# Investigation of the selective catalytic reduction of NO by NH₃ on Fe-ZSM5 monolith catalysts

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## Abstract

Fe-ZSM5 coated on cordierite monolith was investigated in the selective catalytic reduction (SCR) of NO with ammonia over a broad temperature range, applying simulated diesel exhaust gas conditions. The catalyst exhibited over 80% $NO_x$ reduction (DeNOx) from 400 to 650 °C at very good selectivity. The dosage of variable amounts of ammonia in the catalytic tests revealed that the SCR reaction is inhibited by ammonia. At very high temperatures DeNOx is reduced due to the selective catalytic oxidation (SCO) of ammonia to nitrogen and the oxidation to NO. Water-free experiments resulted in generally higher DeNOx values, which are explained by the inhibiting effect of water on the NO oxidation capability of Fe-ZSM5. The catalyst was stable upon thermal ageing and only 5–15% loss in DeNOx activity was observed after hydrothermal treatment. This loss in DeNOx is in parallel with a loss of ammonia storage capacity of the aged catalyst. Characterization by NH₃ TPD and MAS ²⁷Al NMR spectroscopy revealed dealumination of the zeolite by hydrothermal ageing, which reduces the Brønsted acidity of the catalyst.
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Keywords: Fe-ZSM5; $NO_x$ conversion; Monolith; Stability; Urea SCR; Ammonia storage

## 1. Introduction

Iron zeolites of the type Fe-ZSM5 are successfully applied as catalysts for several chemical processes, e.g. the direct benzene to phenol hydroxylation [1,2], $N_2O$ decomposition [3,4] and $NO_x$ reduction in exhaust gases [5,6]. Among the latter diesel exhaust gases are especially challenging due to the changing temperatures, flows and concentrations. Currently, the selective catalytic reduction with urea (urea SCR) is judged to have the highest potential for coping the $NO_x$ emission problem of heavy-duty diesel engines [7–9]. Under the hydrothermal conditions in the exhaust pipe urea releases ammonia, which reacts with NO (>90% of $NO_x$ of an exhaust gas is formed by NO) according to the well-known standard SCR reaction [7]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$
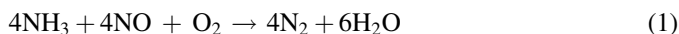
Fe-ZSM5 has been reported to be an active and selective catalyst for the SCR reaction in Refs. [5,6,10–13]. Despite of the valuable information provided in these laboratory investigations, some aspects have not been considered sufficiently for a reliable evaluation of Fe-ZSM5 as SCR catalyst:

1. Water must be present in the basic feed in order to measure the actual performance of the catalyst and to investigate the "real" functionality of the catalyst. However, omitting water may be useful in additional experiments to reveal the reaction mechanism.
2. A good SCR catalyst combines a high $NO_x$ removal efficiency (DeNOx) with a high selectivity and low ammonia emissions after the catalyst. This means that suitable SCR catalysts must have acidic properties, which help to withdraw the ammonia in the catalyst and provide sufficiently high ammonia concentrations at the actives SCR sites at already low ammonia concentrations. Excessive ammonia dosage only slightly increases the ammonia concentration at the active sites. Therefore, the DeNOx remains nearly constant and all excessive ammonia is emitted. By plotting DeNOx versus ammonia slip these important catalyst properties are combined in one graph, e.g.
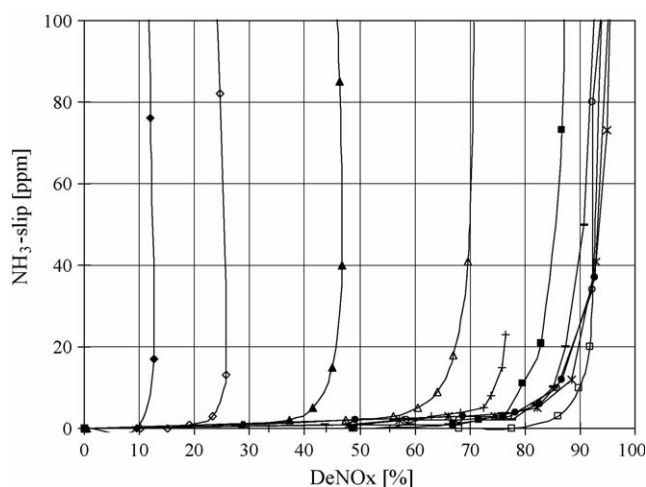
Fig. 1. NH$_3$ slip vs. DeNOx for the fresh Fe-ZSM5 monolith catalyst at (♦) 200 °C, (◇) 250 °C, (▲) 300 °C, (△) 350 °C, (■) 400 °C, (□) 450 °C, (●) 500 °C, (○) 550 °C, (×) 600 °C, (−) 650 °C and (+) 700 °C.

in Fig. 1. The almost rectangular curve shape is a consequence of the high SCR activities at low ammonia slip through the catalyst. Usually, ammonia emissions of about 10 ppm in average are regarded as harmless for automotive applications [14]. This necessitates a dosage control for adding the right amount of ammonia relating to the NO$_x$ concentration and the activity of the catalyst. For catalyst screening experiments dosing a constant amount of ammonia and measuring the activity of the catalyst as a function of temperature is a valuable tool. However, with regard to dosage control in automotive applications a completed description of the catalyst performance is necessary. In our opinion, the temperature dependency of the catalyst activity is best expressed with respect to the allowable ammonia slip of 10 ppm independent of the ammonia to NO$_x$ ratio dosed.

3. Currently, a broad range of engine development strategies are followed, resulting in either low exhaust gas temperatures, e.g. for engines using excessive exhaust gas recycling (EGR), or very high exhaust gas temperatures, e.g. for engines without EGR but with hot diesel particulate filter (DPF) regeneration. Thus, to cover the maximum range of exhaust gas temperatures, the activity and selectivity of the catalysts should be checked from 150 to 700 °C.

4. All above mentioned experimental studies report about Fe-ZSM5 powder catalysts, but monolith investigations are indispensable for gaining experimental data, which are representative of the situation in real world catalytic converters, i.e. low pressure drop, high geometric surface area and short diffusion distances [15].

In this paper we report about Fe-ZSM5 coated on a cordierite monolith in the selective catalytic reduction and selective catalytic oxidation reaction. The experiments were performed mainly in the presence of water over a broad temperature range considering the dependency of DeNOx from the ammonia slip. Moreover, the stability as well as the ammonia storage capacity

## 2. Experimental

A commercially available Fe-ZSM5 powder was used as a model substance. The catalytic material was coated on a cordierite honeycomb of the size 4.66 in. × 4.66 in. × 3 in. with a cell density of 400 cpsi by Umicore automotive catalysts, Germany. For the catalytic investigation, the cordierite monolith was cut into pieces of the size 3.8 cm × 1.7 cm × 1.2 cm fitting to the sample holder of the tube reactor. Details about the plant set up are described in Ref. [14]. The gas hourly space velocity (GHSV = volumetric gas flow/coated monolith volume) was 52,000 h$^{-1}$, which represents the flow conditions in SCR converters on board of diesel vehicles. For tests of the standard SCR reaction, the composition of diesel exhaust gas was approximated by a model feed gas containing 10% O$_2$, 5% H$_2$O 1000 ppm of NO and balance N$_2$. NH$_3$ was added in the range 100–2000 ppm. The selective catalytic oxidation (SCO) reaction of ammonia to nitrogen was tested with a model feed consisting of 10% O$_2$, 5% H$_2$O and 1000 ppm NH$_3$ but no NO. Water was omitted for supplementing investigations The concentrations of NO, NO$_2$, N$_2$O, NH$_3$ and H$_2$O in the gas phase were analysed by HR-FTIR spectroscopy (Nicolet Magna IR 560, OMNIC QuantPad software) equipped with a heated multiple pass gas cell.

The thermal and hydrothermal stability of the Fe-ZSM5 catalyst coated on cordierite was tested by ageing at 650 °C in the presence of 10% oxygen in nitrogen for 50 h (denoted as "dry aged") and by ageing at 650 °C in 10% water and 10% oxygen in nitrogen for 50 h (denoted as "wet aged"), respectively.

The ammonia adsorption capacities of the fresh, the dry aged and the wet aged monolith catalysts were measured at six different temperatures between 200 and 450 °C by two different methods. (a) Thermal desorption: 1000 ppm ammonia was adsorbed on the fresh Fe-ZSM5 monolith catalyst at a fixed temperature in 10% O$_2$, 5% H$_2$O and balance N$_2$. The GHSV was maintained at 52,000 h$^{-1}$. In the desorption procedure, part of the ammonia was removed by purging the sample at the adsorption temperature with pure N$_2$, followed by increasing the temperature up to 450 °C in order to complete the ammonia desorption. (b) Combination of physical desorption and reaction of pre-adsorbed ammonia by NO according to the method of Kleemann et al. [16]: first, ammonia was adsorbed using a nitrogen gas flow containing 10% O$_2$, 5% H$_2$O and 1000 ppm of NH$_3$, at a fixed temperature until this concentration was also reached at the catalyst outlet. Subsequently, the chemically accessible ammonia was removed by stopping the ammonia dosage and simultaneously dosing 10% O$_2$, 5% H$_2$O and 1000 ppm of NO at the same temperature until the NO consumption ceased. The physically desorbed ammonia was measured in parallel. Oxygen and water were always added in order to obtain ammonia storage capacities, being representative for diesel exhaust gas conditions.

Powder samples of the Fe-ZSM5 catalyst were used for characterization. Temperature programmed desorption of ammonia (NH$_3$ TPD) was carried out in a TPD/TPR 2900

conductivity detector. Fifty milligram of sample were degassed at 550 °C for 1 h in a He flow and cooled down to 100 °C. At this temperature adsorption of $NH_3$ took place until saturation. Afterwards, the catalyst was flushed with He for 30 min. TPD measurements were performed from 100 to 650 °C with a heating rate of 20 °C/min, with He as carrier gas.

^{27}Al MAS NMR spectra were obtained on a Bruker Ultrashield 500 spectrometer at a magnetic field of 11.7 T equipped with a 4 mm MAS head probe. The aluminium resonance frequency at this field is 130 MHz. The sample rotation speed was 12.5 kHz. The [27]Al chemical shifts were referenced to a saturated $Al(NO_3)_3$ solution. To obtain NMR spectra as quantitatively as possible in the presence of a heterogeneous distribution of quadrupolar coupling constants, the [27]Al nuclei were excited with a single 20° pulse of 1 μs. Excitation pulses longer than 3 μs were seen to overemphasize the extra-framework aluminium signal intensity relative to the framework aluminium signal. The relaxation delay between the scans was set to 1 s. No saturation effects were observed in the spectrum for relaxation delays longer than 0.5 s.

## 3. Results and discussion

### 3.1. Catalytic performance of Fe-ZSM5 monolith catalysts

#### 3.1.1. Standard-SCR over Fe-ZSM5

From Fig. 1, the high SCR activity of Fe-ZSM5 is clearly discernible, especially at temperatures above 350 °C. In accordance with the expected behaviour of a suitable SCR catalyst nearly all ammonia dosed goes into the SCR reaction, limited either by the activity of the catalyst at a given temperature or the stoichiometry of the SCR reaction. All additional ammonia causes an only marginal increase of the DeNOx. However, having a closer look at the ammonia slip at lower and intermediate temperatures up to 350 °C reveals an interesting behaviour. The steep part of the curves are slightly bent backward, indicating that the $NO_x$ conversion first increases as expected but then decreases again if ammonia is overdosed and ammonia slip is forced. Obviously, the SCR reaction is inhibited by ammonia. This effect is more pronounced in Fig. 2, where DeNOx values are plotted against the stoichiometric ratio $\alpha = NH_{3,in}/NO_{x,in}$ for different temperatures in the range 200–500 °C. These results suggest that the inhibition effect of ammonia could be due to competitive adsorption of ammonia and NO on the active sites. In fact, Eng and Bartholomew [17] and Stevenson et al. [18] observed a similar inhibition by ammonia on H-ZSM5, which was attributed to a competitive adsorption of ammonia and NO.

Fig. 3 illustrates the differences between the DeNOx at 10 ppm $NH_3$ slip and the maximum DeNOx, plotted versus temperature in the range 200–700 °C. In accordance with Fig. 2, the difference between the maximum DeNOx and DeNOx at 10 ppm ammonia slip decreases for lower temperatures due to the ammonia inhibition effect, which prevents that the catalyst activity is increased by adding ammonia in excess. In this temperature range DeNOx is rather limited by the reaction
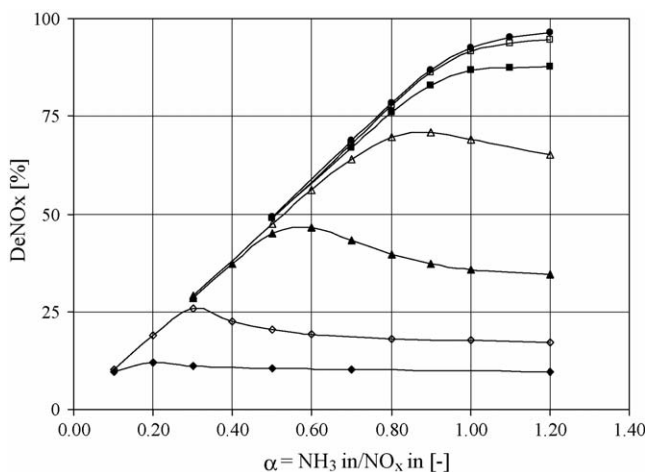


Fig. 2. DeNOx vs. stoichiometric factor $\alpha$ for the fresh Fe-ZSM5 monolith catalyst at (◆) 200 °C, (◇) 250 °C, (▲) 300 °C, (△) 350 °C, (■) 400 °C, (□) 450 °C and (●) 500 °C.

200 to 600 °C, reaching >90% for $T > 450$ °C. It decreases at temperatures beyond 600 °C. However, at 700 °C still around 80% of conversion was achieved.

#### 3.1.2. Possible side-reactions during standard-SCR over Fe-ZSM5

Generally, DeNOx is expected to be limited by the catalyst activity at lower temperatures, the stoichiometry of the SCR reaction at intermediate temperatures and by the catalyst selectivity at high temperatures. With increasing temperatures different side-reactions are conceivable producing $N_2O$ and $NO_x$ as well as increased amounts of nitrogen [19].
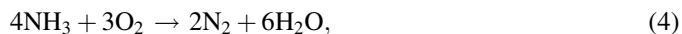
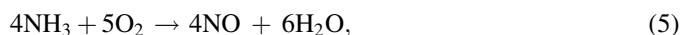For the production of $N_2O$ the direct oxidation of ammonia,

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \tag{2}$$

and the reaction of ammonia with $NO_2$ are discussed [19]:

$$2NH_3 + 2NO_2 \rightarrow N_2O + N_2 + 3H_2O \tag{3}$$
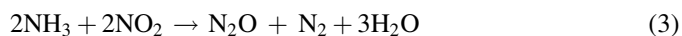
Other potential side-reactions of the SCR process are the selective catalytic oxidation of ammonia to nitrogen (SCO),

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O, \tag{4}$$

and the oxidation of ammonia to NO,

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O, \tag{5}$$

which itself may be further oxidized to $NO_2$.

#### 3.1.3. $N_2O$ formation

Fig. 3 clearly shows that only negligible amounts of $N_2O$ (∼3 ppm) were formed during standard-SCR between 250 and 400 °C and that no $N_2O$ was formed beyond 450 °C. This makes reaction (2) very unlikely, which is expected to produce increasingly amounts of $N_2O$ formation at higher temperatures. The reaction of ammonia with oxygen over Fe-ZSM5 was investigated without the influence of the SCR reaction by dosing ammonia without NO (Fig. 4a). No $N_2O$ was formed at any temperature, ruling out the relevance of reaction (2) for the
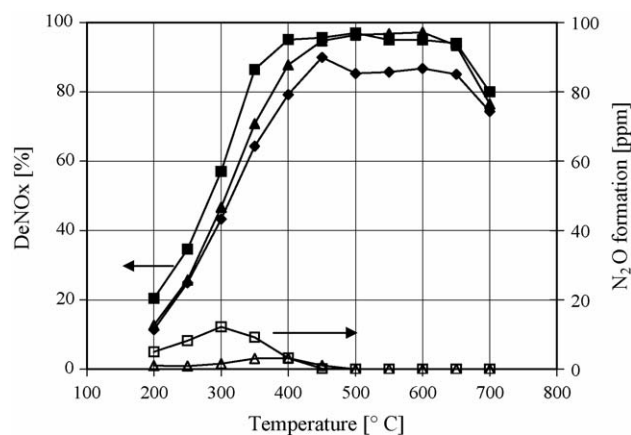
Fig. 3. DeNOx vs. temperature for the fresh Fe-ZSM monolith (◆) at 10 ppm NH$_3$ slip with water in feed, (▲) at maximum conversion with water in feed and (■) at 10 ppm NH$_3$ slip without water. (△) N$_2$O formation at 10 ppm NH$_3$ slip with water in feed and (□) at 10 ppm NH$_3$ slip without water.

reaction equation the N$_2$O formation should be independent of the NO$_2$ content in the feed. However, experiments with increasing NO$_2$ fractions in the feed, which will be subject of another publication, clearly showed the dependency of the N$_2$O emissions on the NO$_2$ concentration in the gas feed at 250–400 °C. This proves the relevance of reaction (3) for the
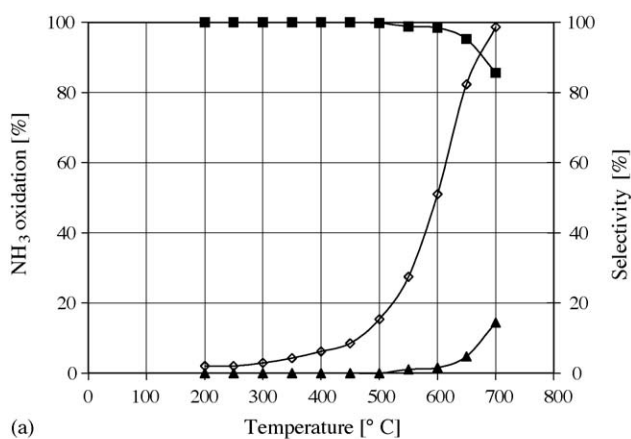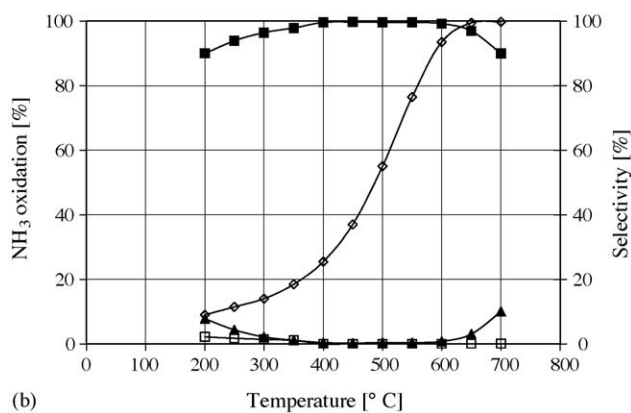


Fig. 4. SCO properties of the fresh Fe-ZSM5 monolith vs. temperature (a) in the presence of water and (b) without water. (◇) NH$_3$ oxidized, (▲) selectivity

formation of N$_2$O on Fe-ZSM5. However, having a closer look at the underlying chemistry, the contribution of reaction (2) cannot be strictly ruled out, as N$_2$O might be formed as a short living intermediate at higher temperatures. In fact, Fe-ZSM5 shows strongly increasing N$_2$O decomposition activity at $T > 400\ °C$

$$2N_2O \rightarrow 2N_2 + O_2 \tag{7}$$

and N$_2$O SCR activity at $T > 350\ °C$ [20]

$$3N_2O + 2NH_3 \rightarrow 4N_2 + 3H_2O \tag{8}$$
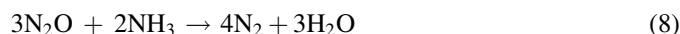
explaining the general absence of N$_2$O at higher temperatures independent of the reaction conditions or the feed composition.

### 3.1.4. SCO reaction and NO formation

The investigation of the ammonia oxidation over Fe-ZSM5 showed that ammonia conversion strongly increases with temperatures (Fig. 4a). Around 50% of the ammonia was oxidized at $T = 600\ °C$ and nearly 100% at 700 °C. The selectivity towards N$_2$ was almost 100% till 600 °C, but beyond 600 °C the selectivity towards nitrogen decreased accompanied with an increase in NO formation. The formation of NO beside the main product N$_2$ in the ammonia oxidation experiment gives occasion to the assumption that during SCR over Fe-ZSM5 NO is not only consumed but also produced on the catalyst by reaction of ammonia with oxygen. This NO cannot be distinguished from the NO in the feed and, especially, if it is formed at the catalyst entrance it may also react downstream in the standard SCR reaction (1). Based on the observed products, it not possible to decide, if the oxidation of ammonia to nitrogen is a straightforward reaction or if it proceeds via NO as intermediate.

### 3.1.5. NO$_2$ formation

Fe-ZSM5 has a distinct NO oxidation capability as shown in Fig. 5. The NO$_2$ fraction increases with temperature as expected, but decreases again at higher temperatures due to the thermodynamic equilibrium between NO and NO$_2$ lying on the side of NO. NO$_2$ is essential for SCR activity of ZSM5-
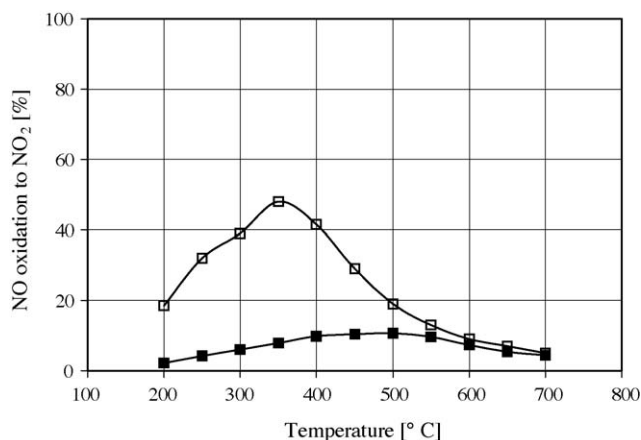


Fig. 5. NO oxidation to NO$_2$ for the fresh Fe-ZSM monolith (■) with water in

based catalysts [21], but, as the $NO_2$ formed from NO is not observed under standard-SCR conditions (Fig. 3) it may be concluded that it is only a short living intermediate, which is immediately consumed. The decisive function of $NO_2$ on the SCR reaction over Fe-ZSM5 was confirmed by adding $NO_2$ to the feed, which drastically increased the DeNOx values up to $NO_2/NO_x = 0.5$, especially at low temperatures [22]. The SCR reaction involving $NO_2$ is called fast-SCR [19] and is described by reaction equation (9). It may be regarded as the *actual* and *general* SCR stoichiometry over zeolite based catalysts, because either $NO_2$ in the feed or the presence of an oxidation functionality in the zeolite for the oxidation of NO to $NO_2$ is a pre-requisite for SCR activity:

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \qquad (9)$$
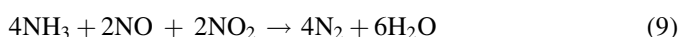
### 3.1.6. SCR stoichiometry

The problem for the investigation of the SCR reaction is, that all reactions end up directly or via intermediates in nitrogen or NO, which cannot be distinguished from the feed components. Moreover, nitrogen cannot be detected by infrared spectroscopy. However, the contribution of all these side-reactions results in an increased consumption of ammonia relatively to the 1:1 stoichiometry of the SCR reaction. This excess consumption is derived from the curves in Fig. 6, showing the ratio of consumed ammonia to consumed $NO_x$ versus the ratio of dosed ammonia to dosed $NO_x$ at 200–700 °C, which is a direct scale for the compliance of the SCR stoichiometry. The values of 1–1.1 between 200 and 600 °C clearly demonstrate that Fe-ZSM5 follows the ideal SCR stoichiometry over a broad temperature range and that a maximum of 10% ammonia is consumed by ammonia oxidation. However, at 700 °C, values of about 1.5–1.7 were observed, indicating that the catalyst consumed an increasing part of ammonia mainly due to the oxidation to nitrogen at very high temperatures.
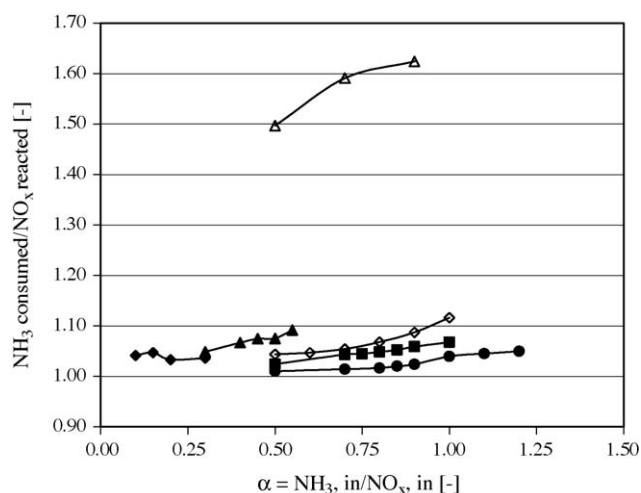


Fig. 6. Observed ammonia to $NO_x$ stoichiometry vs. dosed ammonia to $NO_x$ ratio at (◆) 200 °C, (▲) 300 °C, (■) 400 °C, (●) 500 °C, (◇) 600 °C and (△)

### 3.1.7. Water-free experiments

In order to obtain a clearer picture of the functionality of the catalyst also water-free experiments have been performed. From Fig. 3 it is clearly discernible that Fe-ZSM5 shows a generally higher DeNOx activity if water is omitted. However, also much more $N_2O$ is formed reaching a maximum of 12 ppm at intermediate temperatures. As stated above this side-product is typically formed in larger amounts at intermediate temperatures if $NO_2$ is present in the gas feed [22]. It is obvious from Fig. 5 that also much more $NO_2$ is formed under water-free conditions than with water in the feed. Thus, the increase in $N_2O$ formation under water-free conditions is easily explained by the elevated concentration of $NO_2$ on the catalyst.

The higher oxidation capability of the catalyst under water free conditions, observable from the elevated $NO_2$ concentrations in Fig. 5, is also apparent in the investigation of the ammonia oxidation without water as shown in Fig. 4b. By omitting the water, elevated $NH_3$ conversions are observed over the whole temperature range. At lower temperatures the occurrence of NO and $N_2O$ is remarkable, which was not observed in the presence of water. Apparently, the ammonia oxidation to NO is promoted more than the following SCR reaction, resulting in the production of NO beside the main product $N_2$. With increasing temperature NO decreases as the SCR reaction accelerates faster than the ammonia oxidation.

Long and Yang [23] investigated the SCO reaction over powdered iron zeolites at temperatures up to 450 °C. They also found, that under water-free conditions the selectivity of the SCO reaction to nitrogen increases with temperature at the expense of a decrease in NO formation. This was explained by NO being the intermediate of the SCO reaction, which is reduced to nitrogen by $NH_3$ in the SCR reaction.

The formation of $N_2O$ seems to be coupled to the presence of gas phase NO. Due to the high oxidation capability of Fe-ZSM5, it is very likely, that part of the NO formed is further oxidized to $NO_2$ due to the strong oxidizing properties of the catalyst under water-free conditions. The $NO_2$, however, is not observable, as it is rapidly converted to nitrogen according to the "fast-SCR" reaction already at 200 °C [22]. Thus, the observed formation of $N_2O$ would be a side-product of the "fast-SCR" reaction at low temperatures.

### 3.2. Stability of Fe-ZSM5 monolith catalysts

Stability under real-world conditions is an important parameter for the assessment of the suitability of a catalyst. Therefore, Long and Yang [24] investigated the durability of Fe-ZSM5 powder catalysts, aged in $SO_2$ and $H_2O$ for 60 h at 350 °C. They observed a 20% loss in NO conversion. Feng and Hall [25] studied the durability of the Fe-ZSM5 powder catalyst for a period of 2500 h at 500 °C. They observed a minimal loss in NO activity in a simulated exhaust gas stream. We checked both the thermal and hydrothermal stability of Fe-ZSM5, but coated on the cordierite honeycomb. Fig. 7a compares the $NO_x$ conversion at 10 ppm ammonia slip versus reaction temperature of the aged catalysts with the results of the fresh catalyst

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