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Journal of Catalysis 218 (2003) 354–364

JOURNAL OF
CATALYSIS

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Selective catalytic reduction of NO_x with NH_3 over zeolite H–ZSM-5: influence of transient ammonia supply

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Received 20 November 2002; revised 20 March 2003; accepted 21 March 2003

Abstract

The effect of ammonia supply on the selective catalytic reduction of NO_x over zeolite H–ZSM-5 was investigated using step response experiments between 200 and 500 °C. For inlet $NO:NO_2$ ratios > 1, the activity for NO_x reduction transiently increased when NH_3 was removed from the feed. For $NO:NO_2$ ratios $\leqslant 1$, the NO_x reduction however decreased. By pulsing NH_3 to the feed, the activity for NO reduction was enhanced up to five times compared to continuous supply of ammonia. For $NO:NO_2$ ratios exceeding one, also the selectivity towards N_2O formation was lower with transient ammonia supply. Temperature programmed reaction experiments with preadsorbed NH_3 showed highest initial NO_x reduction activity when ammonia had been adsorbed at 300 or 250 °C compared to 200 °C. A minimum in NO reduction was observed at 130 °C independent of the ammonia adsorption temperature. For $NO:NO_2$ ratios > 1, the results strongly indicate that NO oxidation is the rate determining step in the ammonia selective catalytic reduction (NH_3-SCR) reaction over H–ZSM-5.

Keywords: H–ZSM-5; Selective catalytic reduction; NO_x reduction; Ammonia transients; Lean deNO_x

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1. Introduction

Today diesel and lean-burn engines are attractive alternatives to Otto engines due to lower fuel consumption and hence lower emissions of CO_2. However, a great disadvantage with these alternatives is that they operate at high air-to-fuel ratios that give oxygen excess in the exhaust gas and thus makes it difficult to reduce the NO_x ($NO + NO_2$) formed during the combustion. Ammonia can act as a reducing agent for NO_x in oxygen excess and techniques for adding ammonia to the exhaust gas in a controlled manner are currently being developed. The use of ammonia to reduce NO_x is referred to as ammonia selective catalytic reduction (NH_3-SCR) and is one of the most promising methods for meeting the future legislation demands concerning NO_x emissions from diesel vehicles [1]. The technique has been commercially used for many years in stationary applications and the most commonly used catalysts are vanadia–titania-based materials, which have high activity and selectivity between 270 and 450 °C [2]. At temperatures higher than 420 °C these materials catalyse the oxidation of NH_3 by oxygen, which lead to a loss in SCR activity [3]. Vanadia-based catalysts are also known to catalyse the oxidation of SO_2 to SO_3, which contributes to the formation of particulates [3]. For applications in automotive exhaust after treatment systems, there has been significant interest in developing catalysts that can operate in a wider temperature range from below 200 °C up to 600 °C. Several studies have focused on zeolite materials, which are typically active in a wider temperature range and less of a disposal problem compared to poisonous vanadia-based materials. Although most reports have been devoted to different ion exchanged zeolites [4–9], several authors have reported that zeolites in their acidic form, such as H–mordernite and H–ZSM-5, are also active as NH_3-SCR catalysts, particularly at high temperatures [10–16], but also under ambient conditions [17]. Recently, very high NO_x conversions have also been reported at temperatures around 200 °C over H-form zeolites with preadsorbed NH_3 and for zeolites in their ammonium

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doi:10.1016/S0021-9517(03)00148-9

form [14,18]. In these reports it was observed that the NO oxidation was suppressed when gaseous NH_3 was present in the zeolite suggesting that oxidation of NO is the rate-determining step in the SCR reaction over acidic zeolites for feeds with high NO content [16,19]. It has also been shown that the SCR reaction with equimolar amounts of NO and NO_2 is much faster than with only NO and more selective than with only NO_2 over acidic zeolites [12].

In the present investigation the selective catalytic reduction of NO_x was studied for different inlet NO:NO_2 ratios over zeolite H–ZSM-5 using transient ammonia supply to limit the presence of gaseous NH_3 in the zeolite. Transient supply of NH_3 is expected to give higher activity for the oxidation of NO to NO_2, which in turn should improve the total NO_x reduction activity. Temperature programmed reaction studies were performed to further investigate the role of the temperature during adsorption of NH_3. In order to reduce the complexity of the system and to understand the role of ammonia, a reduced model gas composition was used containing only NO, NO_2, NH_3, and O_2.

2. Experimental methods

2.1. Material

A sample of H–ZSM-5 (EZ 476) was used as obtained from Eka Chemicals AB, Sweden. The SiO_2:Al_2O_3 molar ratio was determined to be 33.2 and the zeolite contained impurities of iron, manganese, and titanium in amounts corresponding to 0.06 wt% Fe_2O_3, 0.02 wt% MnO, and 0.02 wt% TiO_2 as determined by X-ray fluorescence analysis according to the supplier. The specific surface area of the zeolite was 358 m^2/g as determined by N_2 adsorption in accordance with the BET method using a Micromeretics ASAP 2010 instrument.

2.2. Catalytic test procedure

The catalytic measurements were performed at atmospheric pressure using 0.10 g of the zeolite powder. The sample was placed on a small piece of quartz wool supported by a porous quartz plate in a vertically mounted fixed bed quartz reactor (i.d. 7 mm). The same catalyst sample was used in all experiments. The temperature was measured using a thermocouple inside the catalyst bed, and measured and controlled by a thermocouple placed 6 mm after the catalyst bed. The heating unit consisted of a heating coil (1 mm diameter Kanthal wire) in direct contact with the reactor. The reactor and heating coil were insulated by quartz wool and aluminum foil. Feed gases were mixed from Ar (99.998%, air liquid), O_2 (99.95%, air liquid), NO (1.02% in Ar, air liquid), NO_2 (4865 ppm in Ar, AGA), and NH_3 (1.01% in Ar, AGA) and introduced to the reactor via individual mass flow controllers (Brooks). The inlet of NO was placed close to the reactor inlet to avoid oxidation of NO before the catalyst. A total flow of 100 ml/min was used in all experiments, corresponding to a space velocity of 30,000 h^{-1}. The composition of the gas at the reactor outlet was monitored continuously by a quadrupole mass spectrometer (Balzers QMS 200). The ion currents analysed were $m/e = 17$ (NH_3, H_2O), 18 (H_2O), 28 (N_2, N_2O), 30 (NO, N_2O, NO_2), 40 (Ar), 44 (N_2O), and 46 (NO_2). These were measured every 22 s and fragmentation patterns, determined experimentally from calibration gases, were used to quantitatively analyse the data. Some of the mass spectrometer (MS) signals were too complex to convert to concentrations due to cross sensitivities for different gases. This concerned especially the nitrogen oxides, and for these the MS data were only used for qualitative analysis. Instead the outlet concentrations of nitrogen oxides were quantified using a chemiluminescence instrument (CLD 700 EL th, TECAN) for NO and NO_x detection and an IR instrument (UNOR 6N, Maihak) for detection of N_2O. The gas flow into these instruments was diluted with air by a factor of 9.5 to comply with the operating conditions of the NO/NO_x analyser. Prior to each experiment the zeolite was pretreated with 10% O_2 in Ar at 500 °C for 20 min.

The effect of transient ammonia supply was investigated for temperatures between 200 and 500 °C in a series of experiments varying the NO:NO_2 ratio between 100% NO, 25% NO + 75% NO_2, 50% NO + 50% NO_2, and 100% NO_2. The experiments were divided in two sections. In the first section step responses were studied for six different 30-min steps in NO_x and NH_3 concentration. In the second section the pulse responses for six types of ammonia pulses, varying in duration and concentration of ammonia, were studied. The experiments were performed at constant temperature (200–500 °C) and with a constant O_2 concentration of 10%. During the step response experiments the NO_x and NH_3 concentrations were 1000 ppm whenever introduced. In the subsequent pulse response experiments the NO_x concentration was kept constant at 1000 ppm while the ammonia was supplied as pulses according to Table 1. The ammonia concentration was adjusted so that the total amount of ammonia was in stoichiometric proportion to the amount of NO_x over each cycle.

The adsorbed amount of ammonia was quantified at different temperatures and subsequently reacted with NO_x and O_2 by either temperature programmed reaction (TPR) experiments or reaction at constant temperature. In the TPR experiments the zeolite was first saturated with NH_3 at 200,

Table 1
Concentration and duration of ammonia pulses

Pulse type	NH_3 concentration (ppm)	NH_3 pulse length (min)	Time without NH_3 (min)	Times repeated
5/10	3000	5	10	3
5/5	2000	5	5	3
1/4	5000	1	4	5
5/1	1200	5	1	5
1/1	2000	1	1	5
1/0.5	1500	1	0.5	10

250, or 300 °C, and thereafter flushed with Ar for 25 min whereby the temperature was lowered to 50 °C. Finally, the sample was exposed to 1000 ppm NO_x (100% NO or 50% NO + 50% NO_2) and 10% O_2 and the temperature was raised from 50 to 600 °C at 20 °C/min. The NH_3 storage capacity of the zeolite was determined by integrating the ammonia MS signal. The stored amount of ammonia was compared with the reacted amount of NO_x, determined from the integrated NO_x signal from the NO_x analyser. In the second type of preadsorption experiments the sample was first saturated with NH_3 at 150, 200, or 300 °C, and thereafter flushed with Ar for 15 min whereby the temperature was adjusted to 200 °C. Finally the sample was exposed to 1000 ppm NO and 10% O_2 at a constant temperature of 200 °C.

Some comments regarding the reactor system and the product gas analysis are necessary for the interpretation of the results. Most important was the interference from NH_3 in the NO/NO_x analyser resulting in a reduction of the NO_x signal when high amounts of both NO_x and NH_3 were present in the gas feed. This is due to the fact that the SCR reaction occurs in the part of the instrument where NO_2 is converted to NO for NO_x analysis. Empty reactor experiments showed that a mixture of 1000 ppm NH_3 and 1000 ppm NO resulted in a decrease in the NO_x signal corresponding to 140 ppm NO_x. Experiments with only NH_3 also showed that NH_3 gave a contribution to the NO_x signal of about 4–8% of the NH_3 concentration due to NH_3 oxidation to NO_x in the same part of the NO/NO_x instrument. It was further found that the empty reactor oxidised about 13% NO to NO_2 likely as a result of homogeneous and wall catalysed NO oxidation in the system. It is not clear exactly where in the system the oxidation occurred but it is probable that about half the amount was oxidised before and half after the reactor due to exposure to approximately equal lengths of room tempered steel pipes on each side of the reactor.

3. Results

3.1. Step response experiments

Fig. 1 shows the outlet concentrations of NO, NO_x, N_2O, NH_3, and H_2O during step changes in the inlet concentrations of NH_3 and NO_x (introduced as NO) for three different temperatures. The experiments started with a 30-min period where the inlet gas mixture contained NO, O_2, and Ar. In all three experiments the outlet NO concentration was lower than the total NO_x concentration, which is consistent with NO oxidation over the zeolite. It was also observed that the NO oxidation was higher for higher temperatures and in all cases the oxidation decreased slightly with time. After subtracting the amount of NO that was oxidised in the unheated steel pipes before and after the reactor (i.e., 13%), the NO oxidation at the end of the 30-min NO step was estimated to be 16% at 200 °C, 23% at 250 °C, and 27% at 300 °C of the total NO_x concentration. After the first 30 min, NH_3 was added to the gas feed resulting in a slow increase in the NH_3 and H_2O outlet concentrations and an immediate decrease in the NO_x concentration going through a minimum (for 250 and 300 °C) before levelling out at a new steady state, with lower NO and NO_x levels for higher temperatures. The continuous NO_x reduction at the end of this step was 4% at 200 °C, 6% at 250 °C, and 18% at 300 °C after the NO_x signals have been adjusted for the influence of NH_3, as discussed in the experimental section. Considering that the steady-state NO_x signal between 40 and 60 min was approximately 14% too low, due to the influence of NH_3, there was in fact a minimum in the outlet NO_x concentration also in the 200 °C case. Most of the NH_3 was adsorbed in the zeolite during the first 5 min after ammonia was added to the feed and hence the NO_x signal was only marginally influenced by NH_3 during the minimum. Analysis of the MS signal $m/e = 30$ confirmed that also the outlet NO_x concentration at 200 °C increased after about 5 min, similar to the experiments performed at 250 and 300 °C. After 30 min with only NH_3 and O_2 in the feed, NO was added to the feed at 90 min in Fig. 1 and the steady-state conversion was rapidly reached for all three temperatures. When NH_3 was removed from the feed 30 min later (at 120 min in Fig. 1), there was a rapid decrease in the NO and NO_x concentrations at 300 °C, a somewhat slower decrease at 250 °C, and markedly slower at 200 °C. At 200 °C an initial increase of the NO_x level seemed to precede the minimum. However, considering again that the NO_x concentration was about 14% higher just before the NH_3 was turned off, it is obvious that there was no increase in NO_x concentration. The MS signal $m/e = 30$ also confirmed that the NO_x concentration started to decrease at the point where the NH_3 supply was switched off. The removal of NO_x proceeded until the NH_3 concentration reached zero, whereupon the outlet NO_x concentration started to increase and finally reached the inlet NO_x concentration. The NO_x level at the minimum was 290, 330, and 640 ppm for 300, 250, and 200 °C, respectively, and the minimum was reached 2, 5, and 16 min, respectively, after the NH_3 was switched off. For all three experiments the water concentration closely resembled the NO_x removal profile during this step. The NO concentration levels at the end of this step (at 150 min) were similar to the corresponding outlet NO concentrations at 30 min. In the sixth and final step, NH_3 was added to the feed after 30 min with only NO, which is equivalent to the second step. The outlet NO and NO_x concentration profiles during this step were almost identical to the corresponding outlet concentration profiles during the second step.

The influence of the $NO:NO_2$ ratio on the SCR reaction is shown in Fig. 2, where the same experiments as shown in Fig. 1 were performed at 250 °C for three different inlet NO_x compositions (i.e., 75% NO + 25% NO_2, 50% NO + 50% NO_2, and 100% NO_2). The highest steady-state SCR activity was observed for equimolar amounts of NO and NO_2 in the feed, where the NO_x conversion exceeded 90% (Fig. 2B). An interesting observation from this experiment was that the

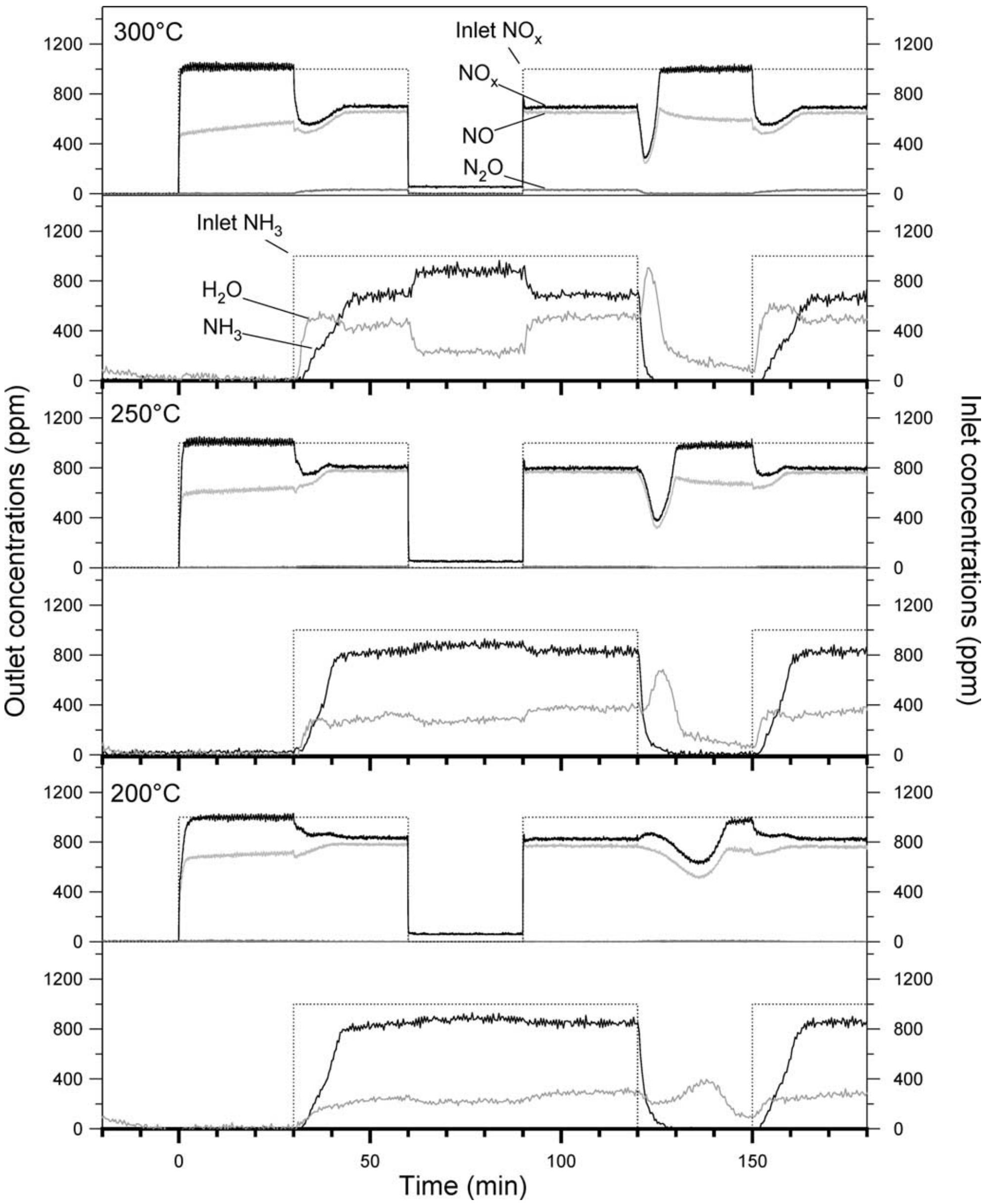

Fig. 1. Step responses for outlet concentrations of NO (light grey curve), NO_x (black curve), N_2O (dark grey curve), NH_3 (black curve), and H_2O (grey) after six different steps in inlet NH_3 (dashed line) and NO_x (dashed line) concentrations. The experiments were performed at 200, 250, and 300 °C by exposing H–ZSM-5 for 0–1000 ppm NH_3, 0–1000 ppm NO and 10% O_2 with Ar as balance.

maximum conversion was not obtained until approximately 10 min after NH_3 was added to the feed. During this period the unreacted NH_3 was accumulated in the zeolite, which was confirmed by MS analysis of the m/e signal 17 and 18 showing no slip of NH_3 at all. The SCR reaction continued for a few minutes after NH_3 was removed from the feed (at 120 min in Fig. 2B), which also proves that NH_3 was accumulated in the zeolite during the SCR reaction. The experiment with only NO_2 as the inlet NO_x source (Fig. 2C) showed relatively high conversion of NO_x, but accompanied by a high outlet concentration of N_2O. The selectivity to N_2O, calculated as the formed amount of N_2O in percentage of the reduced amount of NO_x, was in this experiment as high as 36%, compared to less than 5% for the experiment with equimolar amounts of NO and NO_2. An increased activity upon removal of NH_3 from the feed, similar to the case with 100% NO shown in Fig. 1, was only seen in the experiment where the inlet NO_x consisted of 75% NO + 25% NO_2 (Fig. 2A).

3.2. Pulse response experiments

The effect of transient supply of NH_3 for NO_x reduction was investigated in the second section of the experiments discussed above, by following the outlet NO_x, NO, N_2O, NH_3, and H_2O concentrations during pulsing of the NH_3 feed. The experiments were performed with constant inlet

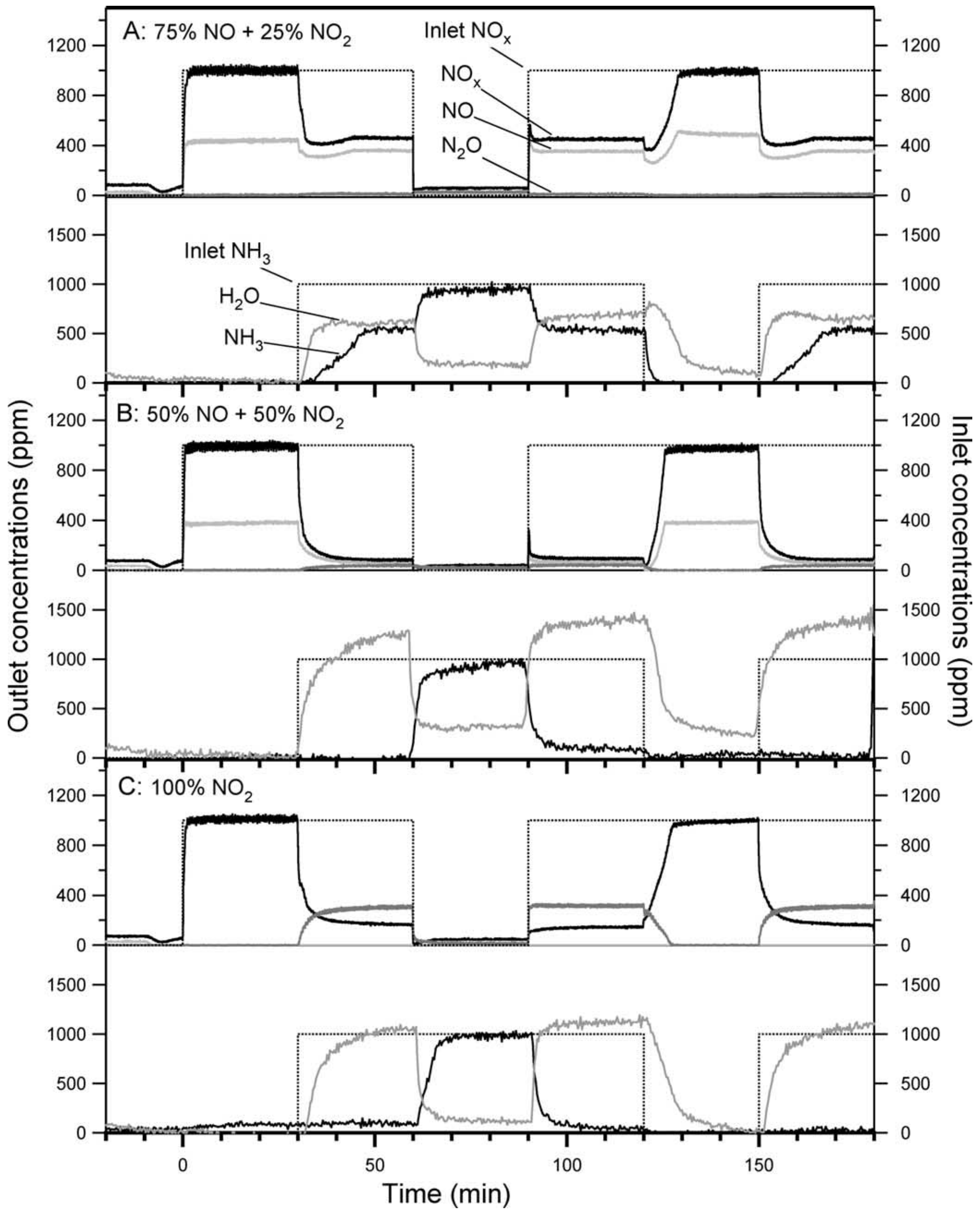

Fig. 2. Step responses for outlet concentrations of NO (light grey), NO_x (black), N_2O (dark grey curve), NH_3 (black curve), and H_2O (grey) after six different steps in inlet NH_3 (dashed line) and NO_x (dashed line) concentrations. The experiments were performed at 250 °C by exposing H–ZSM-5 for 0–1000 ppm NH_3, 0–1000 ppm NO_x and 10% O_2 with Ar as balance. The inlet NO_x consisted of (A) 75% NO + 25% NO_2, (B) 50% NO + 50% NO_2, and (C) 100% NO_2.

NO_x concentration for different NO:NO_2 ratios and temperatures. The pulse responses were investigated for different pulse lengths and frequencies in the six sets of ammonia pulse-cycles described in the experimental section. The case with 100% NO as the inlet NO_x source is presented for 200, 250, and 300 °C in Fig. 3. As observed in the step response experiments, it was clear that the SCR activity increased faster with higher temperature. The average NO_x reduction and selectivity to N_2O formation over the different sets of pulse cycles are summarised in Table 2, where the conversions have been adjusted for the influence of NH_3 on the outlet NO_x signal. It was shown in these experiments that a transient supply of NH_3 yields higher total NO_x conversion and less formation of N_2O, compared to continuous supply of NH_3, for all temperatures and pulse types studied. The type of pulse that yielded the highest NO_x reduction depended on the temperature. The most pronounced differences between transient and continuous NH_3 supply was observed at 250 °C where transient supply of ammonia yielded a NO_x reduction more than five times higher than a continuous NH_3 supply for the pulse type 5 min with NH_3 followed by 10 min without NH_3. During the longer pulse-cycles at

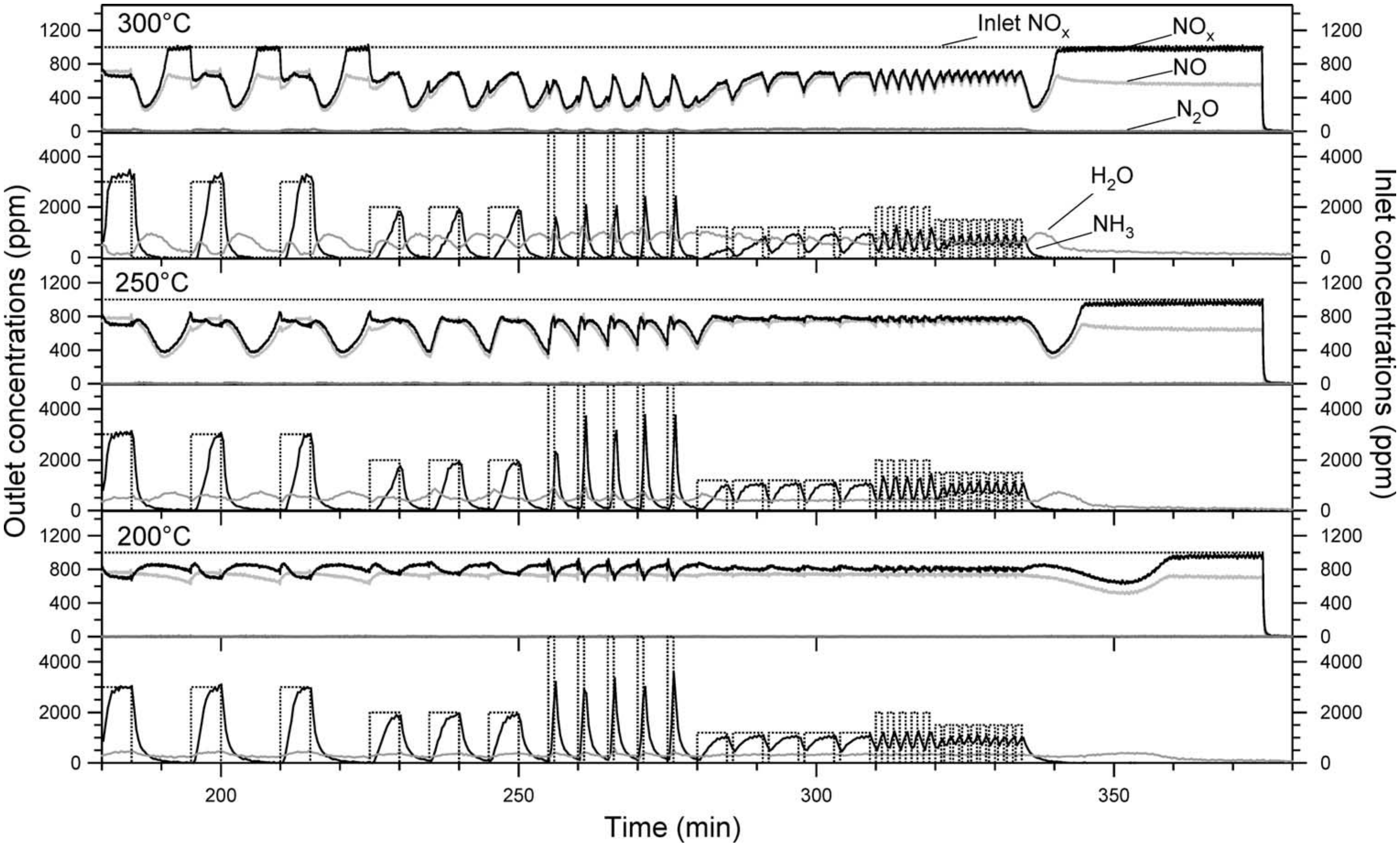

Fig. 3. Pulse responses for outlet concentrations of NO (light grey curve), NO_x (black curve), N_2O (dark grey curve), NH_3 (black curve), and H_2O (grey) for six sets of ammonia pulses (dashed grey line). The experiments were performed at 200, 250, and 300 °C by exposing H–ZSM-5 for 0–5000 ppm NH_3, 1000 ppm NO, and 10% O_2 with Ar as balance. For pulse characteristics, see Table 1.

Table 2
Average NO_x reduction and N_2O selectivity (formed N_2O in percentage of the reduced NO_x) for different temperatures and type of NH_3 pulses. The inlet NO_x feed consisted of 100% NO and the outlet NO_x signal were adjusted for NH_3 influence

Type of pulse[a]	Temperature (°C)			Temperature (°C)		
	200	250	300	200	250	300
	NO_x reduction (%)			Selectivity to N_2O (%)		
5/10	16	33	28	0.9	0.7	2.9
5/5	11	27	41	0.6	1.1	3.4
1/4	17	30	56	0.5	1.2	1.9
5/1	7.1	11	27	0.6	3.1	8.8
1/1	10	16	30	0.4	2.2	8.6
1/0.5	10	13	25	0.4	2.0	10
Continuous	3.6	6.3	18	1.6	9.2	17

[a] 5/10 means 5 min with NH_3 followed by 10 min without NH_3.

Table 3
Average NO_x reduction and N_2O selectivity (formed N_2O in percentage of the reduced NO_x) for different temperatures and type of NH_3 pulses. The inlet NO_x feed consisted of 50% NO and 50% NO_2

Type of pulse[a]	Temperature (°C)					Temperature (°C)				
	200	250	300	400	500	200	250	300	400	500
	NO_x reduction (%)					Selectivity to N_2O (%)				
5/10	63	58	51	37	33	2.4	2.9	4.1	5.0	0.6
5/5	79	82	76	56	51	2.5	3.0	4.0	3.4	0.3
1/4	85	86	77	43	26	2.1	2.0	2.5	3.2	0.5
5/1	81	92	96	91	86	2.7	3.5	4.0	2.5	0.2
1/1	78	93	97	82	63	3.8	3.5	3.4	2.3	0.2
1/0.5	78	92	98	88	81	3.8	3.9	3.6	2.4	0.2
Continuous	81	92	98	99	99	3.4	4.7	4.4	3.2	1.0

[a] 5/10 means 5 min with NH_3 followed by 10 min without NH_3.

Table 4
Average NO_x reduction and N_2O selectivity (formed N_2O in percentage of the reduced NO_x) for different temperatures and type of NH_3 pulses. The inlet NO_x feed consisted of 100% NO_2

Type of pulse[a]	Temperature (°C)		Temperature (°C)	
	200	250	200	250
	NO_x reduction (%)		Selectivity to N_2O (%)	
5/10	63	60	35	38
5/5	70	75	32	40
1/4	68	74	34	42
5/1	76	83	25	38
1/1	73	82	29	41
1/0.5	75	84	26	39
Continuous	77	86	20	37

[a] 5/10 means 5 min with NH_3 followed by 10 min without NH_3.

250 and 300 °C, the same maximum conversion was reached as when NH_3 was removed from the feed in the step response experiments (at 120 min, Fig. 1). At 200 °C, however, the time without NH_3 supply was too short for maximum NO_x conversion to be reached for all pulse cycles. Another interesting observation from the pulse experiments was that the selectivity to N_2O formation was lower for all pulse cycles compared to continuous NH_3 supply.

The effect of increasing the NO_2 fraction of the supplied NO_x was investigated in the pulse response experiments presented in Fig. 4. Increased total NO_x reduction was observed as a result of pulsing the NH_3 supply in the case where the inlet NO_x consisted of 75% NO and 25% NO_2 (Fig. 4A). The improvement was, however, not as high as that observed with 100% NO. For equimolar amounts of NO and NO_2 in the feed (Fig. 4B), transient NH_3 supply resulted in a lower total NO_x reduction, compared to continuous NH_3 supply. The results from experiments performed at five temperatures, 200, 250, 300, 400, and 500 °C, with equimolar amounts of NO and NO_2 as the NO_x source are summarised in Table 3, where the average NO_x conversion and selectivity to N_2O formation are presented. It is clear that continuous NH_3 supply resulted in the highest NO_x conversion at all temperatures and that increased temperature resulted in increased activity. The corresponding data for the case with 100% NO_2 as the NO_x source are presented in Fig. 4C and summarised for 200 and 250 °C in Table 4. Here a considerably higher selectivity to N_2O formation was observed compared to the corresponding experiment with equimolar amounts of NO and NO_2. For the case with only NO_2 as the NO_x source the continuous NH_3 supply showed the highest NO_x reduction activity in combination with the lowest N_2O selectivity compared to all pulse cycles.

3.3. Ammonia adsorption studies

The experiments where NH_3 preadsorbed at 200, 250, and 300 °C reacted with NO and O_2 during a subsequent temperature ramp are presented in Fig. 5. The experiments showed that H–ZSM-5 preadsorbed with NH_3 showed SCR activity already at 50 °C, since the outlet NO_x concentration (top graph) was lower than the inlet NO_x concentration (1000 ppm). Formation of N_2 was observed in analysis of the MS signal $m/e = 28$, which also verified that the SCR reaction occurred. The figure also clearly shows that the NO_x reduction activity of the zeolite was initially higher with higher preadsorption temperature. As the temperature increased, the NO reduction declined and reached a minimum in activity around 130 °C, in all three experiments. Thereafter, the activity increased again and passed through a maximum. The maximum appeared at the lowest temperature for the experiments with NH_3 preadsorbed at 250 and 300 °C. The highest maximum in activity was observed in the experiment with NH_3 preadsorbed at 200 °C, however, the SCR activity remained very low after the minimum until the temperature exceeded 200 °C. Above 200 °C ammonia was found to desorb. The amount of desorbed NH_3 was highest after preadsorption at 200 °C. When comparing the NO and NO_x signals in the three experiments in Fig. 5, it was observed that the NO signal was almost equal to the NO_x signal until no further NO_x reduction was observed, indicating that almost all NO_2 formed reacted with adsorbed ammonia until all ammonia was consumed. Thereafter, the NO response followed the same trend in all three experiments.

The same type of experiments was performed also for equimolar amounts of NO and NO_2 as the NO_x source

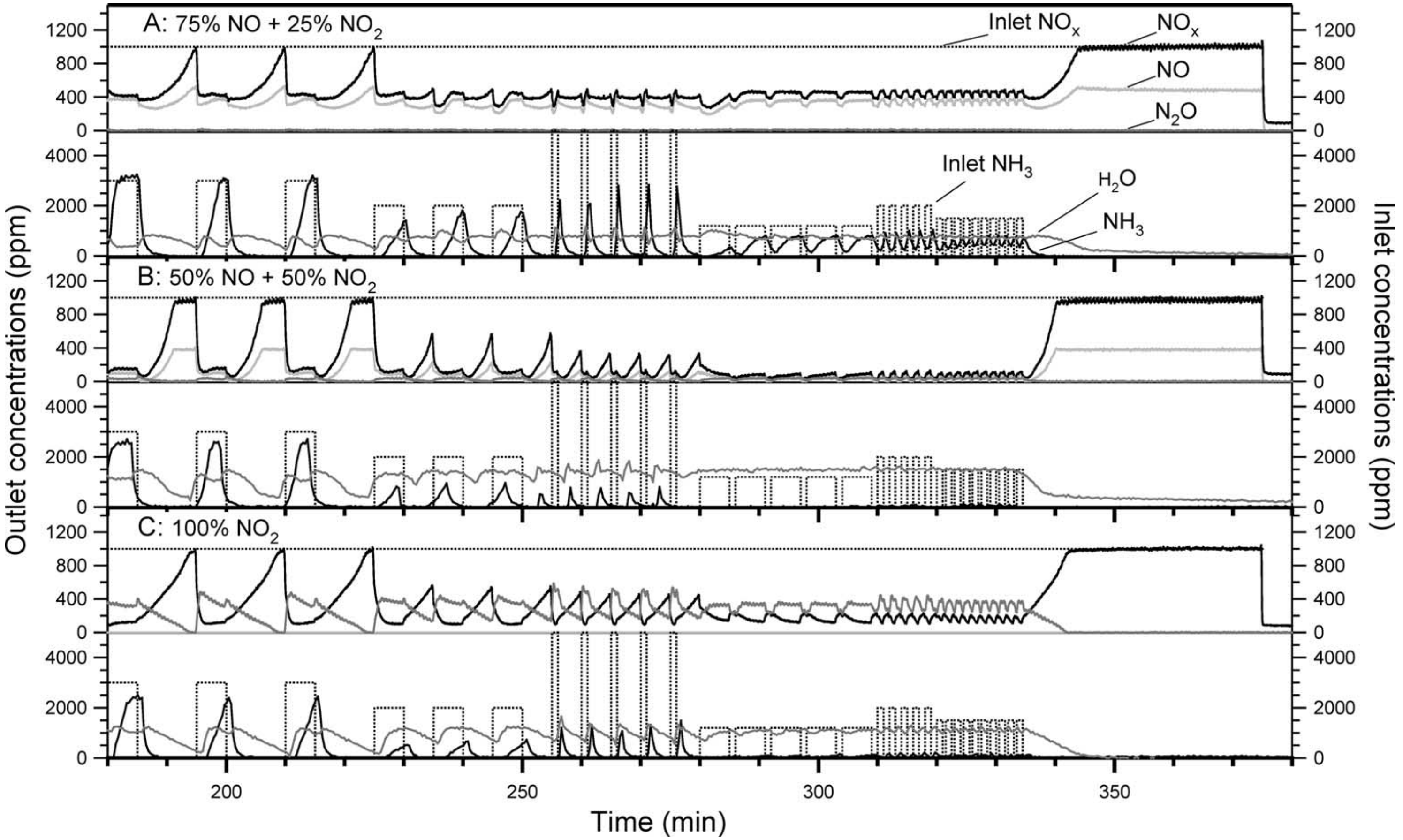

Fig. 4. Pulse responses for outlet concentrations of NO (light grey), NO$_x$ (black), N$_2$O (dark grey curve), NH$_3$ (black curve), and H$_2$O (grey) for six sets of ammonia pulses (dashed line). The experiments were performed at constant temperature 250 °C exposing H–ZSM-5 for 0–5000 ppm NH$_3$, 1000 ppm NO, and 10% O$_2$ with Ar as balance. The inlet consisted of (A) 75% NO + 25% NO$_2$, (B) 50% NO + 50% NO$_2$, and (C) 100% NO$_2$. For pulse characteristics, see Table 1.

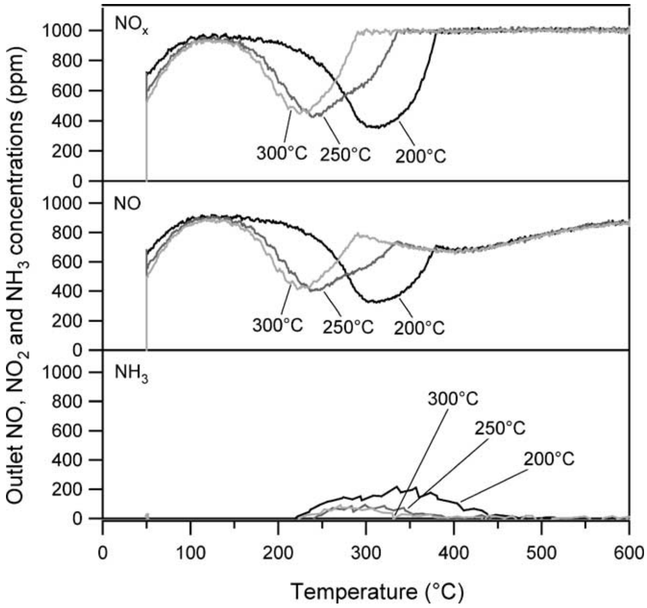

Fig. 5. TPR profiles of NO_x, NO, and NH_3 after preadsorption of NH_3 at 200, 250, and 300 °C for 1000 ppm NO_x (= 1000 ppm NO) and 10% O_2, at a heating rate of 20 °C/min.

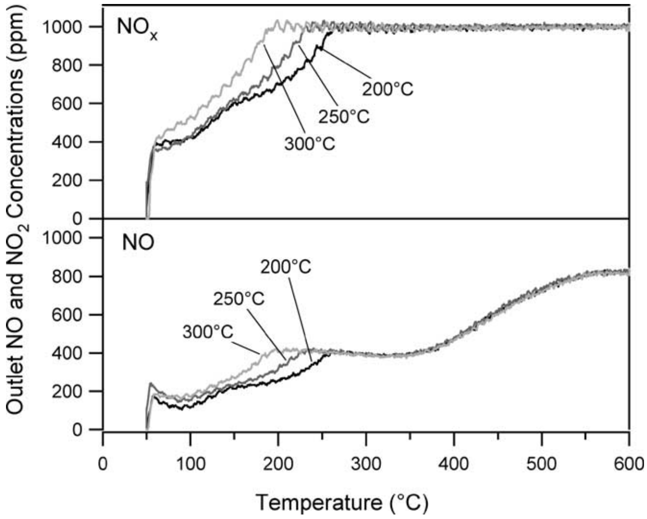

Fig. 6. TPR profiles of NO_x and NO after preadsorption of NH_3 at 200, 250, and 300 °C for 1000 ppm NO_x (= 500 ppm NO + 500 ppm NO_2) and 10% O_2, at a heating rate of 20 °C/min.

(Fig. 6). In these experiments a high NO_x reduction activity was observed already at the lowest temperature of the ramp, 50 °C, which then decreased while the adsorbed ammonia was consumed. In this case the initial NO_x reduction activity seemed to be less dependent on the NH_3 preadsorption temperature. It was observed that the outlet NO concentration was slightly lower than 50% of the total outlet NO_x concentration, meaning that oxidation of NO occurred in the system. When the temperature exceeded 400 °C, the outlet NO:NO_2 ratio followed the thermodynamic equilibrium. At 150 °C, the NO_x concentration levelled out temporarily in the experiment with NH_3 preadsorbed at 200 °C. This was not observed when NH_3 was preadsorbed at 300 or 250 °C.

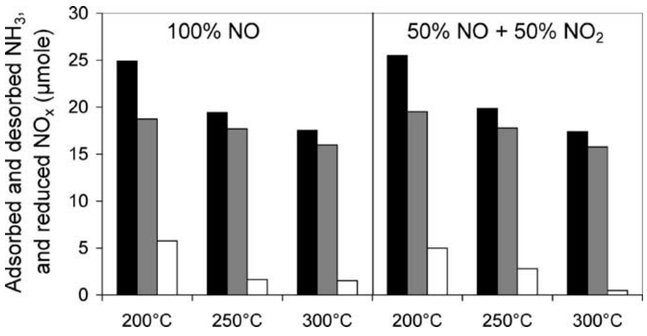

Fig. 7. Amount of adsorbed NH_3 (black), amount of reduced NO_x (grey) and desorbed NH_3 (white) during the temperature ramp in the experiment in Figs. 5 (left) and 6 (right).

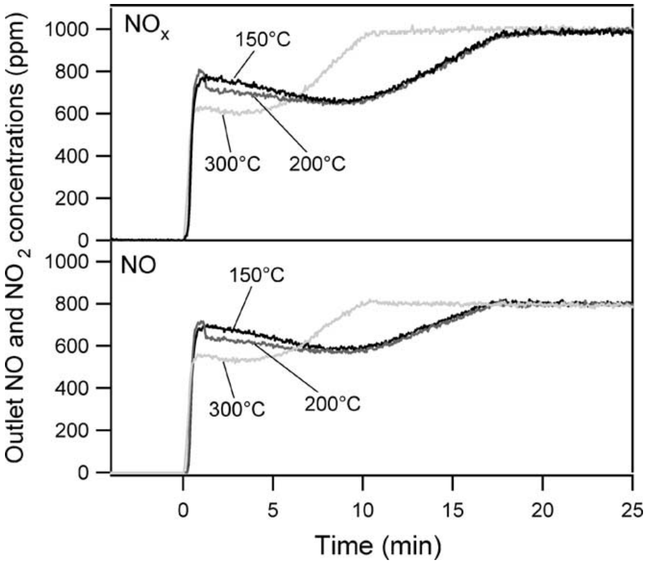

Fig. 8. Reaction of 1000 ppm NO and 10% O_2 at 200 °C over H–ZSM-5 preadsorbed with NH_3 at 150, 200, and 300 °C.

In Fig. 7, the amounts of preadsorbed NH_3 have been calculated from the experiments in Figs. 5 and 6 and are compared with the amount of reduced NO_x calculated from the same experiments. The figure shows that when NH_3 was adsorbed at 250 and 300 °C, roughly 91% of the amount of ammonia adsorbed reacted with the NO_x. However, when the NH_3 was adsorbed at 200 °C the reacted amount of NO_x was approximately 20% less than the amount of adsorbed NH_3. Ammonia desorption peaks starting at 200 °C were observed by MS analysis of m/e signals 17 and 18 (Fig. 5), and the calculated amount of desorbed NH_3 was in good agreement with the observed amount of unreacted NH_3 (Fig. 7).

To further investigate the influence of adsorption temperature, experiments were performed where NO and O_2 reacted at a constant temperature of 200 °C, with NH_3 preadsorbed in the zeolite at three different temperatures: 150, 200, and 300 °C (Fig. 8). A higher NO_x reduction activity was observed for the zeolite preadsorbed with NH_3 at 300 °C compared to the other two experiments, which showed similar activities. In the first few minutes the activity slightly increased in all three experiments and this slow increase in activity was comparable to the slow increase in NO_x reduction after NH_3 was removed in the step response experiment performed at 200 °C (at 30 min in Fig. 1). Additionally the amount of reacted NO in these experiments was very similar to the amount of preadsorbed NH_3.

4. Discussion

The efficiency of zeolite H–ZSM-5 to catalyse the NH_3-SCR reaction was found to be strongly dependent on the relative ratio of NO and NO_2 in the feed. The reaction proceeded with high activity and low selectivity towards N_2O when equimolar amounts of NO and NO_2 were used. When NO was present in excess of NO_2 the reaction proceeded much slower, although with a low selectivity towards N_2O, whereas when NO_2 was in excess the activity was still high, but the selectivity towards N_2O formation was undesirably large. This is in agreement with the high formation of N_2O previously reported for high amounts of NO_2 over zeolite-based catalysts [12,20]. It was further found that, for the cases when NO was in excess, a transient supply of NH_3 increased the activity and selectivity of the SCR reaction. For these cases where NO_2 was in excess of NO the activity was however not improved and the selectivity towards N_2O was increased, with transient supply of ammonia. These results point towards the importance of the NO:NO_2 balance and confirm that the oxidation of NO to NO_2 is the rate determining step of the NH_3-SCR reaction when NO is in excess of NO_2. The improvement by transient supply of NH_3 in these cases suggests that the presence of ammonia in the zeolite hinders the oxidation of NO to NO_2. Blocking the sites for NO oxidation by ammonia is most likely the explanation for this behaviour and it is plausible to assume that the NO oxidation in the zeolite occurs at the Brønstedt acid sites where NH_3 adsorbs as NH_4^+ ions [21,22] and that NH_3 adsorbs more strongly to these sites than NO. Hence, the NO oxidation declines when NH_3 also is present in the zeolite. Another explanation is that physisorbed or weakly bound NH_3 blocks the oxidation sites. It is however most likely that adsorbed NH_4^+ ions hinder the NO oxidation. An indication of this is given by the step response study of NO_x reduction at 300 °C (Fig. 1) where maximal NO_x reduction was not obtained until 5 min after NH_3 was removed from the feed. Physisorbed NH_3 is not likely to be present in the zeolite after this period and still the NO_x reduction increased. When no gas phase NH_3 is present there will be sites available for NO oxidation as soon as NH_4^+ species are consumed in the SCR reaction. An increased number of sites available for NO oxidation will give an increased amount of NO_2 and thus a higher activity for the SCR reaction until the amount of NH_4^+ ions becomes limited. There was also an initial increase in NO_x reduction during the first few minutes in the preadsorption experiments with subsequent NO + O_2 exposure at 200 °C, when no gaseous NH_3 was present in the feed. However, the increase in NO_x reduction was not as pronounced as in the step response experiments and thus hindrance of the NO oxidation by physisorbed or weakly adsorbed NH_3 is also likely to be of importance.

In the case with equimolar amounts of NO and NO_2, however, physisorbed NH_3 present in the zeolite did not inhibit the SCR reaction, since a very high steady-state conversion was observed already at 200 °C and the activity decreased as soon as NH_3 was removed from the feed. This supports the oxidation of NO being the rate-determining step when NO_2 is deficient in the gas mixture.

Even though experiments showed a very high reduction of equimolar amounts of NO and NO_2 there was a time delay for reaching maximal NO_x reduction (Fig. 2B). One explanation for this is that the SCR activity increases with a higher amount of active NH_4^+ species present in the zeolite. Another explanation is that rearrangement of the adsorbed NH_4^+ species into a more active form is rate limiting for the SCR reaction. The adsorbed NH_4^+ ions form either two or three hydrogen bonds with the zeolite sites (referred to as 2H and 3H, respectively) [23] where the 2H structure is more stable at lower temperatures and the 3H structure at higher temperatures. The 3H structure was suggested by Eng et al. to be the more active structure for NO_x reduction [14]. It has also been argued that the time delay may be due to the formation of an intermediate NO_x–NH_4^+ complex [14]. However, after the period without NO_x in the feed (Fig. 2) the NO_x reduction maximum was achieved almost immediately when NO_x was added to the feed. The rate-limiting step should thus be related to the formation of the active NH_4^+ species and not to the formation of the NO_x–NH_4^+ complex.

According to the discussion about different SCR activity between NH_4^+ coordinated in 2H and 3H structures, the adsorption temperature for NH_3 should influence the activity of acidic zeolites. A higher initial NO_x reduction activity was indeed observed in the experiments where NH_3 was preadsorbed at higher temperatures and NO_x was added as NO (see Figs. 5 and 8). However, this effect was not found in the experiment of equimolar addition of NO and NO_2 (Fig. 6), indicating that the type of coordination is of less importance or that a restructuring of 3H to 2H occurs upon lowering the temperature to 50 °C. It points to the higher activity observed in Fig. 5 being due to a higher number of available oxidation sites after preadsorption of NH_3 at higher temperatures. However, a more favourable NH_4^+ coordination with higher adsorption temperature cannot be ruled out as an explanation for the higher SCR reaction at 200 °C (Fig. 8).

It was found in the TPR experiments that a considerably higher amount of NH_3 was adsorbed than reacted when NH_3 was preadsorbed at 200 °C, compared to 250 and 300 °C. It was also observed in the TPR experiment that with ammonia preadsorbed at 200 °C, the activity after the oxidation minimum remained low below 200 °C (Fig. 5). These observations support that the weakly bound NH_3 does not react in the SCR reaction but hinders the NO oxidation. They are also in agreement with TPD results by Lónyi et al. [24], who showed that NH_3 was bound to NH_4^+ species forming $NH_4^+ (NH_3)_n$ after NH_3 adsorption in H–ZSM-5 at 150 °C but not at 250 °C. In the present study it was further found that the amounts of reduced NO_x and preadsorbed NH_3 were almost equal when NO and O_2 reacted at 200 °C; see Fig. 8. This observation suggests that it is possible also for the weakly bound NH_3 to react at 200 °C, probably via rearrangement into more active species.

Low temperature NH_3-SCR activity of NO_x over H–ZSM-5 has previously been reported to show an optimum around 30–40 °C in the temperature range of 0–100 °C [17]. This is consistent with the minimum in NO_x reduction activity observed at 130 °C in the TPR experiments. The minimum is most likely related to the NO oxidation capacity of the zeolite since this minimum was not observed for the case with equimolar amounts of NO and NO_2. The oxidation of NO over H–ZSM-5 has previously been reported to proceed via a minimum in the same temperature range [21]. When the oxidation of NO increases after the minimum, an increasing amount of NH_4^+ ions is consumed in the SCR reaction resulting in more available active sites for NO oxidation, which further increases the SCR activity until the number of NH_4^+ ions becomes limited and the SCR activity decreases.

5. Concluding remarks

The effects of transient NH_3 supply on the selective catalytic reduction of NO_x over H–ZSM-5 were investigated using flow reactor experiments between 200 and 500 °C. With continuous NH_3 supply the highest NH_3-SCR activity was observed with equimolar amounts of NO and NO_2 in the feed. For inlet NO:NO_2 molar ratios > 1, the activity for NO_x reduction transiently increased when NH_3 was removed from the feed, and by pulsing NH_3 to the feed the activity for NO_x reduction was enhanced up to five times compared to continuous supply of NH_3. Also the selectivity towards N_2O formation was lower with transient supply of NH_3. For NO:NO_2 ratios $\leqslant 1$, however, the same experiment showed a decreased NO_x reduction activity. The selectivity towards N_2O formation was also low for equimolar amounts of NO and NO_2 and high when the NO_x was supplied as NO_2, independent of the pulse type. These results strongly indicate that the oxidation of NO is the rate-determining step in the NH_3-SCR reaction over H–ZSM-5 for NO:NO_2 ratios higher than one. The presence of NH_3 in the zeolite was concluded to suppress the activity for NO oxidation and consequently the SCR activity.

Temperature programmed reaction experiments with preadsorbed NH_3 showed the highest initial NO_x reduction activity after ammonia adsorption at high temperatures. From these results it was however not possible to conclude whether the high activity was a result of a higher number of NO oxidation sites available or more favourably bound NH_3 present in the zeolite after preadsorption at high temperatures. A minimum in the activity for NO_x reduction was observed at 130 °C independent of the ammonia preadsorption temperature. The minimum is most likely connected with the previously observed minimum in NO oxidation activity over H–ZSM-5 around this temperature.

Acknowledgments

This study was performed within the LOTUS-project, which is financially supported by the European Commission (Contract GRD1-1999-11135), and partly within the Competence Centre for Catalysis, which is funded by Chalmers University of Technology, the Swedish Energy Agency, and the following member companies: AB Volvo, Johnson Matthey-CSD, Saab Automobile AB, Perstorp AB, Akzo Nobel Catalysts BV, Swedish Space Corporation, and MTC AB.

References

[1] M. Koebel, M. Elsener, M. Kleemann, Catal. Today 59 (2000) 335.
[2] R.M. Heck, Catal. Today 53 (1999) 519.
[3] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B-Environ. 18 (1998) 1.
[4] E. Ito, R.J. Hultermans, P.M. Lugt, M.H.W. Burgers, H. van Bekkum, C.M. van den Bleek, Stud. Surf. Sci. Catal. 96 (1995) 661.
[5] J.A. Sullivan, J. Cunningham, M.A. Morris, K. Keneavey, Appl. Catal. B-Environ. 7 (1995) 137.
[6] S. Kieger, G. Delahay, B. Coq, B. Neveu, J. Catal. 183 (1999) 267.
[7] R.Q. Long, R.T. Yang, J. Catal. 186 (1999) 254.
[8] B. Coq, M. Mauvezin, G. Delahay, J.B. Butet, S. Kieger, Appl. Catal. B-Environ. 27 (2000) 193.
[9] B. Ramachandran, R.G. Herman, S. Choi, H.G. Stenger, C.E. Lyman, J.W. Sale, Catal. Today 55 (2000) 281.
[10] T. Seiyama, T. Arakawa, T. Matsuda, Y. Takita, N. Yamazoe, J. Catal. 48 (1977) 1.
[11] J.R. Kiovsky, P.B. Koradia, C.T. Lim, Ind. Eng. Chem. Prod. Res. Dev. 19 (1980) 218.
[12] J.G.M. Brandin, L.A.H. Andersson, C.U.I. Odenbrand, Catal. Today 4 (1989) 187.
[13] E.Y. Choi, I.S. Nam, Y.G. Kim, J. Catal. 161 (1996) 597.
[14] J. Eng, C.H. Bartholomew, J. Catal. 171 (1997) 27.
[15] T. Komatsu, T. Ueda, T. Yashima, J. Chem. Soc.-Faraday Trans. 94 (1998) 949.
[16] S.A. Stevenson, J.C. Vartuli, C.F. Brooks, J. Catal. 190 (2000) 228.
[17] D. Roberge, A. Raj, S. Kaliaguine, D. Trong On, S. Iwamoto, T. Inui, Appl. Catal. B 10 (1996) L237.
[18] M. Richter, R. Eckelt, B. Parlitz, R. Fricke, Appl. Catal. B 15 (1998) 129.
[19] S.A. Stevenson, J.C. Vartuli, J. Catal. 208 (2002) 100.
[20] G. Delahay, B. Coq, S. Kieger, B. Neveu, Catal. Today 54 (1999) 431.
[21] I. Halasz, A. Brenner, K.Y. Simon Ng, Catal. Lett. 34 (1995) 151.
[22] F. Lónyi, J. Valyon, Micropor. Mesopor. Mater. 47 (2001) 293.
[23] E.H. Teunissen, R.A. Van Santen, A.P.J. Jansen, F.B. Van Duijneveldt, J. Phys. Chem. 97 (1993) 203.
[24] F. Lónyi, J. Valyon, Thermochim. Acta 373 (2001) 53.