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Selective Catalytic Reduction of Nitric Oxide with Ammonia over ZSM-5 Based Catalysts for Diesel Engine Applications

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Abstract Fe/ZSM-5 and Cu-ZSM-5 were investigated for selective catalytic reduction of NO_x with ammonia. The Fe/ZSM-5 catalyst showed over 90% NO conversion from 350 to 500 °C and Cu-ZSM-5 showed over 90% NO conversion from 250 to 350 °C. After pretreatment in 10% H_2O at 700 °C, the Fe/ZSM-5 still exhibited high activities and stability. On the basis of the experiments, Fe/ZSM-5 and Cu-ZSM-5 seem to be promising candidates for diesel-engine NO_x emission control.

Keywords SCR of NO with NH_3 · Fe/ZSM-5 · Cu-ZSM-5 · Diesel engine NO emission control

1 Introduction

Nitrogen oxides (NO, NO_2 and N_2O) in the exhaust gases from combustion of fossil fuels remain a major source for air pollution. They contribute to photochemical smog, acid rain, ozone depletion, and greenhouse effects. It is known that over 50% of NO_x emissions are from automotive sources, such as gasoline cars and diesel engine trucks, and over 40% of NO_x are from stationary sources, such as power plants fueled by fossil fuel combustion. Diesel engines have many benefits over gasoline engines, such as better fuel economy and less CO_2 production. But they also emit more NO_x. In the United States, the Environmental Protection Agency has addressed this issue by imposing increasingly stringent emission regulations, such as the Tier 2 regulations of light duty vehicles and both the 2004 Rule and 2010 Highway Rule for heavy duty diesel engines, all mobile and on-board applications.

The current technology for reducing nitrogen oxide emissions from power plants is selective catalytic reduction (SCR) of NO_x ($x = 1, 2$) with ammonia, in excess oxygen. Many catalysts have been reported to be active for this reaction, such as vanadia (doped with MoO_3 and/or WO_3) and other transition metal oxides [1–5].

Currently, the selective catalytic reduction with ammonia (i.e., via urea injection) is considered as among the most promising candidates for solving the NO_x emission problem of diesel engines. H-zeolite and ion-exchanged molecular sieves have received much attention for SCR of NO_x by both hydrocarbon and ammonia in recent years. Zeolite based catalysts, such as H-form, Cu-exchanged and Fe-exchange zeolites [6–17] were investigated extensively. Among the catalysts, the Cu-ZSM-5 and Fe-ZSM-5 received much attention because of their high activities and high resistance to SO_2 and H_2O under ammonia-SCR reaction conditions. More recently, we have developed a very simple method to prepare Fe/ZSM-5 (by simple incipient wetness impregnation) which led to the catalyst with the highest activities as compared to all the Fe-ZSM-5 catalysts that were prepared by ion exchange methods (both liquid and vapor phase ion exchange) [18, 19].

In this work, Fe/ZSM-5 and Cu-ZSM-5 were investigated on the selective catalytic reduction of NO_x with ammonia over a broad temperature range, similar to the diesel engine gas exhaust conditions. The experiments were performed mainly in the presence of water vapor over the entire temperature range investigated. Moreover, the hydrothermal stability as well as the effects of ratio of NO_2/NO on SCR activity was also investigated. Compared to Fe/Zeolite, Cu-Zeolite has a lower hydrothermal stability;

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so a highly stable Cu-ZSM-5 prepared from vapor-phase ion-exchange method was also investigated in this work.

2 Experimental

2.1 Preparation of Catalysts

Fe/ZSM-5 catalysts were prepared using NH_4-ZSM-5 (Si/Al = 11, from Alsi-Penta) by incipient wetness impregnation with $FeCl_2$ or $FeCl_3$ solution and then dried at 110 °C overnight [details are given in 18, 19]. The catalysts contained both Fe-oxides nanocrystals/clusters and ion-exchanged Fe-ZSM-5 [18], thus, they can be more appropriately denoted as FeO_x/Fe-ZSM-5. The samples were pretreated in He and then calcined in air at 500 °C for 6 h. The amount of iron is reported as iron metal weight % based on the support. By this method, minimum amount of water is evaporated and no excess solution is needed. Also, no washing is required as in the aqueous ion exchange method. So this method is simpler and should be less costly than the ion-exchange method using aqueous solution.

In order to compare activities, the commercial-type catalyst V_2O_5-WO_3/TiO_2 was also investigated. The V_2O_5-WO_3/TiO_2 catalyst (4.4%V_2O_5-8.2%WO_3/TiO_2) was prepared by incipient wetness impregnation with an aqueous solution of NH_4VO_3 in oxalic acid. The impregnated catalyst was first dried at 120 °C for 4 h, followed by calcination at 500 °C in O_2 for 3 h. The supported WO_3/TiO_2 oxides were prepared by dissolving ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$) in water and impregnating the TiO_2 support. The samples were then dried at room temperature followed by drying at 110 °C overnight and calcination at 450 °C for 2 h. The V_2O_5-WO_3/TiO_2 catalyst had nearly identical SCR activity and behavior as that of the commercial SCR catalyst that was supplied by a major catalyst manufacturer [12].

The Cu-ZSM-5 zeolites were prepared by vapor phase ion exchange following similar procedures reported previously [20, 21]. Layers of 2.0 g of H-ZSM5 zeolite and 0.25 g of CuCl (Cu/Al = 1 in moles) were loaded into a reactor each separated by thin quartz wool walls. The reactor was then heated in an inert, dry atmosphere, from room temperature to 200 °C at 1 °C/min and the temperature was held at that temperature for 6 h. Consequently, the temperature was slowly increased to 650 °C and kept at a pre-specified temperature for another 10 h. The excess CuCl was completely evaporated from within the voids of the zeolite and this was corroborated by the absence of the salt from its original reactor location at the end of the vapor phase ion-exhange process and by a white crystalline ring formed at the reactor outlet. The zeolite was then treated in oxygen at 200 °C for 6 h before cooling down to room temperature. According to literature information [21], the Cu content of Cu-ZSM-5 was around 7.1 wt%, i.e. Cu/Al = 0.9 with vapor phase ion exchange.

Cu-ZSM-5 was also prepared by liquid phase ion exchanges of 2.0 g NH_4-ZSM-5 with 200 ml of 0.05 M $CuCl_2$ solution for 24 h at room temperature [11]. After exchange, the mixture was vacuum filtered and washed in copious amount of deionized water until no free ions were present in the filtrate. The sample was dried and then was calcined in air at 500 °C for 6 h. According to literature information [20], the Cu content of Cu-ZSM-5 was around 1.6 wt%, i.e. Cu/Al = 0.2 with liquid phase ion exchange.

The Cu-ZSM-5 catalysts prepared from vapor phase ion exchange and liquid phase ion exchange methods were designated as Cu-ZSM-5(VPIE) and Cu-ZSM-5(LPIE), respectively.

The hydrothermal stabilities and sulfur resistances of all catalysts were tested by subjecting them to pretreatment under the following conditions: 10% water vapor and 500 ppm SO_2 (when used) in air at 700 °C for 24 h. The reason for pretreatment at 700 °C is that the temperatures of the exhaust gases of diesel engines are usually below 600 °C; thus, the treatment above is considered as a good ‘aging’ test.

2.2 Activity Test

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The typical reactant gas composition was as follows: 500 ppm NO, 500 ppm NH_3, 5% O_2, 6% H_2O and balance He. Under typical conditions, 40 mg sample was used in each run. The total flow rate was 500 ml/min (under ambient conditions). Thus, a very high GHSV (gas hourly space velocity) was obtained (5.7×10^5 h^{-1}). The premixed gases (1.01% NO in He, 1.00% NH_3 in He, and 0.99% NO_2 in He) were supplied by Matheson. The water vapor was generated by passing He through a heated gas-wash bottle containing de-ionized water. The tubing of the reactor system was heat traced to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO_2 concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Environmental Instruments Inc. Model 42C). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were also analyzed by a gas chromatograph (Shimadzu, 8A) at 50 °C with 5A molecular sieve column for N_2 and Porapak Q column for N_2O. Before any product analysis, the reactor temperature was kept constant for at least one hour. For a typical experiment, we ran the experiment for two hours at each temperature; and at each temperature, no obvious deactivation was observed.

3 Results and Discussion

3.1 SCR Performance for Different Catalysts

Figure 1 shows the ammonia-SCR activities for two catalysts, 2.5%Fe/ZSM-5 and commercial 4.4%V_2O_5-8.2%WO_3/TiO_2. From Fig. 1, it can be seen that the activities of the Fe/ZSM-5 (fresh and steam-pretreated) are substantially higher than the V_2O_5-WO_3/TiO_2 (fresh and steam-pretreated) catalysts. For the ammonia SCR reaction, it has been generally accepted that ammonia is first adsorbed on the BrØnsted or Lewis acid sites to form, respectively, NH_4^+ or coordinated NH_3, then gaseous or adsorbed nitrogen oxides react with them to form N_2 and H_2O [22]. Hence, surface acidity of the catalyst is important for ammonia SCR reaction because strong surface acidity is beneficial to ammonia adsorption. Our previous study showed that abundant BrØnsted acid sites existed on the Fe/ZSM-5 [18]. When the reactants including NH_3 were introduced to the Fe/ZSM-5 catalyst, NH_3 molecules were adsorbed on these sites to form NH_4^+ ions. The NH_4^+ ions are present in two forms, 3H structure (three hydrogen atoms bonded to the AlO_4 tetrahedron) and 2H structure (two hydrogen atoms bonded to the AlO_4 tetrahedron). The 3H structure is more stable than the 2H structure at high temperatures (>100 °C). The NH_4^+ ions with 3H structure were still observed when the temperature was increased to 400 °C in He, indicating a strong Brønsted acidity on Fe/ZSM-5 [22]. By comparison, ammonia adspecies (both NH_4^+ ions and coordinated NH_3) on V_2O_5/TiO_2 were almost removed at around 300 °C and above [23]. This may be one of the reasons that Fe/ZSM-5 showed much higher SCR activities than vanadia catalysts.

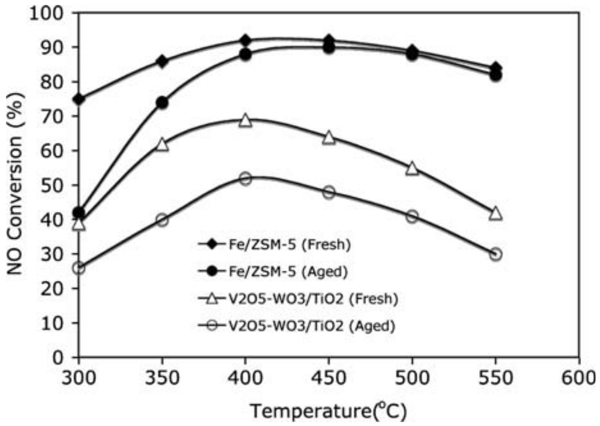

Fig. 1 Catalytic activities for NO reduction by ammonia on 2.5%Fe/ZSM-5 and 4.4%V_2O_5–8.2%WO_3/TiO_2 catalysts. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = 5.7 × 10^5 h^{-1} (based on ambient conditions)

Because the resistance to H_2O is an important issue for the SCR reaction, we also investigated the aging effect of H_2O on the catalytic performance of the 2.5%Fe/ZSM-5 and 4.4%V_2O_5-8.2%WO_3/TiO_2 catalysts. Taking into account the temperature of exhaust gas of diesel engine is usually less than 600 °C, the aging temperature was selected at 700 °C, as an accelerated test. After pretreatment of Fe/ZSM-5 in 10% H_2O at 700 °C for 24 h, the NO conversion decreased significantly in the low temperature range; however, at temperature higher than 400 °C, the NO conversion was almost the same on the fresh and steam-pretreated Fe/ZSM-5. It is known that steam treatment at elevated temperatures will cause dealumination or aluminum migration in the ZSM-5 framework structure [24, 25]. The dealumination of ZSM-5 results in an increase in the Si/Al ratio and a decrease in the surface acidity of the zeolite, thus the observed deactivation of Fe/ZSM-5. In addition, the aging treatment also leads to the decrease of active iron species due to the formation of iron agglomerates and thus the deactivation of Fe/ZSM-5 [24–26]. It is considered that a high Si/Al ratio would increase the bond strength of NH_4^+ on the zeolite whereas a low Si/Al ratio would increase the adsorption capacity [26]. After hydrothermal aging, the bond strength of ammonia on the zeolite would increase due to dealumination. This could be the reason that higher NO conversions (i.e., less deactivation) were observed on the Fe/ZSM-5 at high temperatures than that at lower temperatures (Fig. 1). These results are similar with that of Toloene et al. [26].

From the experimental results, even after ageing with steam at 700 °C for 24 h, the Fe/ZSM-5 catalyst still showed high activities for NO conversion at the reaction temperature range of 400–550 °C. Therefore, Fe/ZSM-5 catalyst prepared from the simple one-step incipient wetness impregnation with $FeCl_2$ in this work exhibits high hydrothermal stability and that Fe/ZSM-5 is a promising catalyst for diesel engine applications (with urea injection).

The NO conversions on Fe/ZSM-5 with different Fe loadings are shown in Fig. 2. It was found that the activity increased with increasing Fe loading, but the increase nearly diminished when the Fe loading was > 2.5%, which was very similar to our previous report [18, 19]. It was known that the catalytic activities of Fe/ZSM-5 catalysts were from Fe^{2+}, Fe^{3+} and highly dispersed iron oxide species [18]. Our previous XRD results showed that only a hematite (α-Fe_2O_3) phase was detected on these Fe/ZSM-5 catalysts [15]. Some ion exchange (of Fe^{2+}) occurred during the incipient wetness impregnation process but the ion exchange of Fe^{2+} was incomplete because of the excess Fe contents in the 5%Fe/ZSM-5 and 7.5%Fe/ZSM-5

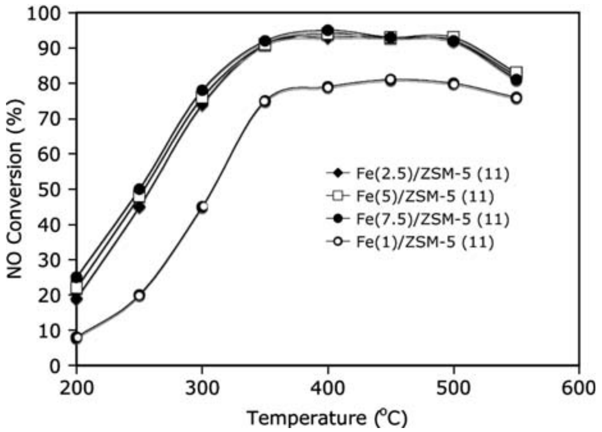

Fig. 2 Catalytic activities for NO reduction by ammonia on Fe/ZSM-5 with different Fe loadings. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = 5.7 × 10^5 h^{-1} (based on ambient conditions). *Notes*: The number in parentheses after Fe indicates the Fe metal content (in percent by weight); the number in parentheses after ZSM-5 indicates the Si/Al ratio in the zeolite

catalysts. This showed that the active sites increased with increasing the Fe content in Fe/ZSM-5 catalyst. When the Fe loading was more that 2.5%, however, the exposed active sites on the catalyst reached the largest amount. Therefore, the catalytic activities of Fe/ZSM-5 showed almost the same level when the Fe loading was above 2.5%.

Figure 3 shows the ammonia-SCR activities of 2.5%Fe/ZSM-5 catalysts prepared from zeolites with different Si/Al ratios and different iron salts (used for incipient wetness impregnation). From Fig. 3, it can be seen that the activity of the Fe/ZSM-5 with a lower Si/Al ratio is higher than that of the Fe/ZSM-5 with a higher Si/Al ratio. The relative order of NO conversion follows: 2.5%Fe/ZSM-5 (11) > 2.5%Fe/ZSM-5 (25) > 2.5%Fe/ZSM-5 (40) where the number in the parentheses indicates the Si/Al ratio. These results showed that ratio of Si/Al had a strong effect on NO conversion for the Fe/ZSM-5 catalysts in the temperature range of 200–550 °C. Although the Fe contents were the same in these Fe/ZSM-5 catalysts, the NO conversions varied with the Si/Al ratio. The same conclusion can be obtained in comparison with our previous study on 1.59%Fe-ZSM-5 (10) catalyst with Si/Al = 10 [12]. It was shown that the NO conversion was more than 95% in the range of 400–550°C on 1.59%Fe-ZSM-5 (10) catalyst, although the iron content of 1.59%Fe-ZSM-5 (10) was lower than that of 2.5%Fe/ZSM-5 in this work. For the SCR of NO with ammonia, the reaction path involves the adsorption of ammonia on the BrØnsted or Lewis acid sites and reaction between the ammonia adspecies and nitrogen oxides [1, 2]. In this reaction, surface acidity is important because strong acidity is beneficial to NH_3 adsorption. It is known that ZSM-5 zeolite with a lower Si/Al ratio has a higher BrØnsted acidity so that a higher SCR activity will be achieved on the Fe/ZSM-5 with lower Si/Al ratio in ZSM-5 zeolite.

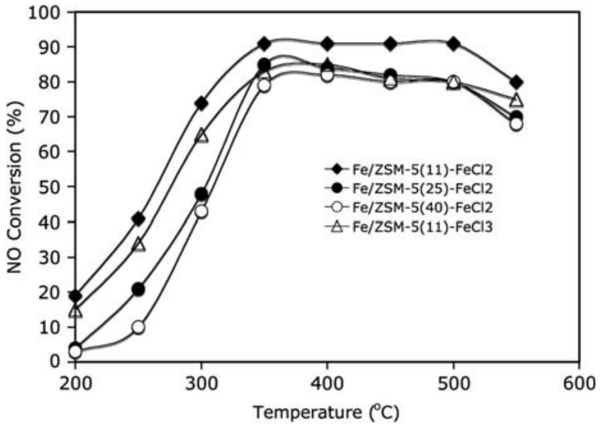

Fig. 3 Catalytic activities for NO reduction by ammonia on 2.5%Fe/ZSM-5 with different Si/Al ratio of ZSM-5. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = 5.7 × 10^5 h^{-1} (based on ambient conditions). *Notes*: The number in parentheses after ZSM-5 indicates the Si/Al ratio in the zeolite

The activity of Fe/ZSM-5 prepared from $FeCl_3$ is also shown in Fig. 3. It was found that a higher activity was obtained from the catalyst prepared from $FeCl_2$ than that from $FeCl_3$. Our previous results [18, 19] indicated that different iron salts ($FeSO_4$, $FeCl_2$ and $Fe(NO_3)_3$) affected the activity significantly. The use of $FeCl_2$ resulted in the highest activity compared to the Fe/ZSM-5 prepared with the other two iron sources. The order of the activity of different catalysts is: Fe/ZSM-5 ($FeCl_2$) > Fe/ZSM-5 ($FeCl_3$) > Fe/ZSM-5 ($FeSO_4$) > Fe/ZSM-5 ($Fe(NO_3)_3$).

Because the combustion gases from diesel engines always contain water vapor and SO_2, we further studied the aging effect of H_2O and SO_2 on the catalytic performance of 2.5%Fe/ZSM-5 catalyst. Before the tests, the 2.5%Fe/ZSM-5 catalyst was pretreated under 10% water vapor and 500 ppm SO_2 (when used) in flowing air at 700 °C for 24 h. Figure 4 shows the results of SCR activities with aged 2.5%Fe/ZSM-5 catalysts. It can be seen that after pretreatment in 10% H_2O at 700 °C for 24 h, the NO conversion decreased significantly in the low temperature range; whereas at temperatures higher than 400 °C, the NO conversion was almost the same between the fresh and the steam-pretreated 2.5%Fe/ZSM-5 catalysts. Similar results were obtained on the effects of pretreatment in SO_2 + H_2O. It is clear that the effect of SO_2 is almost negligible. From Fig. 4, it appears that Fe/ZSM-5 is promising for diesel engine applications particularly at temperatures above 300 °C.

The effect of NO_2 addition on the SCR activity was also investigated. The results are shown in Fig. 5. It is seen that

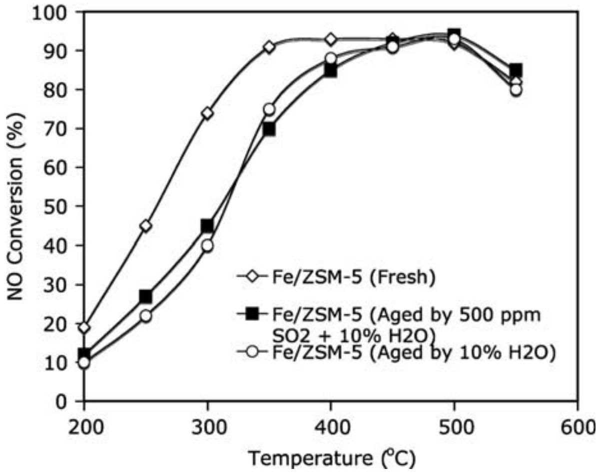

Fig. 4 Catalytic activities for NO reduction by ammonia on fresh and pretreated 2.5%Fe/ZSM-5 catalysts. The pretreatments were at 700 °C for 24 h in air with 10% H_2O and 500 ppm SO_2 (when used). Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = $5.7 \times 10^5\ h^{-1}$ (based on ambient conditions)

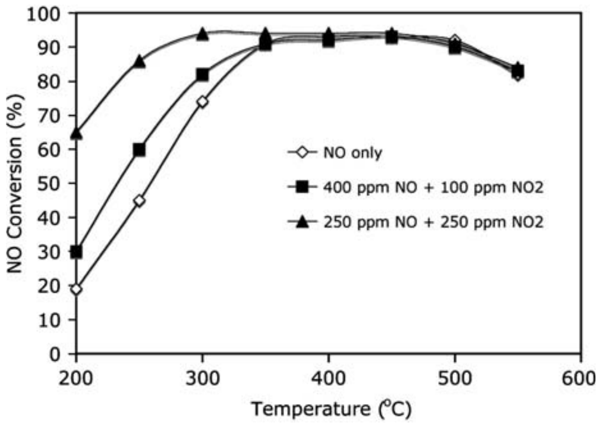

Fig. 5 Effect of NO_2 on catalytic activities for NO reduction by ammonia on 2.5%Fe/ZSM-5. Reaction conditions: 500 ppm (NO + NO_2 total), 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = $5.7 \times 10^5\ h^{-1}$ (based on ambient conditions)

the addition of NO_2 increases the activity, and that the effects are mainly at lower temperatures. In fact, there is nearly no effect by the NO/NO_2 ratio at temperatures higher than 400 °C, as long as the total NO_x concentration is the same and the NH_3/(NO + NO_2) = 1. In the range of the concentrations studied, the highest SCR activity was obtained when the ratio of NO/NO_2 was 1. The results of IR study in our previous work indicated that both NO and NO_2 were involved in the ammonia SCR reaction [18]. During the SCR reaction, gaseous NH_3 molecules are adsorbed quickly onto the BrØnsted acid sites to form NH_4^+ ions and NO molecules are oxidized to NO_2 by O_2. Then NO_2 diffuses to adjacent ions to form the active complex, $NO_2(NH_4^+)_2$. The active complex subsequently reacts with one molecule of NO to produce N_2 and H_2O, thus completing the catalytic cycle. Therefore, the addition of NO_2 can promote the NO conversion in SCR reaction by ammonia.

To investigate the effect of NO_2 addition on the NO conversion under excess NH_3 conditions, NO conversion for NH_3/(NO + NO_2) >1 was shown in Fig. 6. It can be seen that the catalytic activities of 2.5%Fe/ZSM-5 for NO conversion decreased with increasing NO_2 concentration in the reactant. However, the effect of NO_2 addition became smaller at higher temperatures. The difference in NO conversions for these two reactions became less in the range of 400–550 °C.

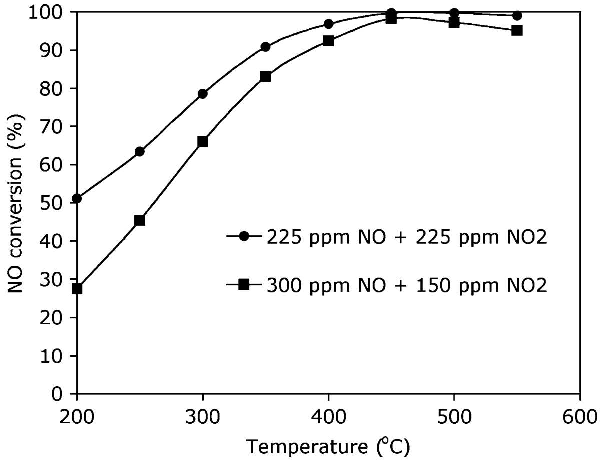

Fig. 6 Effect of NO_2 on catalytic activities for NO reduction by ammonia on 2.5%Fe/ZSM-5. Reaction conditions: 450 ppm (NO + NO_2 total), 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = $5.7 \times 10^5\ h^{-1}$ (based on ambient conditions)

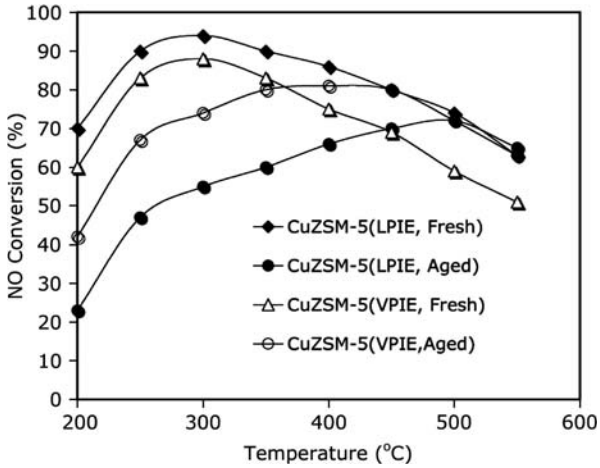

Fig. 7 Catalytic activities for NO reduction by ammonia on fresh and aged Cu-ZSM-5 catalysts prepared from liquid and vapor phase exchange method. All pretreatments were at 700 °C for 24 h with 10% H_2O in air. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5% O_2, 6% H_2O, balance He, and GHSV = $5.7 \times 10^5\ h^{-1}$ (based on ambient conditions)

Figure 7 shows the activity result of ammonia SCR on different ion-exchanged Cu-ZSM-5 catalysts. Cu-zeolite was found to have higher NO_x conversions than Fe/zeolite at temperatures below approximately 300 °C, with the opposite being true at temperatures above 300 °C. Figure 7 also shows that the activity on the fresh Cu-ZSM-5 prepared from liquid phase ion-exchange method is higher than that prepared from vapor phase ion-exchange method; whereas for the aged Cu-ZSM-5, the opposite is true.

The experimental results indicated that Cu-ZSM-5 prepared from vapor phase exchange in this work had higher hydrothermal stability than that prepared from liquid phase exchange methods. Similar to the aged Fe/ZSM-5 catalyst, the deactivation of the aged Cu-ZSM-5 catalyst was attributed to framework dealumination in ZSM-5 and a decrease in active copper species due to the migration or clustering of copper ions [28–32]. It is known that the exchange level of copper ions is higher in Cu-ZSM-5(VPIE) than that in Cu-ZSM-5(LPIE) [20]. The high exchange level of copper ions results in more active Cu^{2+} ions on the surface of Cu-ZSM-5(VPIE) catalyst [20, 32]. Thus, less sites are available for migration of the copper ions on the surface of the aged Cu-ZSM-5(VPIE) catalyst. This can explain why the hydrothermal stability of Cu-ZSM-5(VPIE) is higher than that of Cu-ZSM-5(LPIE). Park et al. studied the hydrothermal stability of Cu-ZSM-5 aged by steam at 700 °C and also found that the stability of Cu-ZSM-5 decreased with reducing the copper content [32]. In comparison with the results of Park et al., it can be seen that by increasing the copper content of the catalyst, the stability of the catalyst fpr NH_3-ammonina SCR is also increased.

From the results shown above, it is concluded that Cu-ZSM-5 shows better performance in the lower temperature range than Fe/ZSM-5; then the Cu-ZSM-5 is more suitable for light duty diesel engines in which the exhaust gas temperature is relatively lower compared to the heavy duty diesel engines. In addition, it can also be anticipated that the wider temperature window with higher NO conversions can be obtained by a combined use of Fe/ZSM-5 and Cu-ZSM-5 catalysts.

4 Conclusions

The Fe/ZSM-5 catalyst exhibited over 90% NO conversion from 350 to 500 °C and Cu-ZSM-5 catalyst exhibited over 90% NO conversion from 250 to 350 °C, respectively, which both reactions are at a very high space velocity (5.7×10^5 h^{-1}). For the Fe/ZSM-5 catalyst, the effects of Si/Al ratio, different iron salts precursors, hydrothermal aging pretreatment and the ratio of NO_2/NO were investigated. It was found that the Fe/ZSM-5 catalyst could maintain high stability in the range of 400 to 550 °C even though the catalyst was aged in 500 ppm SO_2 and 10% H_2O. It was also found that the ammonia-SCR activity of the Fe/ZSM-5 samples, which contained equal iron content, increased with decreasing Si/Al ratio in the ZSM-5 support. This showed that Si/Al ratio has a strong effect on the NO conversion for Fe/ZSM-5 catalysts in the temperature range of 200–550 °C. For Cu-ZSM-5, different preparation methods, including liquid phase ion-exchange and vapor phase ion-exchange, were studied and found that the Cu-ZSM-5 catalyst prepared from vapor phase ion-exchange showed higher hydrothermal stability than that prepared from liquid phase ion-exchange method.

On the basis of experimental results, it can be concluded that Fe/ZSM-5 and Cu-ZSM-5 are promising candidates for NO_x removal for diesel engines. With the combined use of the two catalysts, a potential catalyst for applying to a wide temperature range can be expected.

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