

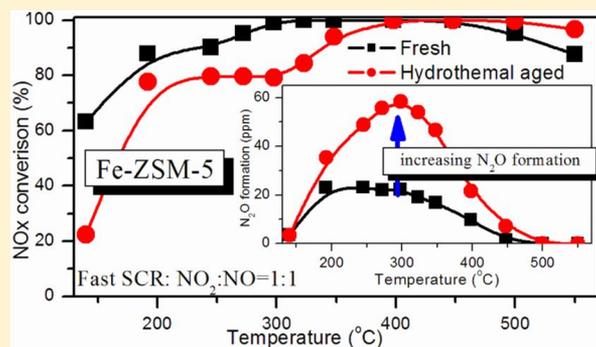
NH₃-SCR Performance of Fresh and Hydrothermally Aged Fe-ZSM-5 in Standard and Fast Selective Catalytic Reduction Reactions

Xiaoyan Shi, Fudong Liu, Lijuan Xie, Wenpo Shan, and Hong He*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

S Supporting Information

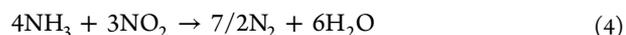
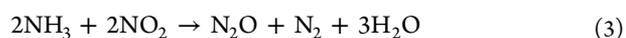
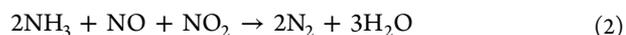
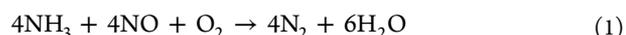
ABSTRACT: Hydrothermal stability is one of the challenges for the practical application of Fe-ZSM-5 catalysts in the selective catalytic reduction (SCR) of NO with NH₃ (NH₃-SCR) for diesel engines. The presence of NO₂ in the exhaust gases can enhance the deNO_x activity because of the fast SCR reaction. In this work, a Fe-ZSM-5 catalyst was prepared by a solid-state ion-exchange method and was hydrothermally deactivated at 800 °C in the presence of 10% H₂O. The activity of fresh and hydrothermally aged Fe-ZSM-5 catalysts was investigated in standard SCR (NO₂/NO_x = 0) and in fast SCR with NO₂/NO_x = 0.3 and 0.5. In standard SCR, hydrothermal aging of Fe-ZSM-5 resulted in a significant decrease of low-temperature activity and a slight increase in high-temperature activity. In fast SCR, NO_x conversion over aged Fe-ZSM-5 was significantly increased but was still lower than that over fresh catalyst. Additionally, production of N₂O in fast SCR was much more apparent over aged Fe-ZSM-5 than over fresh catalyst. We propose that, in fast SCR, the rate of key reactions related to NO is slower over aged Fe-ZSM-5 than over fresh catalyst, thus increasing the probabilities of side reactions involving the formation of N₂O.



1. INTRODUCTION

Selective catalytic reduction (SCR) of NO_x by NH₃ (NH₃-SCR) is one of the most efficient technologies used for removing NO_x from stationary sources and diesel exhausts. Fe-exchanged zeolites, especially Fe-ZSM-5, have been proven to be active catalysts for the NH₃-SCR of NO_x.^{1,2} In typical diesel exhaust, NO_x is composed mainly of NO (>90%), and the SCR of NO with NH₃ according to reaction 1 below is commonly referred to as the standard SCR reaction. The presence of NO₂ in NO_x can enhance the low-temperature activity over Fe-zeolite catalysts, due to the occurrence of the so-called fast SCR reaction (reaction 2), which involves the reaction of NH₃ with an equimolar mixture of NO and NO₂.^{3–13} In practical application, an increase of the fraction of NO₂ in NO_x can be realized by using a preoxidation catalyst located upstream of the SCR catalyst.¹⁴ The activity of the preoxidation catalyst should vary with exhaust temperatures; therefore, the NO₂/NO ratio cannot be a constant. If the NO₂/NO ratio is larger than 1, NO₂ reacts also via alternative NO₂ SCR routes as shown in reactions 3 and 4. Since the SCR performance of Fe-ZSM-5 in the presence of NO₂ is important, the mechanism and kinetics of the NO/NO₂-NH₃ SCR reaction over Fe-ZSM-5 have been studied extensively by transient operations and steady-state measurements.^{4–13} However, the increase in NO_x conversion over Fe-ZSM-5 through the fast SCR reaction is accompanied by the formation of N₂O.^{5,10,12} That is a problem from an environmental point of view, since N₂O is one of the ozone

layer depleting substances and has 310 and 21 times the global warming potential (GWP) of CO₂ and CH₄, respectively.^{15,16}



Fe-ZSM-5 catalysts can be deactivated by hydrothermal aging at high temperatures, and their limited hydrothermal stability is one of the challenges for practical application.^{17–21} Recent investigations suggested that the activity of Fe-ZSM-5 in standard SCR could be decreased by hydrothermal aging.^{19–21} It has been known that hydrothermal aging leads to the dealumination of framework aluminum ions and the migration of Fe ions to form Fe_xO_y clusters.^{19–21} Additionally, hydrothermal aging resulted in the decrease of NO oxidation activity and the Brønsted acidity of Fe-ZSM-5.^{19–21} Rahkamaa-Tolonena et al. reported that hydrothermally aged Fe-ZSM-5 and Fe-β gave higher NO_x conversions in fast SCR with NO₂/NO = 4:6 than in standard SCR, but they did not compare the SCR performance of fresh catalysts with aged catalysts in the

Received: October 30, 2012

Revised: March 5, 2013

Accepted: March 11, 2013

Published: March 11, 2013

presence of NO_2 .²² In fact, to our knowledge, few studies have investigated the SCR performance and the formation of N_2O over hydrothermally aged Fe-ZSM-5 in fast SCR with different NO_2/NO ratios.

In this work, the SCR performance of fresh and hydrothermally aged Fe-ZSM-5 catalysts was investigated in standard SCR and in fast SCR with $\text{NO}_2/\text{NO}_x = 0.3$ and 0.5. The differences between fresh and aged Fe-ZSM-5 catalysts in the SCR performance and in the mechanism of N_2O formation were compared and discussed.

2. EXPERIMENTAL SECTION

Fe-ZSM-5 catalyst with 3.5 wt % Fe loading ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) was prepared by a solid-state ion-exchange method as described in our previous work.²¹ Fe-ZSM-5 was deactivated at 800 °C in 10% $\text{H}_2\text{O}/\text{air}$ for 8 h. Powder X-ray diffraction (XRD) measurements were carried out on a Analytical X-ray diffractometer (The Netherlands, X'Pert PRO MPD), with $\text{Cu K}\alpha$ as the radiation resource. The data were collected for 2θ from 5° to 60° with a step size of 0.02°. UV–visible diffuse reflectance spectroscopy (UV–vis DRS) spectra were recorded with a Hitachi UV3010 (Japan). BaSO_4 was used as the reference material. The Fe-ZSM-5 catalysts were diluted with BaSO_4 at a ratio of 1:4. The spectra were converted with the Kubelka–Munk (KM) function $F(R)$ for comparison.

In situ diffuse reflectance IR Fourier transform spectroscopy (DRIFTS): Experiments of NH_3 adsorption over Fe-ZSM-5 catalysts were performed on an FTIR spectrometer (Nicolet Nexus 670) in order to investigate the Brønsted acidity of the catalysts.^{22,23} Each sample was pretreated at 550 °C in a flow of 20 vol % O_2/N_2 for 20 min, then purged with pure N_2 for 20 min, and cooled down to 150 °C in N_2 . Then, the samples were exposed to a flow of 1% NH_3/N_2 , and the spectra were recorded until NH_3 adsorption saturation occurred.

The catalytic activity data were measured at steady state. The SCR reaction conditions were controlled as follows: 500 ppm NO_x ($\text{NO} + \text{NO}_2$), 500 ppm NH_3 , 5 vol % O_2 , N_2 balance; total flow rate of 500 mL/min. 50 mg of samples (40–60 mesh) was placed in a quartz tube reactor (4 mm i.d.) with a gas hourly space velocity (GHSV) of 320 000 h^{-1} . The effluent gas was analyzed using an FTIR spectrometer (Nicolet Nexus 670). NO_x conversion (X_{NO_x}) was calculated as follows:

$$X_{\text{NO}_x} = (1 - ([\text{NO}] + [\text{NO}_2])_{\text{out}} / ([\text{NO}] + [\text{NO}_2])_{\text{in}}) \times 100\% \quad (\text{E1})$$

3. RESULTS

3.1. Catalytic Characterization. Figure 1a shows the XRD patterns of fresh and aged Fe-ZSM-5 catalysts, H-ZSM-5, and a mechanical mixture of 5 wt % $\alpha\text{-Fe}_2\text{O}_3$ with H-ZSM-5. The typical XRD peaks of $\alpha\text{-Fe}_2\text{O}_3$ can be observed in the patterns of Fe-ZSM-5, at 2θ of 33.1°, 35.6°, 40.9°, and 49.5°.^{24,25} It can be seen that the XRD pattern of aged Fe-ZSM-5 showed little difference from that of fresh catalyst. This indicates that the current hydrothermal deactivation caused no damage to the zeolite framework of Fe-ZSM-5. The KM converted UV–vis spectra of the fresh and aged Fe-ZSM-5 are compared in Figure 1b. Generally, UV–vis spectra can be ascribed to different Fe species over the Fe-ZSM-5: to isolated Fe^{3+} species (bands below 300 nm), oligomeric clusters (between 300 and 400 nm), and Fe_2O_3 particles (above 400 nm).^{21,26,27} The intensity of the bands below 300 nm decreased, and the intensity of the bands

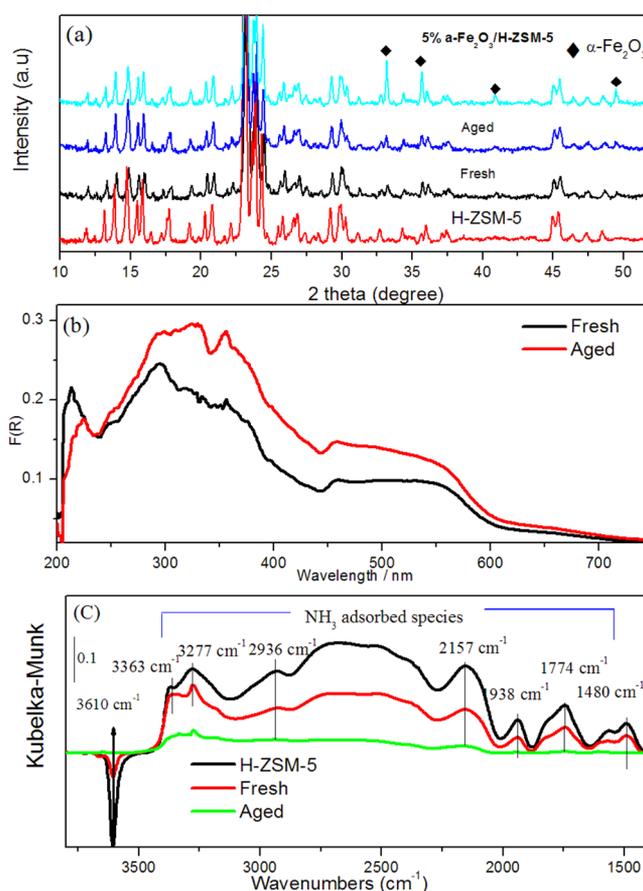


Figure 1. Catalytic characterizations of fresh and aged Fe-ZSM-5: (a) XRD patterns; (b) UV–vis spectra (absolute KM function); (c) in situ DRIFTS results for catalysts after NH_3 adsorption.

above 300 nm increased for aged catalysts, which indicates that hydrothermal aging led to the migration of isolated Fe^{3+} species from iron-exchange sites and the formation of small iron clusters. After deconvolution of the UV–vis spectra, a decrease of percentage of isolated Fe^{3+} species and an increase in the percentage of oligomeric clusters and Fe_2O_3 particles in the catalyst can be observed on aged Fe-ZSM-5 (Supporting Information, Figure S1 and Table S1). Figure 1c shows the DRIFTS spectra of various samples after NH_3 adsorption saturation. The negative band at 3610 cm^{-1} was assigned to the OH stretch of Brønsted acidic sites due to the interaction of surface hydroxyls with NH_3 , which can reflect the relative concentration of Brønsted acidic sites over the Fe-ZSM-5.^{20,21,23} The bands related to adsorbed NH_3 species appear at 3500–1400 cm^{-1} . The band at 1480 cm^{-1} is assigned to the symmetric bending vibration of the NH_4^+ that is chemisorbed on the Brønsted acidic sites.^{28,29} The decrease in intensity of bands related to the adsorbed NH_3 species over aged Fe-ZSM-5 indicates that the concentrations of Brønsted acidic sites and the adsorbed NH_3 species on Fe-ZSM-5 were significantly decreased by hydrothermal aging.

3.2. Catalytic Activity in Standard SCR. The steady-state results of NO_x and NH_3 conversion and N_2O production in the standard SCR reaction over fresh and hydrothermally aged Fe-ZSM-5 catalysts are compared in Figure 2. Compared with fresh catalyst, the aged Fe-ZSM-5 showed a significant decrease in the low-temperature activity and a slight increase in the high-temperature activity in accordance with our previous study.²¹

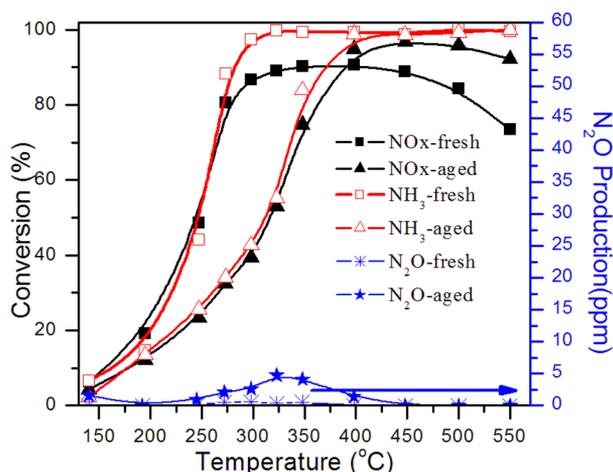


Figure 2. SCR performances of fresh and hydrothermally aged Fe-ZSM-5 catalysts under standard SCR: conversions of NO_x and NH₃, N₂O formations. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5 vol % O₂, N₂ balance.

The NH₃ conversion curve is very close to the NO conversion curve at low temperatures, proving the excellent selectivity of Fe-ZSM-5 in the standard SCR reaction as shown in reaction 1. At high temperatures, conversion of NH₃ exceeded that of NO due to the oxidation of NH₃ to N₂ over Fe-ZSM-5. Figure 3a,b shows that both the NH₃ oxidation and NO oxidation activities of Fe-ZSM-5 were decreased by hydrothermal aging. It is commonly recognized that the NO oxidation to NO₂ is the rate-determining step in standard SCR at low temperatures.^{7,13,30} It is suggested that all Fe species on Fe-ZSM-5 can catalyze the standard SCR reaction and isolated Fe oxo species should be the most active sites at low temperature (generally below 300 °C).^{11,20,24} Moreover, it is also suggested that the presence of Brønsted acid sites has a promoting effect on the low-temperature activity of Fe-ZSM-5 in standard SCR.^{30–32} Thus, the decrease in low-temperature activity of aged Fe-ZSM-5 can be explained by the decrease of NO oxidation activity, Brønsted acidity, and isolated Fe³⁺ species by hydrothermal aging. The slight increase in high-temperature activity of aged Fe-ZSM-5 can be attributed to the formation of Fe₂O₃ clusters, which favored the high-temperature activity and the decrease in the oxidation of NH₃ at high temperatures.^{20,21,33} In standard SCR, the formation of N₂O is a problem for vanadium titanic-based catalysts and Cu-zeolite

catalysts, while Fe-ZSM-5 is known for its high N₂ selectivity without N₂O formation.^{2,10,34} However, a certain amount of N₂O can be observed over aged Fe-ZSM-5 as shown in Figure 2.

3.3. Catalytic Activity in Fast SCR Reaction. Figure 4 presents the conversions of NO_x, NO, NO₂, and NH₃ and the formation of N₂O in the fast SCR reaction with NO₂/NO_x = 0.3 and 0.5 over fresh and aged Fe-ZSM-5. As expected, the presence of NO₂ in the feed significantly increased the NO_x conversions for both fresh and aged Fe-ZSM-5, as shown in Figure 4a,b. However, even in fast SCR, the fresh Fe-ZSM-5 catalyst still showed higher NO_x conversion than for the aged catalyst at low and intermediate temperatures. The difference in NO_x conversion can be basically attributed to the different NO conversion of fresh and aged Fe-ZSM-5, since the NO₂ conversion was near 100% for all catalysts above 200 °C, and the NO_x conversion was calculated from the results of NO and NO₂ as shown in equation E1. Moreover, the NO conversion over aged Fe-ZSM-5 increased very slowly with increasing temperature in the range of 190–400 °C. The rate constant for NO conversion over aged Fe-ZSM-5 almost did not change from 190 to 300 °C (Supporting Information, Figure S2). This indicates that, in the presence of NO₂, some reaction channel involving NO consumption was blocked over aged Fe-ZSM-5 at low temperatures.

The formation of N₂O increased with the increase in proportion of NO₂ in NO_x, as shown in Figure 4c. The aged Fe-ZSM-5 is more favorable toward production of N₂O. Below 300 °C, the N₂O production over aged Fe-ZSM-5 increased with increasing temperature. In fast SCR with NO₂/NO_x = 0.5, the aged Fe-ZSM-5 gave the highest N₂O production with a maximum concentration of 60 ppm at around 300 °C. On the other hand, the formation of N₂O over fresh catalyst reached the highest amount (20 ppm) at around 190 °C and then gradually decreased, quite different from the aged catalysts.

4. DISCUSSION

4.1. Mechanism Analysis. The mechanism of NH₃-SCR of NO_x has been studied by many researchers. Long and Yang proposed a mechanism for standard SCR, in which the oxidation of NO to NO₂ is the rate-determining step and the reaction of NO₂(NH₄⁺)₂ (postulated intermediate) with NO to yield N₂ taking place on the Brønsted acid sites.³⁰ This mechanism was supported by Devadas et al., and they further suggested that NO₂(NH₄⁺)₂ could be a general intermediate in the SCR reaction over ZSM-5 catalyst.¹⁰ Grossale et al.

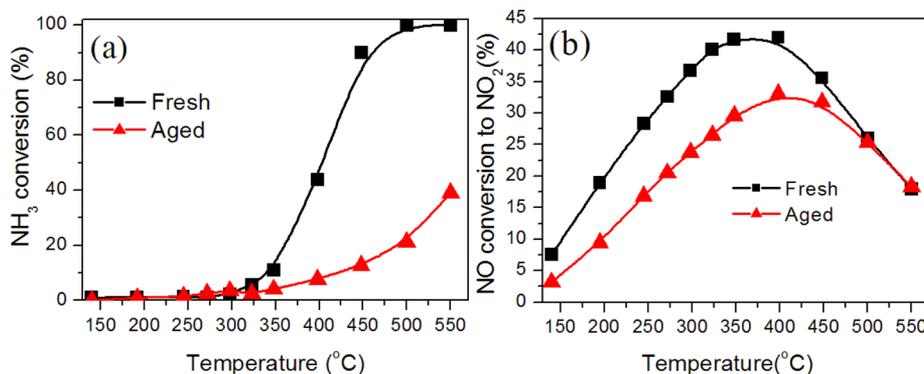


Figure 3. (a) NH₃ oxidation and (b) NO oxidation activities of fresh and hydrothermally aged Fe-ZSM-5. Reaction conditions: (a) 500 ppm NH₃, 5% O₂, N₂ balance; (b) 500 ppm NO, 5% O₂, N₂ balance.

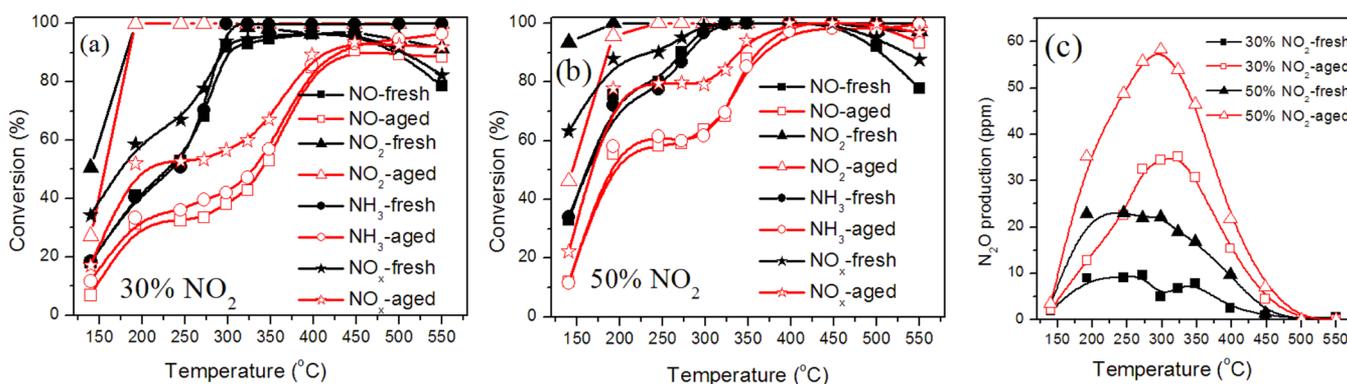
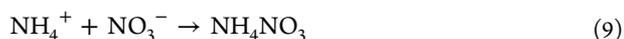
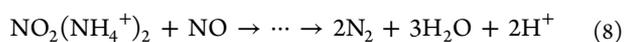
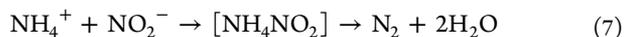
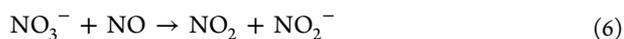


Figure 4. Comparison of fast SCR over fresh and hydrothermally aged Fe-ZSM-5 catalysts. (a) NO, NO₂, NH₃, and NO_x conversion (NO₂/NO_x = 0.3); (b) NO, NO₂, NH₃, and NO_x conversion, NO₂/NO_x = 0.5; (c) N₂O production. Reaction conditions: 500 ppm NO_x (NO + NO₂), 500 ppm NH₃, 5 vol % O₂, N₂ balance; 50 mg of catalyst, total flow of 500 mL/min, and GHSV of 320 000 h⁻¹.

proposed that, in the fast SCR reaction, the role of NO₂ is to form surface nitrites and nitrates and the role of NO is to reduce nitrates to nitrites.^{5,8} They further proposed that the rapidly selective decomposition of unstable ammonium nitrites to yield N₂, and the rate of fast SCR, was dependent on the rate of nitrate reduction by NO at low temperatures.^{5,8} Iwasaki et al. suggested that the formation of surface NH₄NO₃ adspecies from the adsorbed NO₂ is a common reaction in standard SCR, fast SCR, and NO₂ SCR and the rate-determining step of fast SCR is considered to be reduction of NH₄NO₃ by NO.^{12,13} The above conclusions can be summarized as follows: both standard SCR and fast SCR involve the formation of nitrates and nitrites from NO₂, and ammonium nitrite should be the postulated intermediate; N₂ can be produced through the decomposition of ammonium nitrite or through the reaction of NO₂(NH₄⁺)₂ with NO; the slow step is related to the reactions involving NO. The following mechanism analysis is based on the above knowledge.^{5,10,11} The basic reaction steps are given as reactions 5–9:^{5,10,11}



To our knowledge, few studies consider the role of Brønsted acidity and iron sites over Fe-ZSM-5 when they discuss the fast SCR mechanisms over Fe-ZSM-5. In this study, the current hydrothermal deactivation caused no damage to the zeolite framework of Fe-ZSM-5 but resulted in the significant decrease of Brønsted acidity, the migration of isolated Fe³⁺ species, and the decrease of NO oxidation activity. Since the NO oxidation activity is not required in presence of NO₂, the significant decrease of Brønsted acidity and migration of isolated Fe³⁺ sites might be responsible for the limited promotion effect of NO₂ on NO_x reduction over aged Fe-ZSM-5. It is suggested that the decomposition of NH₄NO₂ can be accelerated by zeolite Brønsted sites,³⁰ which is important to low-temperature activity in standard SCR.^{29,30} Schwidder et al. proposed that the fast SCR taking place on Brønsted acid sites can be strongly accelerated over isolated Fe oxo sites.¹¹ It is noted that, although the Brønsted acidity almost disappeared completely,

aged Fe-ZSM-5 still showed good activity in fast SCR. The parent H-ZSM-5, which has the largest amount of Brønsted acidity sites, showed a remarkable performance in fast SCR but cannot be competitive with aged Fe-ZSM-5 (Supporting Information, Figure S3). On the basis of these findings, we propose that the Fe sites over Fe-ZSM-5 play a more important role in fast SCR than Brønsted acidity, which is in agreement with results in the literature.²³

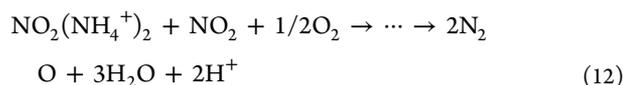
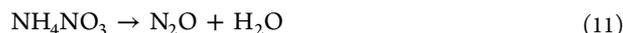
Hydrothermal deactivation resulted in a significant decrease of the NO conversion but showed little effect on the NO₂ conversion. In the case of fast SCR with 50% NO₂ (NH₃ = 500 ppm, NO = NO₂ = 250 ppm), if we assume that all the NO consumption takes place through the fast SCR reaction (reaction 2), the NH₃ consumption should be twice the NO consumption. For instance, when the conversion is 50%, the NH₃, NO, and NO₂ consumption should be 250, 125, and 125 ppm, respectively. This hypothesis is well supported by the data in Figure 4 and the illustration in Figure S4a (Supporting Information). On the other hand, it should be noted that the NO₂ conversion was much higher than the NO conversion in fast SCR. A similar observation was reported previously over the fresh Fe-ZSM-5 and was explained by the formation of NH₄NO₃.⁵ Since the number of Brønsted acid sites over aged Fe-ZSM-5 was significantly decreased, the formation of NH₄NO₃ cannot explain well the observed behavior. The NO₂ consumption unrelated to fast SCR can be expressed as subtracting the NO consumption from the NO₂ consumption (Supporting Information, Figure S4b). From this expression, we can see that the NO₂ consumption unrelated to fast SCR is higher for aged Fe-ZSM-5 than that for the fresh one. The inconsistency between NO_x and NH₃ conversion is mainly caused by the side reactions for NO₂ consumption without NH₃ consumption. We assume that the side reaction channels resulting in NO₂ consumption unrelated to fast SCR may be consecutive nitrates/nitrites formation as reaction 5 and NO evolution reaction as the following:¹⁰



In fast SCR, the reduction of nitrates to nitrites by NO as in reaction 6 is the slow step. H₂-TPR results showed that the H₂-TPR profiles of aged Fe-ZSM were shifted toward higher temperatures (Supporting Information, Figure S5), implying the decrease of the reducibility of aged Fe-ZSM-5. This indicates that the reduction of nitrates to nitrites by NO is slowed over aged Fe-ZSM-5, which is responsible for the

decreased activity in fast SCR. We assume that the higher NO₂ consumption unrelated to fast SCR for aged Fe-ZSM-5 can be explained as the higher decreasing degree of the fast SCR rate than that of the side reaction rate for aged Fe-ZSM-5. Therefore, the possibility of the NO₂ consumption through side reaction channels was increased over aged Fe-ZSM-5.

4.2. N₂O Production. The production of N₂O is a disadvantage of the strategy of the addition of NO₂ into the feed to enhance the NO_x conversion over Fe-ZSM-5 catalysts. In fast SCR, N₂O can be produced from the thermal decomposition of NH₄NO₃ as in reaction 11^{5,7,10,12} and/or from the reaction of NO₂ with intermediate ammonium nitrites, according to Devadas et al. and Long and Yang^{10,30}



In the fast SCR mechanism proposed by Grossale et al.,⁵ the incomplete reduction of nitrates by NO is responsible for the undesired formation of N₂O at low to intermediate temperatures.⁵ Devadas et al. proposed that, in the presence of NO₂, the intermediate NO₂(NH₄⁺)₂ is easily formed and the reaction of NO₂(NH₄⁺)₂ with NO becomes rate limiting; therefore, the probability of the formation of N₂O from the reaction of NO₂(NH₄⁺)₂ with NO₂ increases.¹⁰ The latter mechanism can explain the observation that the formation of N₂O increased with the increase of the NO₂/NO_x ratio. With a higher NO₂ fraction in NO_x, a higher surface concentration of NO₂(NH₄⁺)₂ is formed that results in increasing N₂O formation.

At very low temperatures below 170 °C, the activity of the fast SCR reaction can be inhibited by the so-called ammonia blocking effect, because of the formation of ammonium nitrate adspecies.^{7,13} The decomposition temperature of NH₄NO₃ over Fe-ZSM-5 is above 170 °C.^{7,10,33} Therefore, in fast SCR reactions, no formation of N₂O was observed over all catalysts at very low temperature (ca. 140 °C), which can be explained as resulting from NH₄NO₃ being formed and deposited on the surfaces of Fe-ZSM-5 catalyst at very low temperature.

The profiles of N₂O concentration with increasing temperature over fresh Fe-ZSM-5 are quite different from those over aged catalysts, as shown in Figure 4c. Over fresh Fe-ZSM-5, the N₂O started to be produced at around 190 °C in high amounts and then gradually decreased. However, over aged Fe-ZSM-5, the concentration of N₂O increased with temperature, reached a maximum at around 300 °C, and then, decreased. This indicated that, over fresh Fe-ZSM-5, the decomposition of deposited NH₄NO₃ starting at 170 °C contributed to most of the formation of N₂O. The quantities of NH₃ adsorption over aged Fe-ZSM-5 were much less than that over fresh catalyst, due to the significant decrease of Brønsted acid sites (Figure 1c). Therefore, the high production of N₂O over aged Fe-ZSM-5 cannot be attributed just to the decomposition of NH₄NO₃ that is deposited over catalysts at very low temperature. It should be noted that the low NO conversion over the aged Fe-ZSM-5 was accompanied by high NO₂ consumption through side reaction channels and high N₂O production in fast SCR, when compared with the fresh one (see the previous section). Taking these things into account, we deduced that the rate-determining steps related to NO are slower over aged Fe-ZSM-5; therefore, the possibility of side reactions involving NO₂

consumption increases that results in the high N₂O formation over aged Fe-ZSM-5.

N₂O started decreasing above 350 °C, and no N₂O was detected at temperatures above 500 °C for all catalysts in fast SCR. The results of Devadas et al.¹⁰ and Delahay et al.²⁵ showed that N₂O reduction by NH₃ (N₂O-SCR) starts at approximately 350 °C and reaches nearly 100% conversion at 550 °C. Thus, the decrease of N₂O above 350 °C can be explained by the fact that the reaction of N₂O-SCR and/or the rate-determining steps related to NO become faster at higher temperatures, thereby decreasing the probability of the N₂O formation side reaction.

According to this study, addition of NO₂ to the feed of the SCR reaction can significantly increase the NO_x conversion over hydrothermally aged Fe-ZSM-5. However, the production of N₂O was much more apparent over aged Fe-ZSM-5 than over fresh catalyst in fast SCR reactions. Since N₂O is one of the ozone layer depleting substances, the increased N₂O formation over aged Fe-ZSM-5 is worthy of attention. The design of the preoxidation catalyst for the optimal NO₂/NO_x ratio and the promotion of the hydrothermal stability of Fe-ZSM-5 may be effectively reducing the N₂O production from the SCR reaction.

■ ASSOCIATED CONTENT

📄 Supporting Information

Catalyst preparation; UV–vis spectra, deconvoluted sub-bands of fresh and aged Fe-ZSM-5 and the percentage of the area of sub-bands derived by deconvolution of the UV–vis spectra; rate constant for NO conversion; comparison of fast SCR over fresh and hydrothermal aged Fe-ZSM-5 catalysts; NH₃ and twice NO consumption in fast SCR and NO₂ consumption unrelated to fast SCR; H₂-TPR profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

✉ Corresponding Author

*Phone: +86 10 62849123; fax: +86 10 62849123; e-mail: honghe@rcees.ac.cn.

📄 Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Science Foundation of China (grant nos. 51078347 and 51278486).

■ REFERENCES

- (1) Brandenberger, S.; Kröcher, O.; Tissler, A.; Althoff, R. The state of the art in selective catalytic reduction of NO_x by ammonia using metal-exchanged zeolite catalysts. *Catal. Rev.* **2008**, *50*, 492–531.
- (2) Liu, F.; Shan, P.; Shi, X.; Zhang, Z.; He, H. Research progress in vanadium-free catalysts for the selective catalytic reduction of NO with NH₃. *Chin. J. Catal.* **2011**, *32*, 1113–1128.
- (3) Grossale, A.; Nova, I.; Tronconi, E. Study of a Fe-zeolite-based system as NH₃-SCR catalyst for diesel exhaust aftertreatment. *Catal. Today* **2008**, *136*, 18–27.
- (4) Colombo, M.; Nova, I.; Tronconi, E.; Schmeißer, V.; Bandl-Konrad, B.; Zimmermann, L. NO/NO₂/N₂O–NH₃ SCR reactions over a commercial Fe-zeolite catalyst for diesel exhaust aftertreatment: Intrinsic kinetics and monolith converter modelling. *Appl. Catal., B* **2012**, *111–112*, 106–118.
- (5) Grossale, A.; Nova, I.; Tronconi, E.; Chatterjee, D.; Weibel, M. The chemistry of the NO/NO₂–NH₃ “fast” SCR reaction over Fe-

ZSM5 investigated by transient reaction analysis. *J. Catal.* **2008**, *256*, 312–322.

(6) Grossale, A.; Nova, I.; Tronconi, E.; Chatterjee, D.; Weibel, M. NH_3 -NO/NO₂ SCR for diesel exhausts aftertreatment: reactivity, mechanism and kinetic modelling of commercial Fe- and Cu-promoted zeolite catalysts. *Top. Catal.* **2009**, *52*, 1837–1841.

(7) Grossale, A.; Nova, I.; Tronconi, E. Ammonia blocking of the “fast SCR” reactivity over a commercial Fe-zeolite catalyst for diesel exhaust aftertreatment. *J. Catal.* **2009**, *265*, 141–147.

(8) Grossale, A.; Nova, I.; Tronconi, E. Role of nitrate species in the “NO₂-SCR” mechanism over a commercial Fe-zeolite catalyst for SCR mobile applications. *Catal. Lett.* **2009**, *30*, 525–531.

(9) Colombo, M.; Nova, I.; Tronconi, E. A comparative study of the NH_3 -SCR reactions over a Cu-zeolite and a Fe-zeolite catalyst. *Catal. Today* **2010**, *151*, 223–230.

(10) Devadas, M.; Kröcher, O.; Elsener, M.; Wokaun, A.; Söger, N.; Pfeifer, M.; Demel, Y.; Mussmann, L. Influence of NO₂ on the selective catalytic reduction of NO with ammonia over Fe-ZSM5. *Appl. Catal., B* **2006**, *67*, 187–196.

(11) Schwidder, M.; Heikens, S.; De Toni, A.; Geisler, S.; Berndt, M.; Brückner, A.; Grünert, W. The role of NO₂ in the selective catalytic reduction of nitrogen oxides over Fe-ZSM-5 catalysts. *J. Catal.* **2008**, *259*, 96–103.

(12) Iwasaki, M.; Shinjoh, H. A comparative study of “standard”, “fast” and “NO₂” SCR reactions over Fe/zeolite catalyst. *Appl. Catal., A* **2010**, *390*, 71–77.

(13) Iwasaki, M.; Yamazaki, K.; Shinjoh, H. Transient reaction analysis and steady-state kinetic study of selective catalytic reduction of NO and NO + NO₂ by NH₃ over Fe/ZSM-5. *Appl. Catal., A* **2009**, *366*, 84–92.

(14) Madaia, G.; Koebel, M.; Elsener, M.; Wokaun, A. The effect of an oxidation pre-catalyst on the NO_x reduction by ammonia SCR. *Ind. Eng. Chem. Res.* **2002**, *41*, 3512–3517.

(15) *Climate Change 1992, The Supplementary Report to the IPCC Scientific Assessment*; Houghton, T., Callander, B. A., Verney, S. K., Eds.; Intergovernmental Panel on Climate Change: Cambridge, U.K., 1992.

(16) Thiemens, M. H.; Troglor, W. C. Nylon production: An unknown source of atmospheric nitrous oxide. *Science* **1991**, *251*, 932–934.

(17) Kröcher, O.; Devadas, M.; Elsener, M.; Wokaun, A.; Söger, N.; Pfeifer, M.; Demel, Y.; Mussmann, L. Investigation of the selective catalytic reduction of NO by NH₃ on Fe-ZSM5 monolith catalysts. *Appl. Catal., B* **2006**, *66*, 208–216.

(18) Pieterse, J. A. Z.; Pirngruber, G. D.; van Bokhoven, J. A.; Booneveld, S. Hydrothermal stability of Fe-ZSM-5 and Fe-BEA prepared by wet ion-exchange for N₂O decomposition. *Appl. Catal., B* **2007**, *71*, 16–22.

(19) Iwasaki, M.; Yamazaki, K.; Shinjoh, H. NO_x reduction performance of fresh and aged Fe-zeolites prepared by CVD: Effects of zeolite structure and Si/Al₂ ratio. *Appl. Catal., B* **2011**, *102*, 302–309.

(20) Brandenberger, S.; Kröcher, O.; Casapu, M.; Tissler, A.; Althoff, R. Hydrothermal deactivation of Fe-ZSM-5 catalysts for the selective catalytic reduction of NO with NH₃. *Appl. Catal., B* **2010**, *101*, 649–659.

(21) Shi, X.; Liu, F.; Shan, W.; He, H. Hydrothermal deactivation of Fe-ZSM-5 prepared by different methods for the selective catalytic reduction of NO_x with NH₃. *Chin. J. Catal.* **2012**, *33*, 454–464.

(22) Rahkamaa-Tolonena, K.; Maunula, T.; Lomma, M.; Huuhtanen, M.; Keiski, R. L. The effect of NO₂ on the activity of fresh and aged zeolite catalysts in the NH_3 -SCR reaction. *Catal. Today* **2005**, *100*, 217–222.

(23) Brandenberger, S.; Kröcher, O.; Wokaun, A.; Tissler, A.; Althoff, R. The role of Brønsted acidity in the selective catalytic reduction of NO with ammonia over Fe-ZSM-5. *J. Catal.* **2009**, *268*, 297–306.

(24) Iwasaki, M.; Yamazaki, K.; Banbo, K.; Shinjoh, H. Characterization of Fe/ZSM-5 DeNO_x catalysts prepared by different methods:

Relationships between active Fe sites and NH_3 -SCR performance. *J. Catal.* **2008**, *260*, 205–216.

(25) Delahay, G.; Valade, D.; Guzmán-Vargas, A.; Coq, B. Selective catalytic reduction of nitric oxide with ammonia on Fe-ZSM-5 catalysts prepared by different methods. *Appl. Catal., B* **2005**, *55*, 149–155.

(26) Brandenberger, S.; Kröcher, O.; Tissler, A.; Althoff, R. Estimation of the fractions of different nuclear iron species in uniformly metal-exchanged Fe-ZSM-5 samples based on a Poisson distribution. *Appl. Catal., A* **2010**, *373*, 168–175.

(27) Kumar, M. S.; Schwidder, M.; Grünert, W.; Brückner, A. On the nature of different iron sites and their catalytic role in Fe-ZSM-5 DeNO_x catalysts: New insights by a combined EPR and UV/VIS spectroscopic approach. *J. Catal.* **2004**, *227*, 384–397.

(28) Qi, G.; Yang, R. T. Ultra-active Fe/ZSM-5 catalyst for selective catalytic reduction of nitric oxide with ammonia. *Appl. Catal., B* **2005**, *60*, 13–22.

(29) Li, J.; Zhu, R.; Cheng, Y.; Lambert, C.; Yang, R. T. Mechanism of propene poisoning on Fe-ZSM-5 for selective catalytic reduction of NO_x with ammonia. *Environ. Sci. Technol.* **2010**, *44*, 1799–1805.

(30) Long, R. Q.; Yang, R. T. Reaction mechanism of selective catalytic reduction of NO with NH₃ over Fe-ZSM-5 Catalyst. *J. Catal.* **2002**, *207*, 224–231.

(31) Schwidder, M.; Kumar, M. S.; Bentrup, U.; Pérez-Ramírez, J.; Brückner, A.; Grünert, W. The role of Brønsted acidity in the SCR of NO over Fe-MFI catalysts. *Microporous Mesoporous Mater.* **2008**, *111*, 124–133.

(32) Li, M.; Yeom, Y.; Weitz, E.; Sachtler, W. H. M. An acid catalyzed step in the catalytic reduction of NO_x to N₂. *Catal. Lett.* **2006**, *112*, 129–132.

(33) Brandenberger, S.; Kröcher, O.; Casapu, M.; Tissler, A.; Althoff, R. The determination of the activities of different iron species in Fe-ZSM-5 for SCR of NO by NH₃. *Appl. Catal., B* **2010**, *95*, 348–357.

(34) Yates, M.; Martín, J. A.; Martín-Luengo, M. A.; Suárez, S.; Blanco, J. N₂O formation in the ammonia oxidation and in the SCR process with V₂O₅-WO₃ catalysts. *Catal. Today* **2005**, *107–108*, 120–125.