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NO_x storage and reduction on Pt-supported BaTiO₃ with alkali washing

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Abstract: In this paper, we prepared Pt/BaTiO_{3-x} catalyst through modified the surface of BaTiO₃ 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_x storage capacity of the catalyst was significantly improved as the sample was washed in alkali for 2 h, meanwhile NO_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_x storage reduction (NSR) activity.

1. Introduction

NO_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_x emissions. Traditional NSR catalysts are composed of Pt/BaO/Al₂O₃, in which Pt is the active component when NO was oxidized into NO₂ in the lean-burn period, and BaO is the storage component, where NO₂ and NO are stored in the form of nitrates. During a rich fuel atmosphere, nitrates are reduced to environmentally friendly N₂ by hydrogen. However, the possible calcination of Al₂O₃ and BaO results in the decrease of NSR activity at high temperature.

Perovskites (ABO₃) 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_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_x storage and reduction have been developed showing good NSR performance. For instance, Li et al.^[1] reported that the La_{0.7}Sr_{0.3}CoO₃ catalyst exhibits good NSR performance and could remove 71.4% NO_x with 100% selectivity to N₂ at 300°C in successively alternative lean/rich atmospheres. In addition, Andonova et al.^[2] found that 20BaO/TiO₂/Al₂O₃ 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^[3, 4]. Peng et al.^[4] modified the surface of La_{0.5}Sr_{0.5}CoO₃ using acetic acid treatment, selectively dissolving the A site and SrCO₃ species. The exposed Sr²⁺ 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.^[5]



Herein, we modified the surface of BaTiO₃ 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 BaTiO₃ was prepared by the citric acid complex method. Ba(NO₃)₂ and citric acid were dissolved into deionized water, which was recorded as solution A; C₁₆H₃₆O₄Ti and (CH₂OH)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 BaTiO₃ (BTO).

After the preparation of the BaTiO₃ 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.^[6] 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 K α radiation ($\lambda=1.5418$ Å) operating at 50 kV and 200 mA. N₂ 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.% O₂/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% O₂ and He, 60 s) and fuel-rich (1% H₂/He, 10 s) flue gas. The concentrations of gas (NO, NO₂ and N₂O) were continually monitored using MKS MultiGas 2030. The NO_x outlet concentration was calculated by integrating both the concentrations of NO and NO₂ 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 % O₂ + He (100 mL/min) at 250 °C.

3. Results and Discussion

3.1. Characterizations

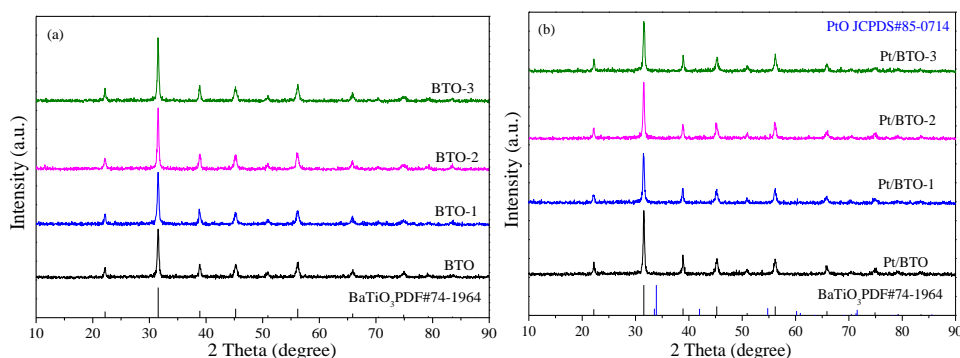


Figure 1. XRD patterns of the (a) BTO and (b) Pt/BTO samples treated with different alkaline washing time.

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 , JCPDS 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 $8.7 \text{ m}^2/\text{g}$ and further increases ($11.4 \text{ m}^2/\text{g}$) after alkaline washing for 1h. However, as the alkaline washing time prolongs to 2 h, the surface area reduces to $8.3 \text{ m}^2/\text{g}$. 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

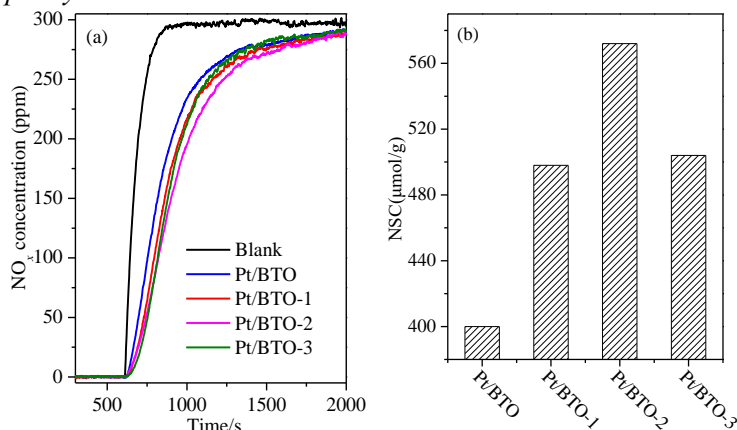


Figure 2. (a) NO_x concentration profiles during NO_x adsorption at 250°C with inlet 300 ppm of NO and 7.5% O_2 and (b) NO_x storage capacity for Pt/BTO catalysts.

Figure 2(a) shows the NO_x storage performance of Pt/BTO catalysts at 250 °C. When NO + O₂ was first introduced, NO_x was stored in the catalyst. With the increase of adsorption time, NO_x adsorption of the catalysts is saturated. NO_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.

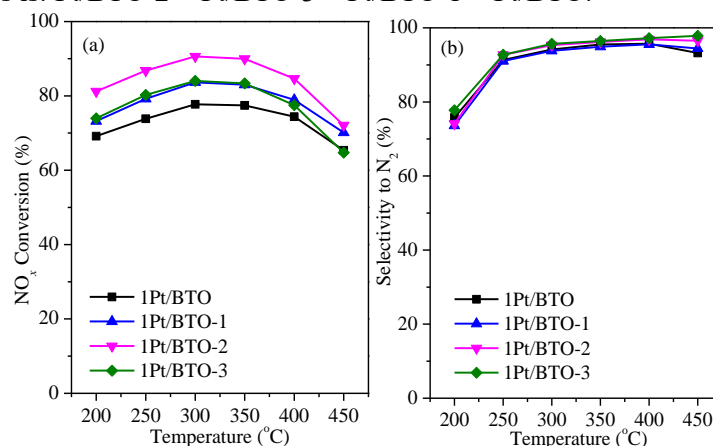


Figure 3. (a) NO_x conversion and (b) N₂ selectivity of Pt/BTO samples in lean (60 s)-rich (10 s) cycles as a function of the operating temperatures.

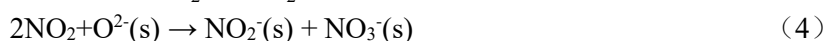
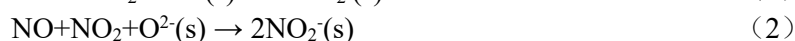
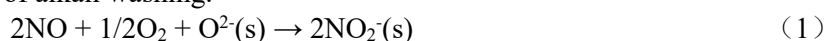
3.3. NSR performance

Figure 3 shows the NO_x conversion and N₂ selectivity of samples in the 200-450 °C with the alternated lean and rich atmospheres. As shown in Figure 3(a), the order of NO_x conversion is: Pt/BTO-2 > Pt/BTO-3 ≈ Pt/BTO-1 > Pt/BTO, similar to that of NO_x storage capacity. Figure 3(b) shows that N₂ selectivity is higher than 90% for all samples above 250 °C.

3.4. In situ IR of NO_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.% O₂/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⁻¹. According to relevant literatures^[7-10], 1213-1223 cm⁻¹ is classified as bridge nitrites, 1260-1300 cm⁻¹ and 1523 cm⁻¹ belong to bidentate nitrates, 1444 cm⁻¹ belongs to ionic nitrate^[8], 1469 cm⁻¹ is assigned to monodentate nitrite^[7], and 1600 and 1630 cm⁻¹ are assigned to adsorbed NO₂^[4,9]. While the inverted peaks at 1352(1353), 1415 and 1560 (1566) cm⁻¹ are decomposition peaks of barium carbonate, belonging to the stretching vibration of C=O^[10].

As observed on Pt/BTO (Figure 4a), the mainly stored NO_x species are in the form of bridged nitrite (1223 cm⁻¹) and bidentate nitrate (1310 cm⁻¹) according to reactions (1)-(4). Negative bands at 1560 and 1415 cm⁻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⁻¹ and 1444 cm⁻¹ gradually increase since the adsorbed nitrites were gradually oxidized to nitrates as expressed in equations (5) and (6)^[11]. Similar yet sharper peaks were observed for Pt/BTO-2, confirming the promoted effect of alkali washing.



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.

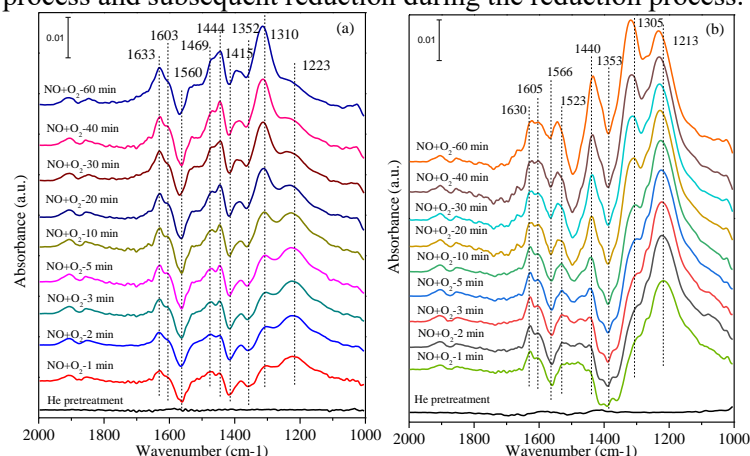


Figure 4. *In situ* IR spectra of (a) Pt/BTO and (b) Pt/BTO-2 during 300 ppm NO + 7.5 vol.% O₂ + He adsorption at 250 °C.

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