

Research Article

A Simulation Study of Effect of Mn-Ce/ γ -Al₂O₃ on NO_x Storage and Reduction over Pt-Ce-Ba/ γ -Al₂O₃ Catalysts

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A series of Pt-Ce-Ba/ γ -Al₂O₃ and Mn-Ce/ γ -Al₂O₃ catalysts were synthesized by a sol-gel method and the samples were characterized by XRD, SEM, and EDS. The effect of Mn-Ce/ γ -Al₂O₃ on the storage and reduction of NO_x over Pt-Ce-Ba/ γ -Al₂O₃ catalysts was studied in a fix-bed reactor with simulation gases NO, O₂, and N₂. The results indicated that NO oxidation to NO₂ was reduced with the increase of inlet NO concentration, which was up to 83% when the concentration of NO was 500 ppm but reduced to 76% with the concentration of NO increasing to 1000 ppm. Comparing with the Pt-Ce-Ba/ γ -Al₂O₃ catalysts, the rate of NO_x storage and reduction was remarkably increased over Pt-Ce-Ba/ γ -Al₂O₃ combined with Mn-Ce/ γ -Al₂O₃ catalysts. However, the reductant used for NO_x reduction reaction over Pt-Ce-Ba/ γ -Al₂O₃ catalysts was consumed under the treatment of Mn-Ce/ γ -Al₂O₃ catalyst, which caused the NO_x conversion to obviously drop, but the rate of NO_x absorption declined slightly.

1. Introduction

Nitrogen oxides emissions as the main pollutants from diesel engine have attracted much attention due to their harmful effect on human health and the environment. The regulations on diesel NO_x emissions have become more stringent and the efforts to reduce the NO_x emissions still remain a challenging topic. NO_x storage and reduction (NSR) is regarded as one of the most practical technologies to remove NO_x from diesel engines. Diesel NO_x emissions typically contain more than 90% NO and less than 10% NO₂. Compared with NO, NO₂ is more promptly to be absorbed on storage components contained in NSR catalyst [1, 2]. NO oxidation to NO₂ is a critical chemical reaction step and benefit for promoting the NO_x storage and reduction over NSR catalyst. Diesel oxidation catalyst (DOC) exhibits good activity for NO oxidation to NO₂. According the oxide catalysts reported, Mn-Ce mixed oxides have evidenced high activity for NO oxidation, which has remarkable effects on the storage and reduction of NO_x emissions.

Pt-Ba [3] mixed oxides are the components mainly used for NO_x storage and reduction, and the sequence capacity of NO_x storage is BaO > Ba(OH)₂ > BaCO₃. It was also reported that Mn-Ce mixed oxides catalysts showed a higher

NO_x storage activity when the content of BaO is within the range of 14~23 (wt%) [4–8]. CeO_x based oxides have been reported to have high activity for NO_x storage and regeneration of NSR catalyst at low temperature [9]. Pt-Me/Al₂O₃ (Me = Ba, Ce, Cu) oxides catalysts have high NO_x storage and reduction activity due to the NO conversion promptly improved by CeO_x oxides [10]. The Mn-Ce based oxides usually have much higher NO oxidation because of the improving of oxidation activity due to the addition of Ce element [11]. Furthermore, the contents of MnO_x-CeO₂ as main components of catalyst also have strong effect on NO oxidation; for example, among all the catalysts, MnO_x (0.4)-CeO₂ shows the highest NO oxidation activity and NO conversion reaches up to 60% at 250°C [12]. For these reasons, it is necessary to develop additives that has the better oxidation activity for NO oxidation combined with NSR catalyst to store and reduce NO_x emissions.

The objective of this paper is to evaluate the effect of Mn-Ce/ γ -Al₂O₃ catalyst on storage and reduction of NO_x over Pt-Ce-Ba/ γ -Al₂O₃ catalyst, which is the combination of a DOC catalyst and a NSR catalyst. A series of NSR catalysts capable of NO_x storage and reduction combined with DOC catalysts were prepared by a sol-gel method that involves the addition of Pt, Ce, Mn, and Ba to Al₂O₃. The activities

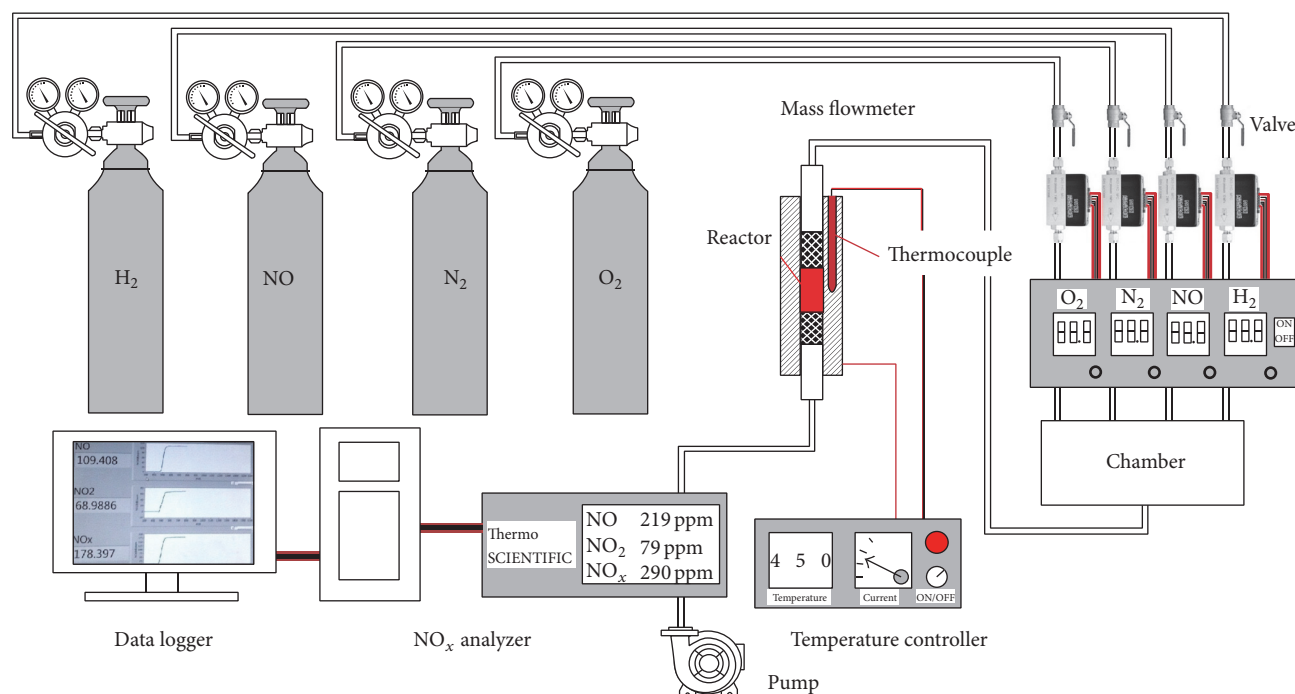


FIGURE 1: Schematic diagram of simulation experiment.

for NO oxidation to NO₂ were measured by temperature programmed reactions. And the simulation experiments were carried out to investigate the storage and reduction of NO_x with and without Mn-Ce/ γ -Al₂O₃ catalyst combined with Pt-Ce-Ba/ γ -Al₂O₃ catalyst.

2. Experimental Section

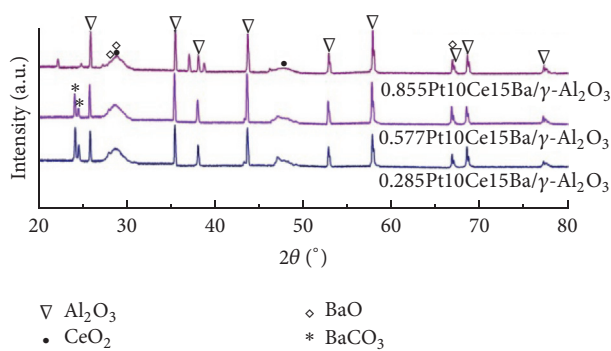
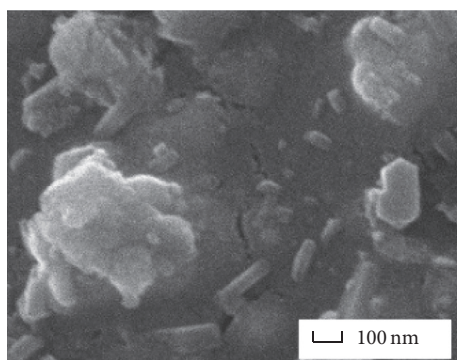
2.1. Catalyst Formulation and Characterization. The Mn-Ce/ γ -Al₂O₃ and Pt-Ce-Ba/ γ -Al₂O₃ catalysts used in this work have been prepared by the sol-gel method. The required amounts of Ce(NO₃)₃·6H₂O, C₄H₆MnO₄·4H₂O, and γ -Al₂O₃ were dissolved in the solution containing deionized water, citric acid, and polyethylene glycol with a mass ratio Mn/Ce 6 : 10, forming homogenous and transparent solution. Stirred at 80°C until transparent gel was obtained, then dried at 110°C for 24 h, decomposed at 300°C for 1 h, and calcined at 500°C for 5 h in air. The catalyst prepared by loading only Pt, Ce, and Ba on γ -Al₂O₃ support is referred to as (x)Pt(y)Ce(25 - y) Ba/ γ -Al₂O₃, where x, y, and (25 - y) mean the weight percent (wt%) of each component that was loaded in the catalyst. The Mn/Ce/Ba mixed oxides reference catalyst was introduced in detail as previously reported. Catalyst powders were characterized by means of an X-ray diffractometer (Bruker D8 Advance) using Cu K α radiation (λ = 0.154068 nm), operating at 40 kV and 40 mA and at a scanning rate of 7°/min, in a 2 θ ranging from 20° to 80° in order to evaluate the achievement of the desired oxides. Field emission scanning electron microscopy (FESEM, JEOL JSM-7001F) equipped with an Oxford Instruments' INCA system was utilized to investigate the morphology and the chemical components of the catalyst samples.

2.2. Experimental Methods. NO to NO₂ oxidation activity experiments were performed and NO_x storage and reduction capacity was evaluated in a fix-bed reactor as shown in Figure 1, composed of simulation gas and control unit, reactor, and NO_x analyzer.

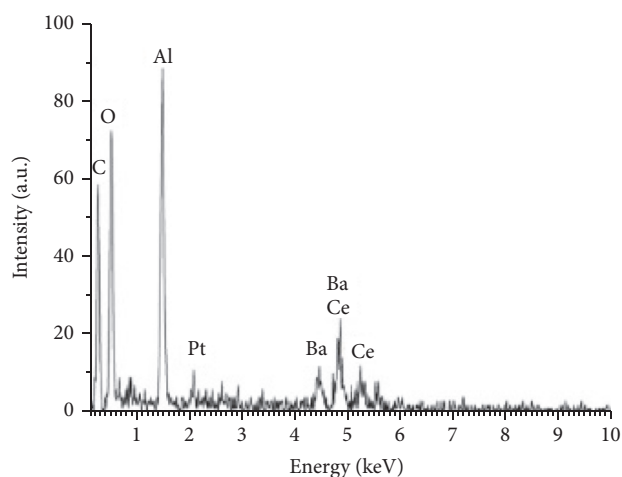
The measurements were then carried out by exposing the catalyst to flowing gas containing 500–1000 ppm NO, 10% O₂, and balance N₂. The NO and NO₂ concentration were followed by the NO_x analyzer. A typical NO_x storage and reduction capacity test was carried out by performing several lean-rich cycles to obtain a steady state working condition for the catalyst, when the catalyst was completely saturated with NO_x. Then a continuous lean flow was admitted to the reactor to evaluate the stored NO_x amounts. Measurements were carried out from 150 to 400°C in 50°C steps. A flow of 1000 ppm NO, 10% O₂, balanced by N₂ was fed during the lean phase, while a flow of 1% H₂, balanced by N₂ was fed during the rich phase. All flow conditions were operated at a gas hourly space velocity (GHSV) of 50,000 h⁻¹.

3. Results and Discussion

X-ray diffractometer of Pt-Ce-Ba/ γ -Al₂O₃ catalysts is shown in Figure 2. The characteristic reflections of Pt and PtO_x were not observed due to the low concentration of Pt in the catalysts and/or the small size of the Pt particles. X-ray diffraction (XRD) analysis showed that the main phases present in Pt-Ce-Ba/ γ -Al₂O₃ were γ -Al₂O₃ (PDF No. 48-0366), CeO₂ (PDF No. 001-0800) located at 28.68° and 47.02°, and BaO (PDF No. 26-0178) located at 28.68° and 66.80°, thereby confirming the decomposition of Ce(NO₃)₃ and Ba(NO₂)₂ into crystalline CeO₂ during catalyst calcination

FIGURE 2: XRD patterns of Pt-Ce-Ba/ γ -Al₂O₃ catalysts.

(a) SEM

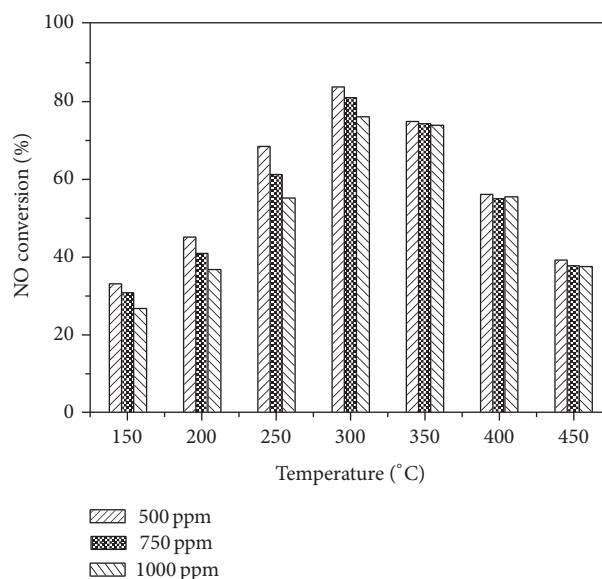


(b) EDS

FIGURE 3: SEM and EDS patterns of Pt-Ce-Ba/ γ -Al₂O₃ catalyst.

[13–16]. In addition, the BaCO₃ phases are also observed as shown in the mark (*) of Figure 2, indicating that Ba(NO₂)₂ converted to BaCO₃ during calcination, in accordance with the results of Kwak et al. [17], in which the crystalline form of BaCO₃ was present as witherite in the catalysts. Therefore, the 0.855Pt10Ce15Ba/ γ -Al₂O₃ (denote as Pt-Ce-Ba/ γ -Al₂O₃) catalyst is chosen as further measurement and evaluation in this work due to its lowest BaCO₃ content contained.

Figure 3 shows the SEM image and EDS spectrum of Pt-Ce-Ba/ γ -Al₂O₃ catalyst. As shown in Figure 3(a), the catalyst

FIGURE 4: Variation of NO conversion with temperature over Mn-Ce/ γ -Al₂O₃ catalyst.

presents the small strip microstructure morphology formed by Pt and/or PtO_x and other irregular agglomerates mainly composed of CeO_x or BaO obtained through the reaction between Pt and Ce oxides, while some larger particles could be observed over the catalyst sample, probably caused by accumulation of γ -Al₂O₃ with CeO_x or BaO. EDS spectra show the presence of various spectra of the catalyst. Each element is identified by the presence of peaks at the characteristic spectrum. As seen in Figure 3(b), strong signals for C and Al elements were detected. Weak signals for Ba, Ce, and P have also been detected. C element was mainly coming from the residual carbon-containing reagents.

Figure 4 shows the variation of NO conversion as a function of catalyst temperature over Mn-Ce/ γ -Al₂O₃ catalyst under 500 ppm, 750 ppm, and 1000 ppm NO, respectively. It can be seen from the figure that NO conversion increases gradually with the rise of temperature in the range of 150–300°C and then decreases after 300°C under each different inlet NO concentration, which can be explained by the fact that partial NO₂ will decompose into NO at high temperature. Additionally, NO conversion decreases with the increase of inlet NO concentration. The total NO conversion is higher under the inlet NO concentration 500 ppm as compared to that of 750 and 1000 ppm NO, which increases from 33% at 150°C to maximum 82% at 300°C. It should be noticed that the difference between NO conversion under different inlet NO concentration experiences little change in the range of 350°C to 450°C, which indicates that the temperature may be responsible for NO oxidation when the temperature is high but not the inlet NO concentration.

Figure 5 shows the variation in NO, NO₂, and NO_x concentration as a function of the time over Pt-Ce-Ba/ γ -Al₂O₃ catalyst with and without the Mn-Ce/ γ -Al₂O₃ catalyst. It can be clearly seen that the NO, NO₂, and NO_x concentration rapidly increase in the initial absorption stage before 1600

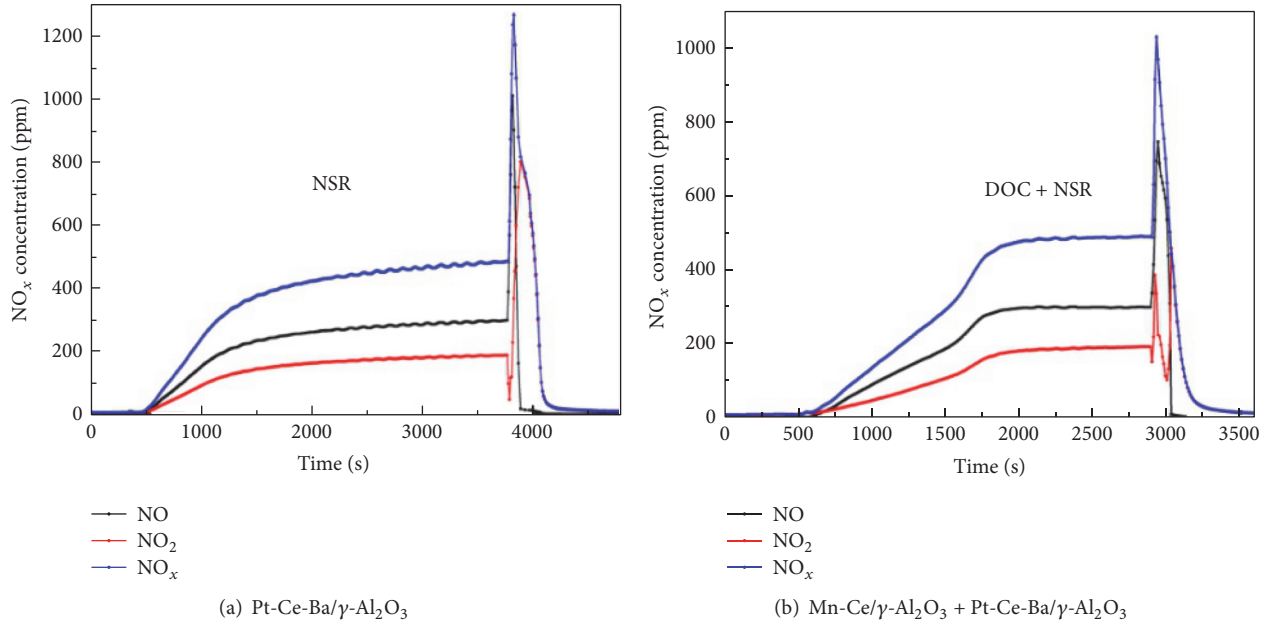


FIGURE 5: Storage and reduction process of NSR catalyst and DOC combined with NSR catalyst technology.

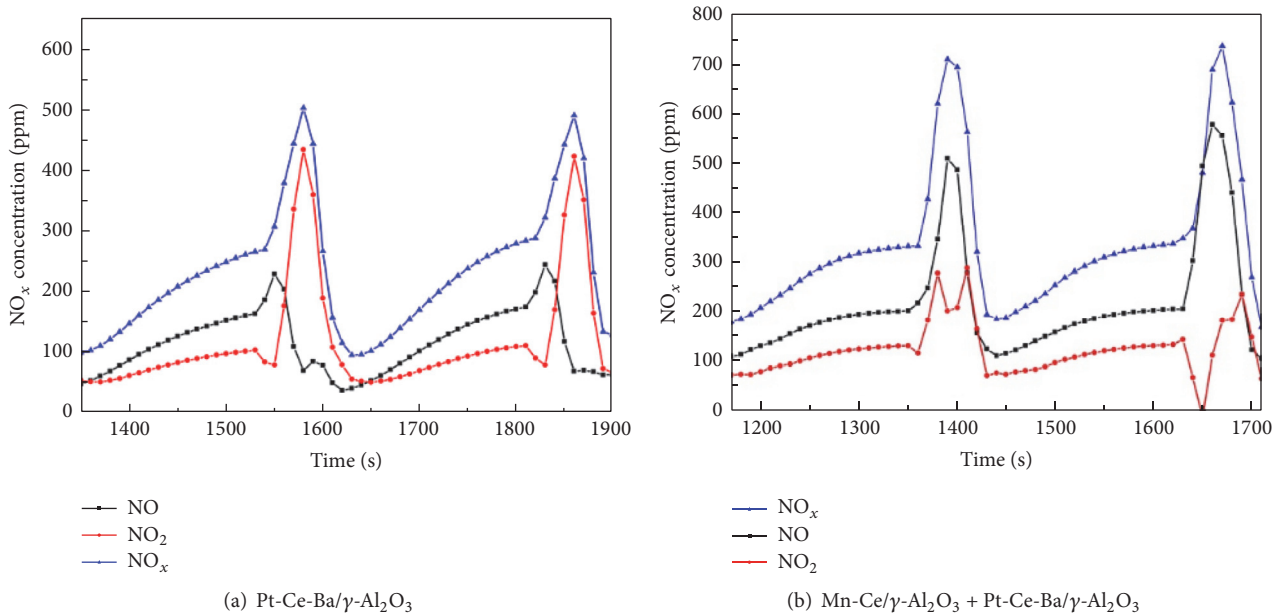


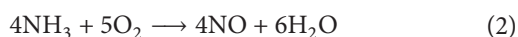
FIGURE 6: Storage-reduction process of (a) NSR catalysts and (b) DOC combined NSR technology.

seconds and remain nearly constant between 1600 and 3600 seconds over Pt-Ce-Ba/γ-Al₂O₃ catalyst. This means that the process from adsorption starting to fully saturated adsorption lasted 1600 seconds. And in the period of rich condition, NO_x concentration decreases remarkably by the reductant reaction with H₂. In comparison to that with Mn-Ce/γ-Al₂O₃ catalyst, NO, NO₂, and NO_x concentration increase occurs somewhat slowly and then becomes very fast between 1600 and 2000 seconds and after that remains the same general trend as the previous analysis. This means it would take a shorter time up to around 2000 seconds for NO and NO₂

adsorbent to be completely saturated, which is caused by the activity of oxidation NO to NO₂ on Mn-Ce/γ-Al₂O₃ catalyst. The present results prove that the oxidation activity of Mn-Ce/γ-Al₂O₃ catalyst can effectively improve the NO_x adsorption rate, but the value of desorption peaks is lower in comparison with the treatment of Pt-Ce-Ba/γ-Al₂O₃ catalyst alone. Therefore, it is difficult to discuss the results only as caused by differences in NO oxidation to NO₂ with oxidation catalyst.

Figure 6 shows NO_x storage and reduction experiments carried out for Pt-Ce-Ba/γ-Al₂O₃ catalyst with and without

Mn-Ce/ γ -Al₂O₃ catalyst samples. Comparing the different experiments, it can be noticed that the rise rate and the peak value of NO_x concentration in the process of desorption reaction were higher and both obviously improved with the Mn-Ce/ γ -Al₂O₃ catalyst, attributed by more heat release from the H₂ oxidation reaction partly consumed by Mn-Ce/ γ -Al₂O₃ catalyst. As can be observed in Figure 6(b), there are more increase of NO concentration and decrease of NO₂ concentration during the process of desorption. This may suggest that NH₃ was formed during the reaction between H₂ and Ce(NO₃)₄ contained in the Mn-Ce/ γ -Al₂O₃ catalyst as shown in reaction (1) [18–20], followed by NO formation where O₂ was available for reacting with NH₃ as shown in reaction (2). In addition, more heat released by the oxidation between H₂ and O₂ will result in the decomposition of nitrate and nitrite oxides contained in Pt-Ce-Ba/ γ -Al₂O₃ catalyst. And this decomposition may also contribute to remarkably improving the NO concentration in the NO_x desorption stage. However, H₂ consumed by the oxidation over Mn-Ce/ γ -Al₂O₃ catalyst resulted in the decrease of NO₂ concentration. More importantly, this reduction was relevant with respect to the total NO₂ concentration needed for NO_x desorption, which had negligible effect on the rate of decomposition reaction.



Lower NO_x conversion and less NO_x storage capacity with Mn-Ce/ γ -Al₂O₃ catalyst can be clearly seen in Figure 6(b) compared to Figure 6(a). As clearly seen in Figure 6(b) compared to Figure 6(a), the NO_x conversion is much smaller and at the same time the NO_x storage capacity experiences less decline. The main reason is that H₂ consumption by oxidation over Mn-Ce/ γ -Al₂O₃ catalyst will lead to the incomplete desorption of NO_x; then the NO_x conversion will be reduced. It is worth noticing that the rate of NO_x storage and reduction is improved by the heat released from the Mn-Ce/ γ -Al₂O₃ catalyst, which is also benefit for making up for NO_x storage capacity.

4. Conclusion

A series of Pt-Ce-Ba/ γ -Al₂O₃ and Mn-Ce/ γ -Al₂O₃ catalysts were prepared and found to exhibit small strip microstructure morphology mainly composed of CeO_x or BaO. The behavior of Pt-Ce-Ba/ γ -Al₂O₃ catalyst was investigated at different lean-rich cycles in NO_x storage and reduction process with and without Mn-Ce/ γ -Al₂O₃ catalyst through simulation experiments. The inlet NO concentration increase was not benefit for NO conversion in the range of low temperature, which will has no effect on NO conversion above high temperature. Compared with Pt-Ce-Ba/ γ -Al₂O₃ catalyst treatment alone, the rate of NO_x storage and reduction both was remarkably increased. The results indicate that Mn-Ce/ γ -Al₂O₃ catalyst can effectively improve the activity of Pt-Ce-Ba/ γ -Al₂O₃ catalyst, especially in the low temperature. However, it is still probable that the reducing agent as H₂ will

be consumed by Mn-Ce/ γ -Al₂O₃ catalyst, which will lead the NO_x conversion to decrease to a certain extent.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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