt/BTO-2 during 300 ppm NO + 7.5 vol.% O_2 + He adsorption at 250 °C.](image)

**Figure 4.** *In situ* IR spectra of (a) Pt/BTO and (b) Pt/BTO-2 during 300 ppm NO + 7.5 vol.% O_2 + He adsorption at 250 °C.

References
[1] Li, X.G., Dong, Y.H., Xian, H., et al. (2011) De-NO_x in alternative lean/rich atmospheres on La_1-xSr_xCoO_3 perovskites. Energy & Environmental Science, 4: 3351-3354.
[2] Andonova, S.M., Senturk, G.S., Kayhan, E., et al. (2009) Nature of the Ti-Ba interactions on the BaO/TiO_2/Al_2O_3 NO storage system. J. Phys. Chem. C, 113: 11014-11026.
[3] Polo-Garzon, F., Fung, V., Liu, X.M., et al. (2018) Understanding the impact of surface reconstruction of perovskite catalysts on CH_4 activation and combustion. ACS Catalysis, 8: 10306-10315.
[4] Peng, Y., Si, W., Luo, J., et al. (2016) Surface tuning of La_0.5Sr_0.5CoO_3 perovskite catalysts by acetic acid for NOx storage and reduction. Environ. Sci. Technol., 50: 6442-6448.
[5] Annika, A., Erik, F., Magnus, S. (2003) Influence of platinum and rhodium composition on the NOx storage and sulphur tolerance of a barium based NOx storage catalyst. Appl. Catal., B, 46: 429-439.
[6] Foo, G.S., Hood, Z.D., Wu, Z.L. (2017) Shape effect undermined by surface reconstruction: ethanol dehydrogenation over shape-controlled SrTiO_3 nanocrystals. ACS Catalysis, 8: 555-565.
[7] Konstantin, H., Vladimir, B., Margarita, K., et al. (1994) Infrared spectroscopy study of the species arising during NO_2 adsorption on TiO_2 (Anatase). Langmuir, 10: 464-471.
[8] Palma Del Valle, S., Marie, O., Nguyen, H.P. (2018) Effect of support material Al_2O_3 vs ZrO_2-TiO_2 on the Ba availability for NSR catalyst: An in situ and operando IR study. Appl. Catal., B, 223: 112-124.
[9] Hadjiivanov, Konstantin, I. (2000) Identification of neutral and charged N_2O_5 surface species by IR spectroscopy. Catal. Rev., 42: 71-144.
[10] Toops, T.J., Smith, D.B., Epling, W.S., et al. (2005) Quantified NO_x adsorption on Pt/K/gamma-Al_2O_3 and the effects of CO_2 and H_2O. Appl. Catal., B, 58: 255-264.
[11] Castoldi, L., Matarrrese, R., Morandi, S., et al. (2018) New insights on the adsorption, thermal decomposition and reduction of NO_x over Pt- and Ba-based catalysts. Appl. Catal., B, 224: 249-263.