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The effect of NO_2 on the activity of fresh and aged zeolite catalysts in the NH_3-SCR reaction

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Abstract

The activity of fresh and hydrothermally aged zeolite-based catalysts in the NH_3-selective catalytic reduction (SCR) reaction with excess of oxygen were studied. In addition, the effect of NO_2 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_2 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_2 is probably the rate-determining step for the SCR reaction.

Keywords: NO_x; NO_2; NH_3; 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_x 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_2 on a hydrolysis catalyst. Then ammonia reacts with NO to form nitrogen and water. The general reaction is as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O.$$

The effectiveness of the SCR technology for the control of NO_x 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_2 has been shown to enhance particularly the low temperature NO_x reduction on conventional V_2O_5-WO_3/TiO_2-based catalysts [1]. However, the performance of V_2O_5-WO_3/TiO_2-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_x [3,4]. It has been claimed that, e.g., Fe-MFI could exhibit higher activity in the SCR of NO by NH_3 at stationary sources compared to the very classical V_2O_5-TiO_2-based commercial catalysts [5]. Zeolite-based catalysts have been studied extensively in NH_3-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_2 ratio determine the catalytic properties of the material. The framework acidity can be modified by variation of the Si/Al_2 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_3-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_2 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_4NO_3, Cu-zeolite catalysts using $(CH_3COO)_2Cu{\cdot}H_2O$, Fe-zeolite catalysts using $FeCl_3$, and Ag-beta using $AgNO_3$, 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_2 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_3 1000 ppm, NO 1000 ppm, H_2O 8%, O_2 10%, and N_2 balance). The total gas flow was 1.2 l min^{-1} at 25 °C and it corresponds to a space velocity of 25000 h^{-1} 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 (Gasmet™ FT-IR Gas Analyser).

The activity experiments, where NO_2 was added into the gas mixture, were also carried out in order to study the effect of NO_2 on the activity. A feed gas mixture contained 600 ppm NO and 400 ppm NO_2, and the other components were the same as in the experiment without NO_2. In the case of fresh H-MOR and Ag-beta, the role of NO_2 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_2. The total amount of NO and NO_2 was 1000 ppm (NO_x).

Table 1
Characteristics of zeolite-based SCR catalysts (M: metal)

Catalyst	Si/Al_2 ratio	M (wt.%)	M/Al (mol/mol)	IER (%)	BET (m^2/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

The catalysts were aged for 20 h at 600 °C in hydrothermal conditions (10% H_2O 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_3 adsorption step. After this the sample was cooled down to 200 °C and the sample was flushed with NH_3 (500 ppm NH_3 in N_2) until the steady state was attained. The total gas flow was 2 l min^{-1} at 25 °C. Thereafter, the sample was flushed with N_2 for 5 min and the reactor temperature was increased to 600 °C with a rate of 20 °C min^{-1} under a 10% O_2/N_2 mixture (TPO). The concentrations of desorbed and formed NH_3, NO, NO_2, and N_2O 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_3 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^2/g, respectively, and the pore volume was 0.23, 0.25, 0.68, 0.18, and 0.45 $cm^3\ g^{-1}$, respectively.

The hydrogen ion exchanged zeolites had a very low activity without NO_2. The maximum NO_x conversion of

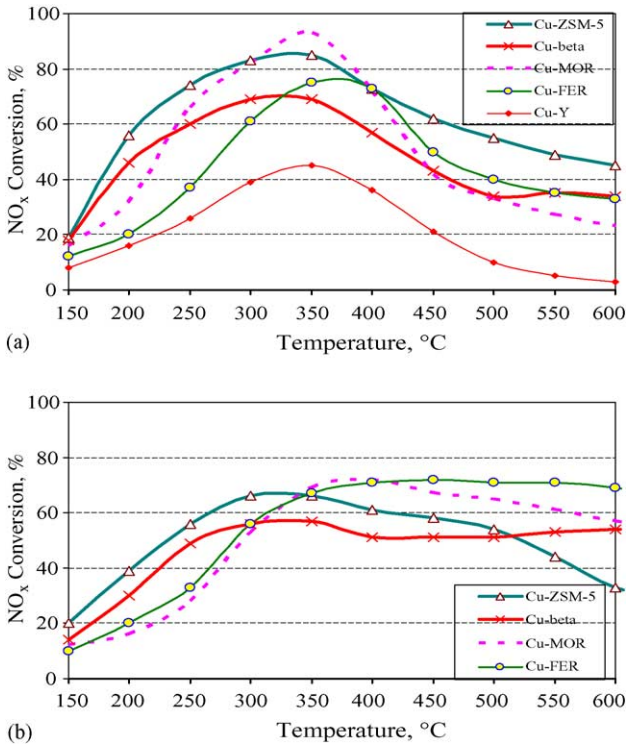

Fig. 1. (a) NO_x conversions of fresh Cu-ZSM-5, Cu-beta, Cu-MOR, Cu-FER, and Cu-Y-zeolites as a fuction of temperature. Conditions: 1000 ppm NO, 1000 ppm NH_3, 8% H_2O, 10% O_2, and balance with N_2. (b) NO_x conversions of hydrothermally aged Cu-ZSM-5, Cu-beta, Cu-MOR, and Cu-FER zeolites as a fuction of temperature. Conditions: 1000 ppm NO, 1000 ppm NH_3, 8% H_2O, 10% O_2, and balance with N_2; hydrothermal aging: 20 h at 600 °C in 10% H_2O in air.

29% was reached with H-beta at 350 °C. The activity of fresh catalysts without NO_2 decreases based on the maximum NO_x 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_x conversion was reached) and wide temperature window, the activity of Cu-ZSM-5 among the Cu-containing catalysts was the highest without NO_2 as can be seen in Fig. 1, where the catalytic activity of the fresh Cu-zeolites for NO_x 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_3 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:

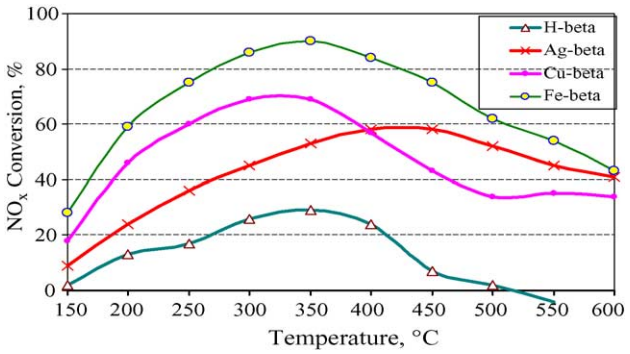

Fig. 2. NO_x conversion over the fresh H-, Ag-, Cu-, and Fe-beta zeolites. Conditions: 1000 ppm NO, 1000 ppm NH_3, 8% H_2O, 10% O_2, and balance with N_2.

Fe > Cu > Ag > H despite the fact that the amount of Ag (n(M)/n(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_2, the NO_x 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_2. The maximum NO_x conversion was 34% at 600 °C whereas the maximum NO_x conversion was around 60% at 350–500 °C in the presence of NO_2. The activity of Cu-MOR was enhanced also at low and high temperatures in the presence of NO_2. 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_2. The presence of NO_2 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_x conversions over a wider temperature range. The activity of most active fresh catalysts with NO_2 decreases based on the maximum NO_x 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_2O in the presence and absence of NO_2 in the inlet flow. Also the other Cu-containing zeolites formed clearly higher amounts of N_2O than the Fe-containing zeolites. This indicates that the selectivity to N_2 is higher over the Fe-containing zeolites. The maximum selectivity to N_2O 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,

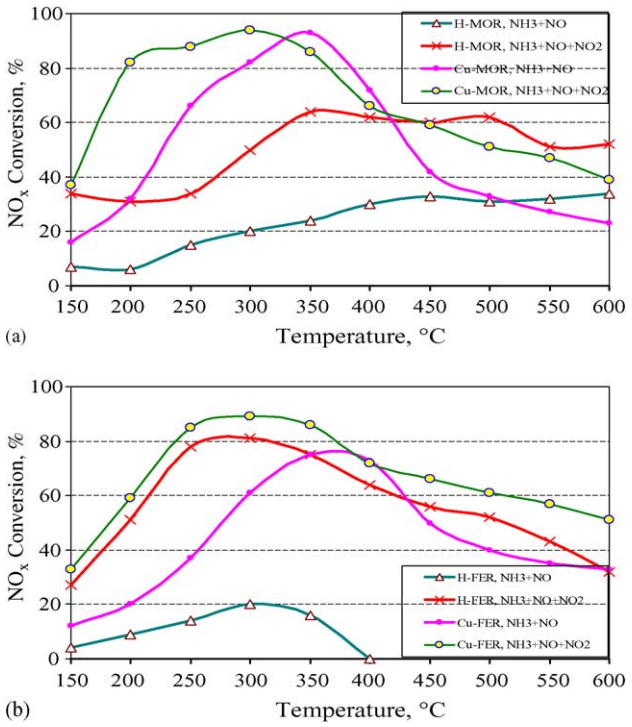

Fig. 3. (a) NO_x conversions of fresh H-MOR and Cu-MOR in the presence and absence of NO_2. Conditions: 600 ppm NO + 400 ppm NO_2 or 1000 ppm NO and 1000 ppm NH_3, 8% H_2O, 10% O_2, and balance with N_2. (b) NO_x conversions of fresh H-FER and Cu-FER in the presence and absence of NO_2. Conditions: 600 ppm NO + 400 ppm NO_2 or 1000 ppm NO and 1000 ppm NH_3, 8% H_2O, 10% O_2, and balance with N_2.

N_2 was the only detectable N-containing product, and no N_2O was observed for Fe-ZSM-5. The formation of undesired N_2O (by N + NO) indicates that NO decomposition has occurred or ammonia is partially oxidized by oxygen. However, the total oxidation activity is not too high because 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 NH_3-SCR as well as not selected for further studies. The activity of hydrogen exchanged zeolites increased also significantly in the presence of NO_2. H-FER had the highest NO_x conversion, 81% at 300 °C (Fig. 3b). H-beta, which was the most active one without NO_2 was now the second most active and had the maximum NO_x conversion of 72% also at 300 °C.

The effect of 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 NO_x conversion enhanced evenly over Ag-beta when the amount of NO_2 in the feed gas mixture was increased from 0 to 400 ppm. Also the maximum NO_x conversion was reached at lower temperatures. The presence of 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 NO_2, ammonia started to oxidize at 500 °C. Therefore, the NO_x conversion decreased at high temperatures. The decrease in the NO_x conversion due to the production of NO as well as the formation NO_2 and N_2O indicates the oxidation on NH_3. According to Alemany et al. [11], a decrease in the activity and selectivity of the V_2O_5-based catalyst, when the temperature of SCR reaction exceeds 400 °C, is mainly due to production of NO and 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 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 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 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 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 NH_3 concentration after the Fe-beta catalyst was 26 ppm. At higher temperatures, the 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 NO_x conversion and highest NH_3 slip. The effect of 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 NO_2 enhanced especially the low temperature activity. The activity of most active hydrothermally aged catalysts with NO_2 decreases based on the maximum 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 NO_2 to the inlet flow increased the catalytic activity of fresh and aged

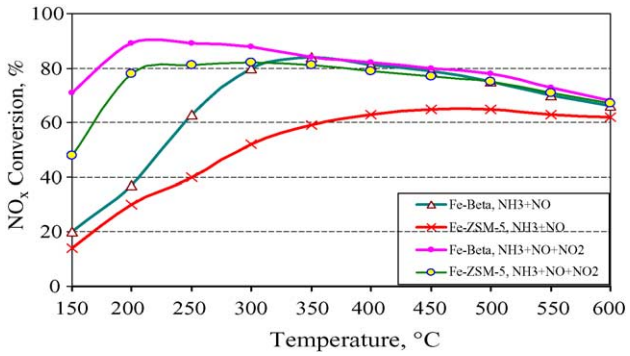

Fig. 4. NO_x conversions of hydrothermally aged Fe-beta and Fe-ZSM-5 in the presence and absence of NO_2. Conditions: 600 ppm NO + 400 ppm NO_2 or 1000 ppm NO and 1000 ppm NH_3, 8% H_2O, 10% O_2, and balance with N_2.

zeolite-based catalysts in NH_3-SCR. The result indicated that most probably the reaction mechanism includes the oxidation of NO to NO_2, which is a slow reaction step on zeolite-only catalysts. Therefore, the presence of 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 NO_2 reacts very fast with NO and NH_3. According to Long and Yang, zeolites' Brönsted acid sites provide sites for ammonia adsorption, generating NH_4^+ ions [4]. It was observed that the reactivity of NH_4^+ ions with NO + 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 NO_2. Therefore, the oxidation activity of Fe-beta is most probably higher than that on Cu-, Ag-, or H-beta (Fig. 2). NO_2 is much more reactive than NO with NH_4^+ ions, and therefore the presence of it enhances the SCR activity. The oxidation of NO to NO_2 is probably the rate-determining step for the SCR reaction.

In the conditions where NH_3 oxidation is low, NH_3 and NO_x react in the stoichiometry 1:1. Therefore, the lower the NO_x conversion is, the higher is the NH_3 slip. If NO_x conversion and NH_3 slip are both low and NO_x conversion even negative, the NH_3 oxidation activity is too high. The NO_x reduction and 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 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 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.

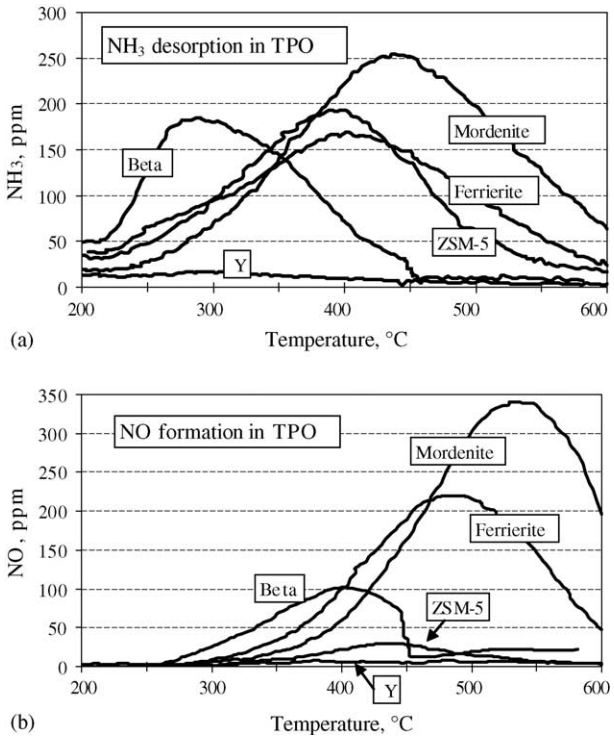

Fig. 5. Desorption of (a) NH_3 and (b) NO over fresh zeolites during TPO (10% O_2 in N_2). Saturated with NH_3 at 200 °C before TPO.

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 NH_3 is desorbed as NH_3 at lower and mainly as NO of nitrogen oxides at higher temperatures in TPO experiments. The formation of N_2O and NO_2 in TPO was small with these catalysts. The selectivity for 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/Al_2 ratio than the other studied catalysts, and thus different acidity. The high Si/Al_2 ratio of Y-zeolite does not promote the formation of the NH_4^+ ions. It is known that a high Si/Al_2 ratio increases the bond strength and a low Si/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 NH_3 during the ammonia adsorption and desorption experiments after hydrothermal aging, because the adsorption capacity was decreased. Dealumination increases the Si/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

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