

# The effect of NO<sub>2</sub> on the activity of fresh and aged zeolite catalysts in the NH<sub>3</sub>-SCR reaction

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## Abstract

The activity of fresh and hydrothermally aged zeolite-based catalysts in the NH<sub>3</sub>-selective catalytic reduction (SCR) reaction with excess of oxygen were studied. In addition, the effect of NO<sub>2</sub> in the gas feed as well as the acidity of the catalysts for the SCR activity was investigated. The studied catalysts were hydrogen, copper, iron and silver ion exchanged ZSM-5, mordenite, beta, ferrierite, and Y-zeolites. The investigation verifies that the zeolite-based catalysts are very promising for the ammonia SCR reaction. Especially, the activity at low and high temperatures was higher than the activity of commercial vanadia-based catalysts. From the studied catalysts, Fe-beta was the most potential one. The presence of NO<sub>2</sub> in the inlet flow enhanced significantly the catalytic activity of fresh and hydrothermally aged zeolite catalysts. This suggests that the oxidation of NO to NO<sub>2</sub> is probably the rate-determining step for the SCR reaction.

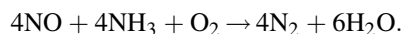
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**Keywords:** NO<sub>x</sub>; NO<sub>2</sub>; NH<sub>3</sub>; Urea; SCR; Zeolites; Hydrothermal stability

## 1. Introduction

Nitrogen oxides remain a major source in air pollution. The emission limit values for heavy-duty vehicles are being made more stringent throughout the world. Engines that operate under lean burn (i.e., oxygen rich) conditions can provide significant fuel economy compared with stoichiometric engines. In the presence of excess oxygen in the exhaust gas, however, NO<sub>x</sub> cannot be sufficiently removed by conventional three-way catalysts. Urea-selective catalytic reduction (SCR) is an attractive and proven after treatment method for future commercial heavy-duty vehicles. Unlike ammonia, the handling, storage, and transport of urea are efficient and safe. In addition, urea is non-toxic even at high concentrations in aqueous solution. Numerous development programs attempt to adapt the SCR technology for mobile diesel engines. In the urea-SCR system, urea will be hydrolyzed to ammonia and CO<sub>2</sub> on a

hydrolysis catalyst. Then ammonia reacts with NO to form nitrogen and water. The general reaction is as follows:



The effectiveness of the SCR technology for the control of NO<sub>x</sub> exhaust, using ammonia as a reductant, has been demonstrated in this study. Therefore, the crucial SCR catalysts can be studied without the effect of the urea hydrolysis variables.

NO<sub>2</sub> has been shown to enhance particularly the low temperature NO<sub>x</sub> reduction on conventional V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-based catalysts [1]. However, the performance of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-based catalysts is not sufficient at low and high temperatures [2]. Many transition metal exchanged zeolites, such as Cu-ZSM-5, Co-ZSM-5, and Fe-ZSM-5, to mention a few, have been studied as a catalyst for the selective catalytic reduction of NO<sub>x</sub> [3,4]. It has been claimed that, e.g., Fe-MFI could exhibit higher activity in the SCR of NO by NH<sub>3</sub> at stationary sources compared to the very classical V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-based commercial catalysts [5]. Zeolite-based catalysts have been studied extensively in NH<sub>3</sub>-SCR systems [6].

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Zeolites are extensively used as shape-selective solid acid catalysts in many industrial processes [7]. Factors such as framework type and Si/Al<sub>2</sub> ratio determine the catalytic properties of the material. The framework acidity can be modified by variation of the Si/Al<sub>2</sub> ratio of the zeolite and the framework type or by substitution of Al by other trivalent elements. Modification of the framework acidity may lead to materials with improved catalytic properties. The acid properties of zeolites are considered as an important factor in controlling the catalytic activity in chemical reactions [8,9]. It is assumed that SCR activity is enhanced by the surface acidity of catalysts.

The aim of this study was to obtain knowledge about the activity of zeolite-based catalysts in the NH<sub>3</sub>-SCR reaction with excess of oxygen. The limited hydrothermal stability of zeolites may restrict their use, and therefore also the hydrothermal stability of catalysts was examined. In addition, the effect of NO<sub>2</sub> in the gas feed as well as acidity of the catalysts for the SCR activity was investigated. The adsorption and desorption experiments of ammonia were used to study the acidity of fresh and aged zeolite catalysts and the influence of the acidity on the activity of zeolite catalysts.

## 2. Experimental

The zeolites used for the catalyst preparation were ZSM-5, mordenite (MOR), beta, ferrierite (FER), and Y-zeolites. The silica to alumina ratio of zeolites were 29, 20, 22, 20, and 80, respectively. The active cation (H, Cu, Fe, and Ag) was added into the zeolite structure by ion exchange. H-zeolite catalysts were prepared using NH<sub>4</sub>NO<sub>3</sub>, Cu-zeolite catalysts using (CH<sub>3</sub>COO)<sub>2</sub>Cu·H<sub>2</sub>O, Fe-zeolite catalysts using FeCl<sub>3</sub>, and Ag-beta using AgNO<sub>3</sub>, respectively. The ion-exchanged metal ratio of aluminium was calculated as molar basis ( $n(M)/n(Al)$ ), the value of which is insensitive to charge and as ion-exchange ratio (IER) in percent, (Table 1, metals analysed by XRF analysis (Philips MagiX)). The silica to alumina ratio of Fe-ZSM-5 was 23. Specific surface areas (BET) were measured by N<sub>2</sub> adsorption using a volumetric Carlo Erba Sorptomatic 1990 analyzer.

The powder sample (0.6 g) was inserted into a tubular quartz reactor heated by IR. The activity of a catalyst sample was examined with a simulated gas mixture (NH<sub>3</sub> 1000 ppm, NO 1000 ppm, H<sub>2</sub>O 8%, O<sub>2</sub> 10%, and N<sub>2</sub> balance). The total gas flow was 1.2 l min<sup>-1</sup> at 25 °C and it corresponds to a space velocity of 25000 h<sup>-1</sup> with a typical monolith catalyst. The steady-state concentration were measured, by each 50 °C, between 150 and 650 °C. Temperature was increased always 50 °C at a time and then it was kept constant for 6 min at the reached temperature. The outlet gas was analysed by a FT-IR analyzer (Gasmeter™ FT-IR Gas Analyser).

The activity experiments, where NO<sub>2</sub> was added into the gas mixture, were also carried out in order to study the effect

Table 1

Characteristics of zeolite-based SCR catalysts (M: metal)

Catalyst	Si/Al <sub>2</sub> ratio	M (wt.%)	M/Al (mol/mol)	IER (%)	BET (m <sup>2</sup> /g)
ZSM-5	29	–	–	–	350
Beta	22	–	–	–	510
MOR	20	–	–	–	375
FER	20	–	–	–	275
Y	80	–	–	–	590
H-ZSM-5	29	–	–	–	343
H-beta	22	–	–	–	480
H-MOR	20	–	–	–	407
H-FER	20	–	–	–	239
H-Y	80	–	–	–	649
Cu-ZSM-5	29	2	0.29	58	332
Cu-beta	22	1.6	0.18	36	433
Cu-MOR	20	1.5	0.15	31	415
Cu-FER	20	1.1	0.11	23	270
Cu-Y	80	0.7	0.27	54	596
Ag-beta	22	3.0	0.34	34	452
Fe-ZSM-5	23	0.7	0.10	28	354
Fe-beta	22	0.9	0.12	36	544

of NO<sub>2</sub> on the activity. A feed gas mixture contained 600 ppm NO and 400 ppm NO<sub>2</sub>, and the other components were the same as in the experiment without NO<sub>2</sub>. In the case of fresh H-MOR and Ag-beta, the role of NO<sub>2</sub> in the feed gas was studied in more detail. In this experiment, the feed gas mixture contained 0, 50, 100, 200, or 400 ppm NO<sub>2</sub>. The total amount of NO and NO<sub>2</sub> was 1000 ppm (NO<sub>x</sub>).

The catalysts were aged for 20 h at 600 °C in hydrothermal conditions (10% H<sub>2</sub>O in air) to evaluate the durability. Activity as well as adsorption and desorption properties of these catalysts were evaluated also after these hydrothermal pretreatments. The catalyst sample was flushed with nitrogen at 300 °C for 20 min before the NH<sub>3</sub> adsorption step. After this the sample was cooled down to 200 °C and the sample was flushed with NH<sub>3</sub> (500 ppm NH<sub>3</sub> in N<sub>2</sub>) until the steady state was attained. The total gas flow was 2 l min<sup>-1</sup> at 25 °C. Thereafter, the sample was flushed with N<sub>2</sub> for 5 min and the reactor temperature was increased to 600 °C with a rate of 20 °C min<sup>-1</sup> under a 10% O<sub>2</sub>/N<sub>2</sub> mixture (TPO). The concentrations of desorbed and formed NH<sub>3</sub>, NO, NO<sub>2</sub>, and N<sub>2</sub>O were measured by a FT-IR gas analyzer. TPO with 10% oxygen was used instead of TPD (inert gas) to simulate the realistic conditions of NH<sub>3</sub> adsorption phenomena in lean SCR applications.

## 3. Results

### 3.1. Fresh samples

The BET surface areas of the parent zeolites ZSM-5, MOR, beta, FER, and Y were 350, 375, 510, 275, and 590 m<sup>2</sup>/g, respectively, and the pore volume was 0.23, 0.25, 0.68, 0.18, and 0.45 cm<sup>3</sup> g<sup>-1</sup>, respectively.

The hydrogen ion exchanged zeolites had a very low activity without NO<sub>2</sub>. The maximum NO<sub>x</sub> conversion of

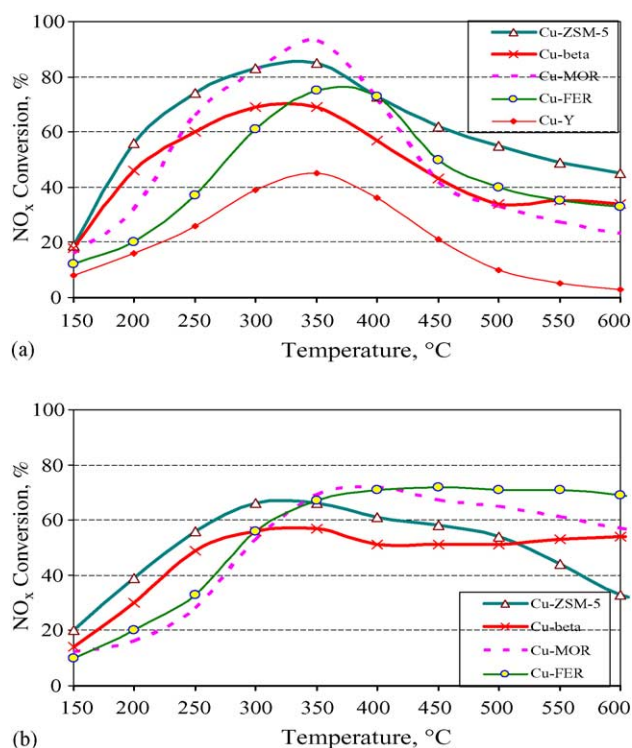


Fig. 1. (a) NO<sub>x</sub> conversions of fresh Cu-ZSM-5, Cu-beta, Cu-MOR, Cu-FER, and Cu-Y-zeolites as a function of temperature. Conditions: 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 8% H<sub>2</sub>O, 10% O<sub>2</sub>, and balance with N<sub>2</sub>. (b) NO<sub>x</sub> conversions of hydrothermally aged Cu-ZSM-5, Cu-beta, Cu-MOR, and Cu-FER zeolites as a function of temperature. Conditions: 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 8% H<sub>2</sub>O, 10% O<sub>2</sub>, and balance with N<sub>2</sub>; hydrothermal aging: 20 h at 600 °C in 10% H<sub>2</sub>O in air.

29% was reached with H-beta at 350 °C. The activity of fresh catalysts without NO<sub>2</sub> decreases based on the maximum NO<sub>x</sub> conversion as follows: Cu-MOR (93%) > Fe-beta (90%) > Cu-ZSM-5 (85%) > Cu-FER (75%) > Fe-ZSM-5 (73%) > Cu-beta (69%) > Ag-beta (58%) > Cu-Y (45%). Based on the reaction initiation temperature (e.g.,  $T_{50}$  temperature, where 50% NO<sub>x</sub> conversion was reached) and wide temperature window, the activity of Cu-ZSM-5 among the Cu-containing catalysts was the highest without NO<sub>2</sub> as can be seen in Fig. 1, where the catalytic activity of the fresh Cu-zeolites for NO<sub>x</sub> as a function of temperature is presented. The activity of Cu-Y-zeolite was substantially lower than the activity of other Cu-containing zeolites. The effect of ion-exchanged metal to the activity of zeolite material was investigated in the case of beta zeolite. As can be seen from Fig. 2, the ion-exchanged metal (Ag, Cu, and Fe) increased considerably the catalytic activity of beta zeolite. Fe-beta had the highest activity. It was active over a wide temperature range and it had the lowest ammonia slip (the concentration of NH<sub>3</sub> after the catalyst) among the fresh catalysts. Cu-beta was more active than Ag-beta at temperatures lower than 400 °C whereas Ag-beta was more active at higher temperatures. Based on these results, it can be concluded that the catalytic activity of ion-exchanged cations on beta decreases as follows:

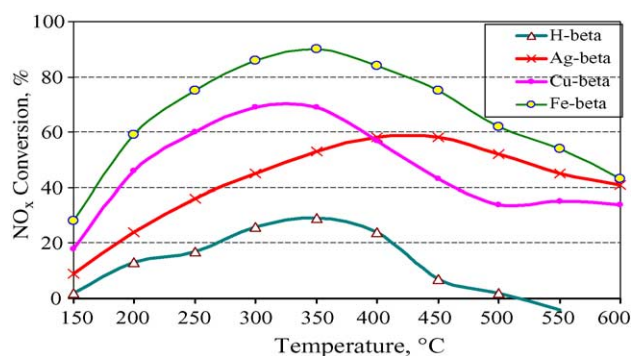


Fig. 2. NO<sub>x</sub> conversion over the fresh H-, Ag-, Cu-, and Fe-beta zeolites. Conditions: 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 8% H<sub>2</sub>O, 10% O<sub>2</sub>, and balance with N<sub>2</sub>.

Fe > Cu > Ag > H despite the fact that the amount of Ag ( $n(\text{M})/n(\text{Al})$ ) was almost three times higher than the amount of Fe and two times higher than the amount of Cu. The following catalysts are the most suitable for high temperatures as fresh and their activity at 600 °C decreases in the following order: Cu-ZSM-5 (45%) > Fe-beta (43%) > Ag-beta (41%) > Cu-beta (34%) > Cu-FER (33%) > Fe-ZSM-5 (26%) > Cu-MOR (23%).

When the reaction gas contained NO<sub>2</sub>, the NO<sub>x</sub> conversion was improved both at low (<300 °C) and at high (>450 °C) temperatures. This phenomenon is presented for H-MOR and Cu-MOR catalysts in Fig. 3a and for H-FER and Cu-FER catalysts in Fig. 3b, respectively. It can be seen that H-MOR had a low activity at lower temperatures without NO<sub>2</sub>. The maximum NO<sub>x</sub> conversion was 34% at 600 °C whereas the maximum NO<sub>x</sub> conversion was around 60% at 350–500 °C in the presence of NO<sub>2</sub>. The activity of Cu-MOR was enhanced also at low and high temperatures in the presence of NO<sub>2</sub>. The same behaviour was observed in the case of H-FER and Cu-FER catalysts. The activity of H-FER zeolite increased dramatically in the presence of NO<sub>2</sub>. The presence of NO<sub>2</sub> in the feed gas also diminished the differences between the catalysts. In addition, it decreases the observed ammonia slip over all the zeolite catalysts. All the catalysts had higher NO<sub>x</sub> conversions over a wider temperature range. The activity of most active fresh catalysts with NO<sub>2</sub> decreases based on the maximum NO<sub>x</sub> conversion as follows: Cu-MOR (94%) > Fe-beta (92%) > Cu-FER (89%) > Cu-ZSM-5 (88%) > Cu-beta (87%) > Fe-ZSM-5 (86%) > Ag-beta (82%) > Cu-Y (61%). Cu-Y-zeolite had again a substantially lower activity than the other catalysts. In addition, Cu-Y catalyst had a high ammonia slip compared to other catalysts and it also formed high amounts of N<sub>2</sub>O in the presence and absence of NO<sub>2</sub> in the inlet flow. Also the other Cu-containing zeolites formed clearly higher amounts of N<sub>2</sub>O than the Fe-containing zeolites. This indicates that the selectivity to N<sub>2</sub> is higher over the Fe-containing zeolites. The maximum selectivity to N<sub>2</sub>O was 3% over the Fe-beta and Fe-ZSM-5 zeolites. Long and Yang [10] had similar findings on Fe-ZSM-5. According to them,

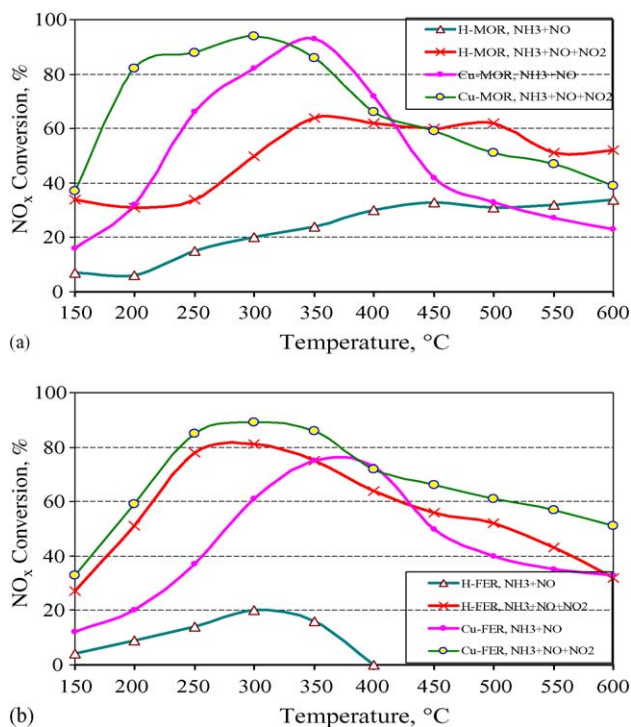


Fig. 3. (a)  $\text{NO}_x$  conversions of fresh H-MOR and Cu-MOR in the presence and absence of  $\text{NO}_2$ . Conditions: 600 ppm NO + 400 ppm  $\text{NO}_2$  or 1000 ppm NO and 1000 ppm  $\text{NH}_3$ , 8%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$ , and balance with  $\text{N}_2$ . (b)  $\text{NO}_x$  conversions of fresh H-FER and Cu-FER in the presence and absence of  $\text{NO}_2$ . Conditions: 600 ppm NO + 400 ppm  $\text{NO}_2$  or 1000 ppm NO and 1000 ppm  $\text{NH}_3$ , 8%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$ , and balance with  $\text{N}_2$ .

$\text{N}_2$  was the only detectable N-containing product, and no  $\text{N}_2\text{O}$  was observed for Fe-ZSM-5. The formation of undesired  $\text{N}_2\text{O}$  (by  $\text{N} + \text{NO}$ ) indicates that NO decomposition has occurred or ammonia is partially oxidized by oxygen. However, the total oxidation activity is not too high because  $\text{NH}_3$  slip still exists except at high temperatures in the case of Cu-Y. Therefore, Cu-Y is not considered as a promising catalyst for  $\text{NH}_3$ -SCR as well as not selected for further studies. The activity of hydrogen exchanged zeolites increased also significantly in the presence of  $\text{NO}_2$ . H-FER had the highest  $\text{NO}_x$  conversion, 81% at 300 °C (Fig. 3b). H-beta, which was the most active one without  $\text{NO}_2$  was now the second most active and had the maximum  $\text{NO}_x$  conversion of 72% also at 300 °C.

The effect of  $\text{NO}_2$  concentration in the inlet flow for the SCR activity was studied in detail with H-MOR and Ag-beta zeolites. It was observed that  $\text{NO}_x$  conversion enhanced evenly over Ag-beta when the amount of  $\text{NO}_2$  in the feed gas mixture was increased from 0 to 400 ppm. Also the maximum  $\text{NO}_x$  conversion was reached at lower temperatures. The presence of  $\text{NO}_2$  increased the reduction rate over the whole temperature range. In the case of H-MOR, the SCR activity did not increase so clearly at high temperatures (Fig. 3a). When the feed gas mixture contained 400 ppm  $\text{NO}_2$ , ammonia started to oxidize at 500 °C. Therefore, the  $\text{NO}_x$  conversion decreased at high temperatures. The

decrease in the  $\text{NO}_x$  conversion due to the production of NO as well as the formation  $\text{NO}_2$  and  $\text{N}_2\text{O}$  indicates the oxidation on  $\text{NH}_3$ . According to Alemany et al. [11], a decrease in the activity and selectivity of the  $\text{V}_2\text{O}_5$ -based catalyst, when the temperature of SCR reaction exceeds 400 °C, is mainly due to production of NO and  $\text{NO}_2$  caused by ammonia oxidation.

### 3.2. Aged samples

The hydrothermal aging at 600 °C for 20 h decreased the activity of zeolite powder catalysts (Fig. 1b). The maximum  $\text{NO}_x$  conversions were lower and they were reached at higher temperatures. Meanwhile, the activity of most of the catalysts was increased at high temperatures ( $T > 450$  °C) compared to their activity as fresh. However, the activity of Cu-ZSM-5 and Ag-beta decreased substantially at high temperatures. Based on the maximum conversions the activity of the aged catalysts without  $\text{NO}_2$  in the feed gas mixture decreases in the following order: Fe-beta (84%) > Cu-FER (72%) > Cu-MOR (72%) > Cu-ZSM-5 (66%) > Fe-ZSM-5 (65%) > Cu-beta (57%) > Ag-beta (38%). From the beta zeolite catalysts, the Fe-beta retained the catalytic activity considerably better than Cu- and Ag-beta after the hydrothermal aging. After aging, the following catalysts are the most suitable for high temperatures and their activity at 600 °C decreases in the following order: Cu-FER (69%) > Fe-beta (66%) > Fe-ZSM-5 (62%) > Cu-MOR (57%) > Cu-beta (54%) > Cu-ZSM-5 (33%) > Ag-beta (22%).

The addition of  $\text{NO}_2$  to the inlet flow increased remarkably also the activity of hydrothermally aged catalysts and diminished the differences between the catalysts. All the copper containing zeolites had the reaction initiation temperature at 160–180 °C. The reaction initiates on Fe-ZSM-5 at around 150 °C and the  $\text{NO}_x$  conversions of Fe-beta was already 70% at 150 °C. Fe-beta had also a very low ammonia slip. At the temperatures lower than 325 °C the maximum  $\text{NH}_3$  concentration after the Fe-beta catalyst was 26 ppm. At higher temperatures, the  $\text{NH}_3$  slip was near to zero. Ag-beta had clearly the highest reaction initiation temperature, which was 250 °C (50% converted). It had also the lowest maximum  $\text{NO}_x$  conversion and highest  $\text{NH}_3$  slip. The effect of  $\text{NO}_2$  in the case of hydrothermally aged Fe-beta and Fe-ZSM-5 is demonstrated in Fig. 4. It can be seen that the presence of  $\text{NO}_2$  enhanced especially the low temperature activity. The activity of most active hydrothermally aged catalysts with  $\text{NO}_2$  decreases based on the maximum  $\text{NO}_x$  conversion as follows: Fe-beta (89%) > Cu-MOR (84%) > Fe-ZSM-5 (82%) > Cu-FER (81%) > Cu-beta (78%) > Cu-ZSM-5 (73%) > Ag-beta (70%).

## 4. Discussion

As was discussed above, the addition of  $\text{NO}_2$  to the inlet flow increased the catalytic activity of fresh and aged



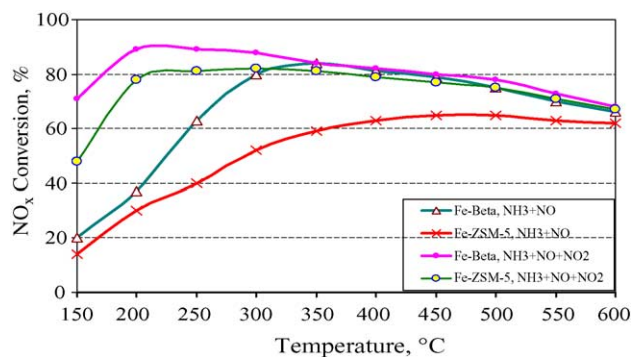


Fig. 4.  $\text{NO}_x$  conversions of hydrothermally aged Fe-beta and Fe-ZSM-5 in the presence and absence of  $\text{NO}_2$ . Conditions: 600 ppm NO + 400 ppm  $\text{NO}_2$  or 1000 ppm NO and 1000 ppm  $\text{NH}_3$ , 8%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$ , and balance with  $\text{N}_2$ .

zeolite-based catalysts in  $\text{NH}_3$ -SCR. The result indicated that most probably the reaction mechanism includes the oxidation of NO to  $\text{NO}_2$ , which is a slow reaction step on zeolite-only catalysts. Therefore, the presence of  $\text{NO}_2$  in the feed gas mixture enhances the SCR reactions. This finding is in good agreement with the results of Coq et al. [12] who observed that  $\text{NO}_2$  reacts very fast with NO and  $\text{NH}_3$ . According to Long and Yang, zeolites' Brönsted acid sites provide sites for ammonia adsorption, generating  $\text{NH}_4^+$  ions [4]. It was observed that the reactivity of  $\text{NH}_4^+$  ions with NO +  $\text{O}_2$  on Fe-ZSM-5 was much higher than that on H-ZSM-5, which is in accordance with the results of our study. The present study verifies that the SCR activity of hydrogen exchanged ZSM-5, MOR, beta, FER, and Y-zeolites was clearly lower than that on corresponding Cu, Fe, or Ag exchanged zeolites (Fig. 3). The addition of Cu, Fe or Ag to the zeolite increased the activities dramatically. The increase is related to the increase in NO oxidation to  $\text{NO}_2$ . Therefore, the oxidation activity of Fe-beta is most probably higher than that on Cu-, Ag-, or H-beta (Fig. 2).  $\text{NO}_2$  is much more reactive than NO with  $\text{NH}_4^+$  ions, and therefore the presence of it enhances the SCR activity. The oxidation of NO to  $\text{NO}_2$  is probably the rate-determining step for the SCR reaction.

In the conditions where  $\text{NH}_3$  oxidation is low,  $\text{NH}_3$  and  $\text{NO}_x$  react in the stoichiometry 1:1. Therefore, the lower the  $\text{NO}_x$  conversion is, the higher is the  $\text{NH}_3$  slip. If  $\text{NO}_x$  conversion and  $\text{NH}_3$  slip are both low and  $\text{NO}_x$  conversion even negative, the  $\text{NH}_3$  oxidation activity is too high. The  $\text{NO}_x$  reduction and  $\text{NH}_3$  oxidation rates are related to the cations and their amounts in zeolites. When the ion-exchange ratio is low, more acidic sites are free for  $\text{NH}_3$  adsorption and cations are finely dispersed. If the amount of cations is high, there is a risk to have out of extra framework cations and metal oxide clusters, which can be too active for  $\text{NH}_3$  oxidation. The studied SCR catalysts were prepared by ion exchange, and therefore the IER (cation concentration) was balanced to the level where the cations are tightly on the zeolite structure.

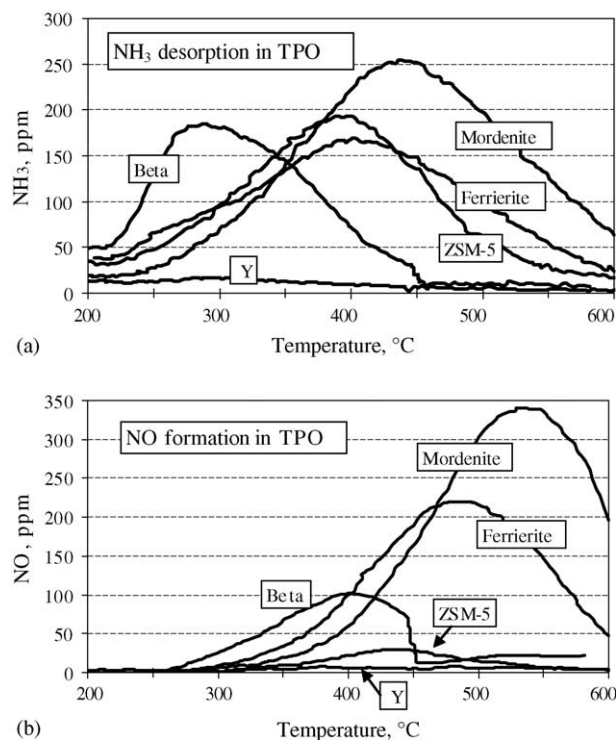


Fig. 5. Desorption of (a)  $\text{NH}_3$  and (b) NO over fresh zeolites during TPO (10%  $\text{O}_2$  in  $\text{N}_2$ ). Saturated with  $\text{NH}_3$  at 200 °C before TPO.

The low SCR activity of H-Y and Cu-Y-zeolites correlates well with the results from ammonia adsorption and desorption in TPO experiments, which show that the parent Y-zeolite does not adsorb or desorb any ammonia (Fig. 5). Adsorbed  $\text{NH}_3$  is desorbed as  $\text{NH}_3$  at lower and mainly as NO of nitrogen oxides at higher temperatures in TPO experiments. The formation of  $\text{N}_2\text{O}$  and  $\text{NO}_2$  in TPO was small with these catalysts. The selectivity for  $\text{NH}_3$  desorption instead of nitrogen oxides was the highest with ZSM-5 and Beta of the non-ion-exchanged zeolites. However, the oxidation tendency was decreased in a few investigated cases when a cation was added into the zeolite (e.g., mordenite with Cu).

The Y-zeolite has considerably higher Si/ $\text{Al}_2$  ratio than the other studied catalysts, and thus different acidity. The high Si/ $\text{Al}_2$  ratio of Y-zeolite does not promote the formation of the  $\text{NH}_4^+$  ions. It is known that a high Si/ $\text{Al}_2$  ratio increases the bond strength and a low Si/ $\text{Al}_2$  ratio increases the adsorption capacity, respectively. Typically, the acidity of zeolites decreases after hydrothermal aging. The decrease in acidity is caused by the decreased surface area and dealumination. This was observed as lower amounts of adsorbed  $\text{NH}_3$  during the ammonia adsorption and desorption experiments after hydrothermal aging, because the adsorption capacity was decreased. Dealumination increases the Si/ $\text{Al}_2$  ratio, which in turn can increase the bond strength of adsorbents. This might explain the observed higher SCR activity at high temperatures after hydrothermal aging in the case of all other catalysts except

Cu-ZSM-5 and Ag-beta. For example, with aged Cu-FER, the desorption of  $\text{NH}_3$ , NO, and minor amount of  $\text{N}_2\text{O}$  was observed at higher temperatures than before the aging. The strong acid sites correspond to the observed high temperature desorption. Another possible reason is the lower  $\text{NH}_3$  oxidation activity after aging. Thus, the formation of oxidation products, NO,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$ , does not decrease the  $\text{NO}_x$  conversion. After aging the highest  $\text{NH}_3$  oxidation activities, 16 and 9%, were observed in the case of Ag-beta and Cu-ZSM-5, respectively. The  $\text{NH}_3$  oxidation activity was calculated by the following Eq. (1):

$\text{NH}_3$  oxidation activity (%)

$$= \frac{\text{desorbed (NO + NO}_2 + \text{N}_2\text{O)}}{\text{adsorbed (NH}_3\text{)}} \times 100. \quad (1)$$

These results are in accordance with the low SCR activity of zeolites after aging. The results allow us to conclude that in SCR reaction of NO with  $\text{NH}_3$ , there is no doubt that the acidic function of the catalyst is one of the main factors which control the high activity. In particular, surface acidity plays an important role in the adsorption and activation of ammonia at high temperatures.

## 5. Conclusions

The activity and hydrothermal stability of zeolite-based catalysts in the  $\text{NH}_3$ -SCR reaction with excess of oxygen

were studied. The results suggest that based on the hydrothermal stability, the best zeolite-based catalysts for  $\text{NH}_3$ -SCR are Fe-beta, Cu-FER, Cu-MOR, and Fe-ZSM-5. These catalysts had the highest  $\text{NO}_x$  conversions and widest temperature windows. Hydrothermal aging modifies the acid properties of zeolites. The higher the acidity retains, the better the hydrothermal stability for the SCR activity. The present study also indicates that the presence of  $\text{NO}_2$  in the feed gas mixture enhances the SCR reactions. The highest increase in the activity by  $\text{NO}_2$  was observed on H and metal promoted zeolites at low temperatures.

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