Research Article

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The Influence Of NO/O₂ On The NO_x Storage Properties Over A Pt-Ba-Ce/γ-Al₂O₃ Catalyst

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Abstract: With the purpose of studying the influence of NO/O₂ on the NO_x storage activity, a Pt-Ba-Ce/γ-Al₂O₃ catalyst was synthesized by an acid-aided sol-gel method. The physical and chemical properties of the catalyst were characterized by X-ray diffraction (XRD) and Transmission Electron Microscope (TEM) methods. The results showed that the composition of the catalyst was well-crystallized and the crystalline size of CeO₂ (111) was about 5.7 nm. The mechanism of NO and NO₂ storage and NO_x temperature programmed desorption (NO-TPD) experiments were investigated to evaluate the NO_x storage capacity of the catalyst. Pt-Ba-Ce/γ-Al₂O₃ catalyst presented the supreme NO_x storage performance at 350°C, and the maximum value reached to 668.8 μmol / g_{cat}. Compared with O₂-free condition, NO oxidation to NO₂ by O₂ had a beneficial effect on the storage performance of NO_x. NO-TPD test results showed that the NO_x species stored on the catalyst surface still kept relatively stable even below 350°C.

Keywords: Diesel engine; NSR; NO_x storage capacity; Mechanism; NO-TPD.

1 Introduction

Diesel and lean-burn engines are becoming increasingly popular, which offer important fuel savings as compared to conventional gasoline engines [1]. In contrast, the presence of excess O₂ in the diesel exhausts renders the classical three-way catalysts, which are effective only under stoichiometric conditions, inefficient in reducing NO_x emissions in the lean-burn engine exhaust [2]. NO_x

storage and reduction (NSR) technology has considered to be a particularly means to reduce NO_x from diesel engines. The principle of NSR is that NO_x stored on the catalyst as nitrates or nitrites when O₂ is in excess. Under rich conditions, with the presence of excessive reductants, NO_x reduction reactions take place [3,4].

Many studies have focused on the optimization of the NSR catalyst for NO_x reduction [5,6]. These NSR catalysts mainly contain precious metals such as Pt/Rh/Pd to facilitate oxidation and reduction reactions, and alkali metal or alkaline earth metals compounds as the NO_x absorbed component on a high surface area support material [7,8,9]. Pt-Ba/γ-Al₂O₃ catalyst is considered to be the most commonly studied formulation of NSR catalyst, which exhibits high NO_x storage capacities in the low-temperature region within 200–400°C [10,11]. Besides, with the addition of ceria to Pt-Ba-Al catalysts is reported to improve NO_x storage capacity at low temperatures under 300°C [12]. Shi et al. compared the NSR behaviour of Pt-Ba-Al₂O₃, Pt-Ba-CeO₂ and Pt-Ba-CeO₂(25%)/Al₂O₃ catalysts, and found that ceria containing catalysts could improve NO_x conversions at low temperatures (200 °C), which indicated that CeO₂ could be a helpful assistant material for NO_x storage under low temperature [3].

Literature reports have proved that many factors in diesel exhausts had a great impact on the properties of NO_x storage and reduction. In particular, NO oxidation to NO₂ over the precious metal is an essential precursor for NO_x storage [13,14,15] due to that NO₂ is more easily to be adsorbed on the trapping material in the form of nitrites/nitrates [16]. Ceria has the capacity to increase mobility of O₂ on the surface of catalysts and sometimes affects the oxidation performance of other elements and the incorporation of ceria are beneficial to the NO oxidation to NO₂ and NO₂ storage [17,18]. 6Mn10Ce/γ-Al₂O₃ displayed a higher oxidation activity of NO into NO₂ in the temperature range of 150°C–450°C [19]. Various factors have positive effect on the stability of nitrates and the NO_x conversion performance. It has been suggested that the stability of the nitrates is increased by the presence of O₂, which

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otherwise are decomposed resulting in the release of NO_x [20].

With the aim to investigate the properties of NO_x storage under different operating conditions that close to real diesel exhausts, such as temperature, H_2 , CO , O_2 and NO , etc. Such complex mixture would influence the optimum operation of the NSR catalysts under various operating temperature. The present study aims to understand the behavior and the influence of O_2 and NO on the NO_x storage capacity of the Pt-Ba-Ce/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. In the present work, the NO_x storage experiments with the combined feed of $\text{NO}/\text{O}_2/\text{N}_2$ were carried out to focus on the NO_x storage capacity of Pt-Ba-Ce/ $\gamma\text{-Al}_2\text{O}_3$ under different operating conditions.

2 Materials and methods

2.1 NSR Catalyst Preparation

Pt-Ba-Ce/ $\gamma\text{-Al}_2\text{O}_3$ catalyst used in this study was prepared by an acid-aided sol-gel method. First, the required amount of Ba (CH_3COO)₂, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\gamma\text{-Al}_2\text{O}_3$ were dissolved in deionized water, and then stirred for 30 min till to form solution. $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ was added into the solution, the amount of which was twice times of Ba²⁺ and Ce³⁺ molar concentration. Then polyethylene glycol, the quality of which is 10% of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, was introduced into the solution at 80°C in the vigorous magnet-stirring device. After continuously stirring, the obtained transparent gel subsequently was dried as contacted with a homogenous solution of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$, as a precursor for Pt, dried at 110°C for 24 h, calcining then took place at 500°C for 5 h in air. Finally, the powders of 40–60 mesh were obtained by ball milling for further experiments.

2.2 Catalyst Characterization

The XRD diffraction patterns of the samples were obtained with a Bruker D8 ADVANCE X-ray diffractometer. The samples were subjected to Cu K α ($\lambda = 0.154068$ nm) radiation at 40 kV and 40 mA. Powder XRD patterns were recorded at 0.02° per second sampling interval in continuous scan mode from 20 to 90° of 2θ with a scanning velocity of 7°/min. The crystalline size was calculated by Scherrer's formula $D = K\lambda/(\beta \cos\theta)$. Transmission electron microscopy (TEM) images of the catalysts were obtained on a TEM (Philips Tecnai 12) microscope operated at 120 kV. The catalyst samples were ground and dispersed in

anhydrous ethanol by ultra-sonication previously. Then, the resulting suspension solution was dropped on a 200 mesh carbon-coated copper wire and sufficiently dried for TEM test.

2.3 Catalytic Activity

Catalytic activities of Pt/Ba-Ce/ $\gamma\text{-Al}_2\text{O}_3$ measurements for NO_x storage and NO temperature programmed desorption were carried out on the lab apparatus shown in Fig.1. The catalyst sample of 0.3 mL was placed in a fixed-bed quartz reactor and packed between two quartz plugs to prevent the sample blown away. The gas concentrations were continuously detected by Thermo Scientific Model 42i-HL Analyzer. Before the measurement, the catalysts were pretreated at 450°C by imposing a feed of 1% H_2 in N_2 for 1h, and in N_2 for 30 min separately. After cooling down to the required measurement temperatures, the gas flow (500 ppm NO , 10% O_2 and N_2 balance) was feed by calibrated electronic mass flow controllers with a total flow rate of 300ml/min, and a space velocity of 60000 h^{-1} . All measurements have been repeated three times to ensure the experimental errors did not exceed 3%. The NO_x storage efficiency (NSE) and NO_x storage capacity (NSC) were calculated according to the following formula:

$$NSE = \left(1 - \frac{\int_0^{t_s} \varphi(\text{NO}_x) \cdot dt}{\varphi(\text{NO}) \cdot t_s} \right) \times 100\% \quad (1)$$

$$NSC = \alpha \cdot \frac{\int_0^{t_s} [\varphi(\text{NO}) - \varphi(\text{NO}_x)] dt}{g_{cat}} \quad (2)$$

Where $\varphi(\text{NO}_x)$ was the detected NO_x concentration (ppm), $\varphi(\text{NO})$ was the inlet NO concentration (ppm), t_s was the storage time (s), g_{cat} was the mass of the catalyst (g). And α was a constant that converted NSC units from ppm to μmol .

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 Catalyst characterization

The X-ray diffraction pattern of Pt/Ba-Ce/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was shown in Figure 2. As shown in Figure 2, the main

Figure 1: Schematic of experimental system.

Figure 2: XRD pattern of catalyst.

phases present in the sample were BaCO₃ (JCPDS No. 45-1471) and γ -Al₂O₃ (JCPDS No. 47-1770). The main diffraction peaks at $2\theta = 28.59^\circ$, 33.03° , 47.31° , and 56.03° were attributed to the cubic fluorite CeO₂ (JCPDS: PDF43-1002). According to Scherrer's formula, the crystalline size of CeO₂ (111) is 26 nm. The characteristic reflections of Pt were not observed due to the small size of Pt particles in the Pt-Ba-Ce/ γ -Al₂O₃ catalyst.

The TEM image of the Pt-Ba-Ce/ γ -Al₂O₃ catalyst was shown in Figure 3. It's obvious to find that the main structure of the catalyst was strip-shaped with nanoparticles. The small near-spherical particles with the sizes varying in the range of 10-20 nm (marked by the black circles) homogeneously dispersed on the surface of the catalyst, mainly were BaCO₃ or CeO₂ nanoparticles, which were deposited on the surface of γ -Al₂O₃. Besides, there are many nanoparticles small particles in the size range of 1-5 nm (marked by the red circles) might be Pt or PtO_x particles.

3.2 Effect of Temperature on NO_x storage capacity

Results on NO_x storage capacity as a function of temperature over the Pt-Ba-Ce/ γ -Al₂O₃ catalyst were shown in Figure 4. Table 1 showed the values of NO_x storage capacity, NO_x storage efficiency and penetration time of the catalyst at different temperatures. It was obviously found that no NO_x slip was detected at the beginning of the storage period (defined as the penetration time T_c), indicating that the NO_x was completely stored at the active site of the catalyst surface during this process. The NO_x slip began to gradually increase as time increased. NO_x storage capacity of the catalyst was close to saturation when the detected NO_x concentration reached to 500

Figure 3: TEM pattern of catalyst.

Figure 4: NO, NO₂ and NO_x(NO+NO₂) breakthrough profile for 30 min at different temperature with lean feed consisting of 500 ppm NO+10% O₂+balance N₂, 60,000 h⁻¹.

ppm. Tc increased from 1 min to 12 min as the temperature increased from 250°C to 350°C, which was shown to well correspond to the NO_x storage capacity of the catalyst increased from 151.7 μmol / g_{cat} to 668.8 μmol / g_{cat}. The results could be attributed to the fact that the catalyst activity increased with the temperature raised in the region of low temperature, promoted the NO_x storage process. However, when the temperature varied from 350-

Table1: NO_x storage capacity, NO_x storage efficiency, penetration time at different temperatures.

Temperature / °C	NSC/μmol/g _{cat}	NSE / %	Tc / min
250	152	22.6	1
300	382	57.0	2
350	669	99.8	12
400	370	55.3	6
450	138	20.5	2

450°C, Tc decreased with the temperature increased, from 12 min to 2 min, resulting in a decrease in the NO_x storage capacity of the catalyst. NO_x storage capacity decreased was mainly due to an imbalance between the rates of NO_x storage and nitrate decomposition. The catalyst presented the excellent NO_x storage performance in high temperature range. Furthermore, the high temperature would reduce the thermal stability of the NO_x stored on the surface of the catalyst to form the nitrate or nitrite, and the increased decomposition increased would lead to the NO_x storage amount reduced.

3.3 Effect of O₂ on NO_x storage capacity

From the above analysis, Pt-Ba-Ce/γ-Al₂O₃ showed the supreme NO_x storage performance at 350°C. In order to investigate the NO_x storage capacity as a function of O₂ over the Pt-Ba-Ce/γ-Al₂O₃ catalyst, the inlet gas was switched in the range of 0%-10% O₂ at 350°C. The storage patterns of the catalyst under the process of 0% O₂ to 10% O₂ atmosphere at 350°C were shown in Figure 5. As shown in Figure 5, Tc was only 1 min under 0% O₂ condition. The concentration of NO_x slip increased rapidly with the time, and then reached to storage saturation after about 13 min. However, the NO₂ was not detected during the storage process. The results indicated that the catalyst performed poor NO_x storage capacity in the absence of O₂. It should be noted that the NO_x concentration decreased rapidly and the NO_x slip was not detected for about 10 min after switching to 10% O₂ conditions, which indicated that NO_x was completely stored on the catalyst surface. After about 58 min, the catalyst reached to the storage saturation state again, and simultaneously NO₂ was began to be detected, indicating that NO oxidation to NO₂ played the positive role in promoting the NO_x storage capacity over the catalyst.

In order to further study the effect of O₂ on the NO_x storage performance of the catalyst, the O₂ concentration in the experiments was set to 0%, 5%, 10% and 15%,

Figure 5: Adsorption patterns of catalyst under the process of 0% O₂ and 10% O₂ at 350°C.

Figure 6: NO_x (NO/NO₂) breakthrough profile for 70 min at different O₂ concentration with lean feed consisting of 500 ppm NO+O₂+balance N₂, 60,000 h⁻¹.

respectively, and the temperature was fixed at 350°C. NO_x storage capacity as a function of O₂ concentrations over the Pt-Ba-Ce/γ-Al₂O₃ catalyst were shown in Figure 6. As shown in Figure 6, the maximum NO_x storage efficiency was only 31.8% under the condition of 0% O₂. When O₂ concentration was increased to 5%, the penetration time was increased and the NO_x slip rate decreased, and the NO_x saturated storage efficiency was increased to 37.6%. When O₂ concentration was 10%, the NO_x penetration time increases to 12 min, and the NO_x saturated storage efficiency was greatly improved to 51.6%. When O₂ concentration was further increased to 15%, the NO_x saturated storage efficiency was slightly reduced to 40.3%.

Table 2: NO_x adsorption efficiency, NO_x adsorption amount NO₂/NO_x ratio, breakthrough time and adsorption saturation time under different oxygen concentration at 350°C

O ₂ concentration/%	NSC /μmol/g _{cat}	NSE /%	Tc/min
0	129	31.8	1
5	302	37.1	2
10	641	51.6	12
15	586	40.3	8

Figure 7: NO_x (NO/NO₂) breakthrough profile for 65 min at different NO concentration with lean feed consisting of 500 ppm NO+balance N₂, 60,000 h⁻¹.

The values of NO_x storage efficiency, NO_x storage capacity, NO₂/NO_x ratio, penetration time and storage saturation time of the catalyst at different O₂ concentrations were shown in Table 2. As can be seen from the Table 2, the Pt/Ba-Ce/γ-Al₂O₃ catalyst had the highest NO_x adsorption efficiency when the O₂ concentration was 10% at 350°C.

3.4 Effect of NO concentrations on NO_x storage capacity

NO_x storage capacity as a function of NO concentrations over the Pt-Ba-Ce/γ-Al₂O₃ catalyst was shown in Figure 7. As shown in Figure 7, with the increase of NO concentration, the penetration time was gradually decreased to 12 min, 3 min and 1 min, respectively. In addition, the storage saturation time was decreased respectively with the increase of NO concentration to 52 min, 33 min and 26 min, which indicated that the NO_x storage efficiency was decreased as the NO concentration increased. The main

Figure 8: NO - TPO profile of Pt/Ba-Ce/ γ -Al₂O₃ catalyst.

reason was that the active site of NO_x adsorption was constant under the different NO concentration, and then the relative NO adsorption capacity was decreased with the high NO concentration.

3.5 Thermal stability of stored NO_x

The NO-TPD curve of the catalyst was shown in Figure 8. As shown in Figure 8, when the temperature was below 350°C, NO_x was not detected, which indicated that the NO_x species stored on the catalyst surface was relatively stable under the range of low temperature. When the temperature was higher than 350°C, the NO_x slip began to be detected. Furthermore, as the temperature increased, the NO_x slip was increased rapidly. At 450°C, the desorption peak of NO₂ appeared and the desorption peak of NO took place at 470°C. Further analysis results showed that desorption peak value of NO was only 25 ppm, while the NO₂ was up to 764 ppm. In addition, when the temperature was higher than 350°C, the thermal stability of the NO_x stored on the surface of the catalyst was reduced. The involved overall reactions were explained with reaction (1) to (4)

4 Conclusions

In the present work, the Pt-Ba-Ce/ γ -Al₂O₃ catalyst was synthesized by the acid-aided sol-gel method and found to be well crystallized in the size of 5.7 nm. The active components of the catalyst were uniformly dispersed without obvious agglomeration. The catalyst had the optimal NO_x storage performance at 350°C, and the maximum of NO_x storage capacity is 669 $\mu\text{mol} / \text{gcat}$. In addition, with the presence of O₂, NO is oxidized to NO₂, promoting the catalyst on the storage performance of NO_x. Moreover, the relative NO storage capacity of the catalyst was decreased on the high concentration of NO, which resulted in the NO_x storage efficiency reduce. NO-TPD test results showed that when the temperature below 350°C, the NO_x species stored on the catalyst surface was relatively stable. The desorption peaks of NO₂ and NO appear at 450°C and 470°C, respectively.

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Conflict of interest: Authors declare no conflict of interest.

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