Research Article

A Simulation Study of Effect of Mn-Ce/\gamma-Al_2O_3 on NO_x Storage and Reduction over Pt-Ce-Ba/\gamma-Al_2O_3 Catalysts

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A series of Pt-Ce-Ba/\gamma-Al_2O_3 and Mn-Ce/\gamma-Al_2O_3 catalysts were synthesized by a sol-gel method and the samples were characterized by XRD, SEM, and EDS. The effect of Mn-Ce/\gamma-Al_2O_3 on the storage and reduction of NO_x over Pt-Ce-Ba/\gamma-Al_2O_3 catalysts was studied in a fix-bed reactor with simulation gases NO, O_2, and N_2. The results indicated that NO oxidation to NO_2 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/\gamma-Al_2O_3 catalysts, the rate of NO_x storage and reduction was remarkably increased over Pt-Ce-Ba/\gamma-Al_2O_3 combined with Mn-Ce/\gamma-Al_2O_3 catalysts. However, the reductant used for NO_x reduction reaction over Pt-Ce-Ba/\gamma-Al_2O_3 catalysts was consumed under the treatment of Mn-Ce/\gamma-Al_2O_3 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% NO_2. Compared with NO, NO_2 is more promptly to be absorbed on storage components contained in NSR catalyst [1, 2]. NO oxidation to NO_2 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 NO_2. 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 > BaCO_3. 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-\(\text{Me/Al}_2O_3\) (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-\text{CeO}_2 as main components of catalyst also have strong effect on NO oxidation; for example, among all the catalysts, MnO_x(0.4)-CeO_2 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/\gamma-Al_2O_3 catalyst on storage and reduction of NO_x over Pt-Ce-Ba/\gamma-Al_2O_3 catalyst, which is the combination of 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 \(\text{Al}_2O_3\). The activities
for NO oxidation to NO\textsubscript{2} were measured by temperature programmed reactions. And the simulation experiments were carried out to investigate the storage and reduction of NO\textsubscript{2} with and without Mn-Ce/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst combined with Pt-Ce-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst.

2. Experimental Section

2.1. Catalyst Formulation and Characterization. The Mn-Ce/\gamma-Al\textsubscript{2}O\textsubscript{3} and Pt-Ce-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts used in this work have been prepared by the sol-gel method. The required amounts of Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O, C\textsubscript{x}H\textsubscript{y}MnO\textsubscript{z}·4H\textsubscript{2}O, and \gamma-Al\textsubscript{2}O\textsubscript{3} 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 \gamma-Al\textsubscript{2}O\textsubscript{3} support is referred to as \((\mathrm{x} \times \mathrm{Pt} \times \mathrm{Ce} (25 - y) \times \mathrm{Ba} / \gamma - \mathrm{Al}_2\mathrm{O}_3)\), 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\textalpha radiation (\(\lambda = 0.154068\) nm), operating at 40 kV and 40 mA and at a scanning rate of 7°/min, in a 2\theta 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 NO\textsubscript{2} oxidation activity experiments were performed and NO\textsubscript{2} storage and reduction capacity was evaluated in a fixed-bed reactor as shown in Figure 1, composed of simulation gas and control unit, reactor, and NO\textsubscript{2} analyzer.

The measurements were then carried out by exposing the catalyst to flowing gas containing 500–1000 ppm NO, 10% O\textsubscript{2}, and balance N\textsubscript{2}. The NO and NO\textsubscript{2} concentration were measured by the NO\textsubscript{2} analyzer. A typical NO\textsubscript{2} 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\textsubscript{2}. Then a continuous lean flow was admitted to the reactor to evaluate the stored NO\textsubscript{2} amounts. Measurements were carried out from 150 to 400° C in 50° C steps. A flow of 1000 ppm NO, 10% O\textsubscript{2}, balanced by N\textsubscript{2} was fed during the lean phase, while a flow of 1% H\textsubscript{2}, balanced by N\textsubscript{2} was fed during the rich phase. All flow conditions were operated at a gas hourly space velocity (GHSV) of 50,000 h\textsuperscript{-1}.

3. Results and Discussion

X-ray diffractometer of Pt-Ce-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts is shown in Figure 2. The characteristic reflections of Pt and PtO\textsubscript{2} 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/\gamma-Al\textsubscript{2}O\textsubscript{3} were \gamma-Al\textsubscript{2}O\textsubscript{3} (PDF No. 48-0366), CeO\textsubscript{2} (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(NO\textsubscript{3})\textsubscript{3} and Ba(NO\textsubscript{3})\textsubscript{2} into crystalline CeO\textsubscript{2} during catalyst calcination.
Figure 2: XRD patterns of Pt-Ce-Ba/γ-Al2O3 catalysts.

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

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

In this work, the effect of Mn addition on the catalytic performance of this catalyst is further measured and evaluated. The Mn-Ce/γ-Al2O3 catalyst prepared in this work presents the small strip microstructure morphology formed by Pt and/or PtOx and other irregular agglomerates mainly composed of CeOx 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 CeOx 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 maybe responsible for NO oxidation when the temperature is high but not the inlet NO concentration.

Figure 5 shows the variation in NO, NO2, and NOx 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 NOx concentration rapidly increase in the initial absorption stage before 1600
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, NOₓ concentration decreases remarkably by the reductant reaction with H₂. In comparison to that with Mn-Ce/γ-Al₂O₃ catalyst, NO, NO₂, and NOₓ 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 NOₓ 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 NOₓ storage and reduction experiments carried out for Pt-Ce-Ba/γ-Al₂O₃ catalyst with and without
Mn-Ce/γ-Al$_2$O$_3$ catalyst samples. Comparing the different experiments, it can be noticed that the rise rate and the peak value of NO$_3$ concentration in the process of desorption reaction were higher and both obviously improved with the Mn-Ce/γ-Al$_2$O$_3$ catalyst, attributed by more heat release from the H$_2$ oxidation reaction partly consumed by Mn-Ce/γ-Al$_2$O$_3$ catalyst. As can be observed in Figure 6(b), there are more increase of NO concentration and decrease of NO$_2$ concentration during the process of desorption. This may suggest that NH$_3$ was formed during the reaction between H$_2$ and Ce(NO$_3$)$_3$ contained in the Mn-Ce/γ-Al$_2$O$_3$ catalyst as shown in reaction (1) [18–20], followed by NO formation where O$_2$ was available for reacting with NH$_3$ as shown in reaction (2). In addition, more heat released by the oxidation between H$_2$ and O$_2$ will result in the decomposition of nitrate and nitrite oxides contained in Pt- Ce-Ba/γ-Al$_2$O$_3$ catalyst. And this decomposition may also contribute to remarkably improving the NO concentration in the NO$_3$ desorption stage. However, H$_2$ consumed by the oxidation over Mn-Ce/γ-Al$_2$O$_3$ catalyst resulted in the decrease of NO$_3$ concentration. More importantly, this reduction was relevant with respect to the total NO$_3$ concentration needed for NO$_x$ desorption, which had negligible effect on the rate of decomposition reaction.

\[
\text{Ce(NO}_3)_4 + 16\text{H}_2 \rightarrow 4\text{NH}_3 + \text{CeO}_2 + 10\text{H}_2\text{O} \quad (1)
\]

\[
4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \quad (2)
\]

Lower NO$_3$ conversion and less NO$_3$ storage capacity with Mn-Ce/γ-Al$_2$O$_3$ 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$_3$ conversion is much smaller and at the same time the NO$_3$ storage capacity experiences less decline. The main reason is that H$_2$ consumption by oxidation over Mn-Ce/γ-Al$_2$O$_3$ catalyst will lead to the incomplete desorption of NO$_3$; then the NO$_3$ conversion will be reduced. It is worth noticing that the rate of NO$_3$ storage and reduction is improved by the heat released from the Mn-Ce/γ-Al$_2$O$_3$ catalyst, which is also benefit for making up for NO$_3$ storage capacity.

### 4. Conclusion

A series of Pt-Ce-Ba/γ-Al$_2$O$_3$ and Mn-Ce/γ-Al$_2$O$_3$ catalysts were prepared and found to exhibit small strip microstructure morphology mainly composed of CeO$_2$ or BaO. The behavior of Pt-Ce-Ba/γ-Al$_2$O$_3$ catalyst was investigated at different lean-rich cycles in NO$_3$ storage and reduction process with and without Mn-Ce/γ-Al$_2$O$_3$ catalyst through simulation experiments. The inlet NO concentration increase was not benefit for NO conversion in the range of low temperature, which will have no effect on NO conversion above high temperature. Compared with Pt-Ce-Ba/γ-Al$_2$O$_3$ catalyst treatment alone, the rate of NO$_3$ storage and reduction both was remarkably increased. The results indicate that Mn-Ce/γ-Al$_2$O$_3$ catalyst can effectively improve the activity of Pt-Ce-Ba/γ-Al$_2$O$_3$ catalyst, especially in the low temperature. However, it is still probable that the reducing agent as H$_2$ will be consumed by Mn-Ce/γ-Al$_2$O$_3$ catalyst, which will lead the NO$_3$ 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.

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