DeNO$_x$ reactions on Cu-zeolites
Decomposition of NO, N$_2$O and SCR of NO by C$_3$H$_8$ and CH$_4$ on Cu-ZSM-5 and Cu-AlTS-1 catalysts

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Abstract

Cu-ZSM-5 and Cu-AlTS-1 catalysts were prepared by solid state ion exchange and studied in DeNO$_x$ reactions. A NO$_3$ type surface complex was found to be an active intermediate in the decomposition of NO and N$_2$O. Copper was oxidized to Cu^{2+} in the decomposition reactions. Oscillations at full N$_2$O conversion were observed in the gas phase O$_2$ concentration, without any change in the N$_2$ concentration. The oscillation was synchronized by gas phase NO formed from the NO$_3$ complex. The same complex seems to be an active intermediate also in NO selective catalytic reduction (SCR) by methane, whereas carbonaceous deposits play a role in NO SCR by propane. TPD reveals that only 10–20% of the total copper in the zeolites participates in the catalytic cycles. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cu containing zeolites are active in DeNO$_x$ reactions, both in the decomposition and selective catalytic reduction (SCR) by hydrocarbons. Despite the extensive research work in this field the mechanism is still not fully understood and there is a lack in the elucidation of the similarities and differences in the two types of reactions. In the present work we studied the decomposition of N$_2$O and NO as well as SCR of NO by hydrocarbons on the same catalysts using transient kinetic studies combined with in situ temperature programmed desorption of the intermediates.

2. Experimental

Parent zeolites of different Al and Ti content were synthesized using propylamine template. Cu was ion-exchanged into the NH$_4^+$ form of the zeolites from CuCl$_2$·2H$_2$O by using solid state ion exchange. The mixed powders of the zeolite and the copper salt were heated in a stream of nitrogen up to 550 °C using 10 °C/min heating rate and keeping at constant temperature for 2 h. The ion exchange was monitored by measuring continuously the amount of HCl formed. After having cooled the samples were washed with water until no Cl$^-$ was detected in the water. Part of the samples was dissolved in HF and the Cu, Al and Na contents were measured by atomic absorption spectroscopy (AAS). The catalysts are marked as a

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combination of the Si/Al ratio and the exchange level (100% exchange means $Cu/NH_4^+ = 0.5$). Three catalysts were tested in DeNO$_x$ reactions. Two of them were Cu-ZSM-5 with Si/Al = 24 ($NH_4^+ = 0.67$ mmol/g) and $Cu/NH_4^+ = 0.66$ and 0.44, marked as Cu-ZSM-5-24-132 and Cu-ZSM-5-24-88, respectively. The third one was Cu-AlTS-1 with Si/Ti = 82, Si/Al = 55 ($NH_4^+ = 0.29$ mmol/g) and $Cu/NH_4^+ = 0.7$, marked as Cu-AlTS-1-55-140.

The reactions were performed in a fixed-bed quartz tubular flow reactor with 4 mm i.d. About 160 mg of catalyst of the 0.25–0.5 mm sieve fraction was placed between quartz wool plugs. Gas flow rates of 20–40 ml/min were applied. Premixed gases of 1.96% NO/Ar, 1.78% C_3H_8 + 3.8% O_2 in Ar, 2% CH_4/Ar, 2.01% N_2O/Ar and pure O_2 and Ar were further mixed by mass flow controllers. The reaction products were analyzed by a QMS interfaced to the reactor via a differentially pumped capillary and an orifice. FT-IR with a flow through cell was used to distinguish between N_2 and CO as well as CO_2 and N_2O. The reactor could be temperature programmed to perform in situ TPD measurements. In every case the heating rate was 10 °C/min. Details are given in [1–3].

The sequence of the catalytic tests was the following. First the catalyst was heated in 20 ml/min Ar to 600 °C, cooled to 500 °C and contacted with 20 ml/min 1.96% NO/Ar. This is called as first contact with NO. The temperature was stepwise decreased to 200 °C, the gas was switched to 20 ml/min Ar and TPD was started with final temperature of 600 °C. The cycle was repeated several times. After the NO decomposition the N_2O decomposition was studied in a similar way using 20 ml/min 2.01% N_2O/Ar. This was followed by SCR by C_3H_8 and CH_4 using 40 ml/min 0.9% C_3H_8 + 1% NO + 4.4% O_2 balance Ar and 40 ml/min 1% CH_4 + 1% NO + 2.5% O_2 balance Ar mixtures, respectively.

3. Results and discussion

3.1. Decomposition of NO

For the Cu-ZSM-5-24-132 catalyst the first contact with NO at 500 °C is given in Fig. 1. Similar curves were obtained for the other catalysts too. All three
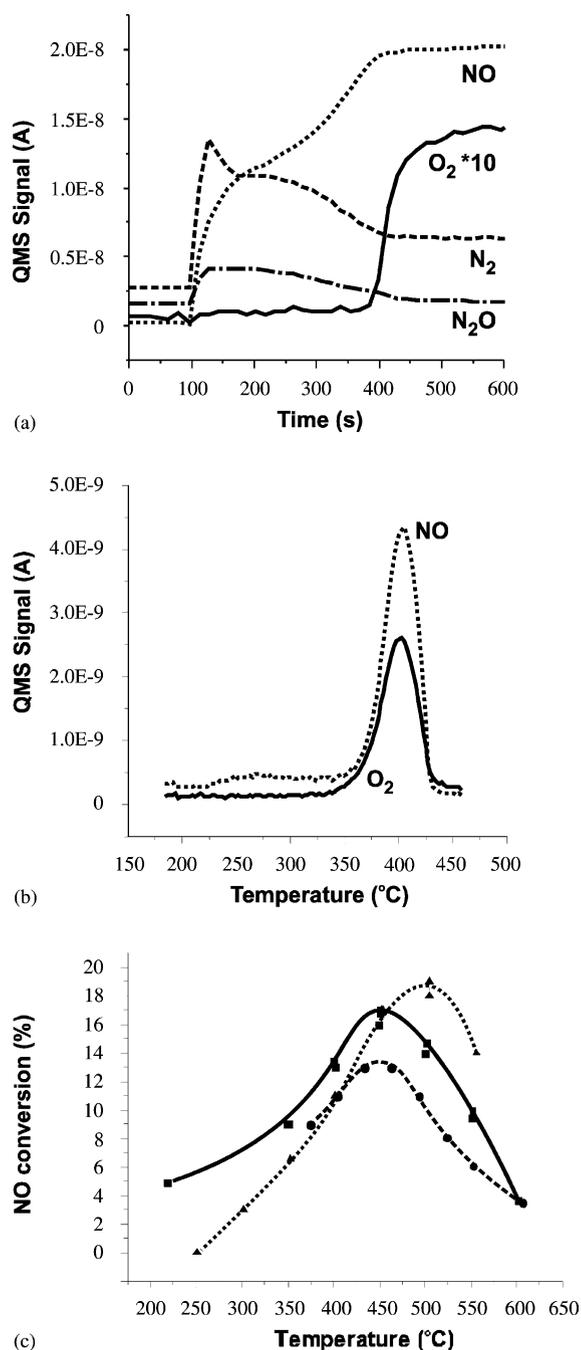
Fig. 1. NO decomposition: (a) first contact of Cu-ZSM-5-24-132 catalyst with 20 ml/min 1.96% NO at 500 °C; (b) TPD after NO decomposition on Cu-ZSM-5-24-132, 20 ml/min Ar 10 °C/min ramp; (c) steady state NO conversion in 20 ml/min 1.96% NO/Ar. (■) Cu-ZSM-5-24-132; (●) Cu-ZSM-5-24-88; (▲) Cu-AlTS-1-55-140.

Table 1
Quantification of the transients and TPDs

Catalyst	Missing O_2 in first NO contact, O_2/Cu	NO TPD		TOF $\times 10^3$, NO/Cu $\times$ s	N_2O TPD		TPD after NO SCR by propane			TPD after NO SCR by methane	
		NO/Cu	O_2/Cu		NO/Cu	O_2/Cu	CO/Cu	CO_2/Cu	NO/Cu	NO/Cu	O_2/Cu
Cu-ZSM-5-24-132	0.15	0.18	0.17	0.72	0.12	0.15	0.04	0.14	0		
Cu-ZSM-5-24-88	0.2	0.18	0.18	1.28	0.09	0.12	0.09	0.17	0	0.19	0.16
Cu-AlTS-1-55-140	0.23	0.29	0.27	1.7	0.18	0.20	0.14	0.26	0.12	0.18	0.18

catalysts take up a substantial amount of oxygen indicated by the delay of the oxygen signal. The same time there is a transient N_2O formation and an overshoot in N_2. These transients indicate a change in the oxidation state of copper. An estimation of the missing oxygen given in Table 1 results in 0.15–0.23 O_2/Cu, i.e. a substantial amount of the copper in the catalyst is oxidized. Copper is stabilized in this oxidized state as this type of transient is observed only after NO SCR by propane in the rich conditions (not presented in this paper), when the reaction mixture is reductive. This also means that during NO decomposition only a small fraction of the copper might be present as Cu^+.

A typical TPD curve after NO decomposition is given in Fig. 1b. NO and O_2 form at about 400–420 °C in equal amounts, which is explained by the decomposition of a NO_3 type surface complex [1]. This complex seems to be an active intermediate in the reaction [3] as NO conversion has a maximum at about 450–500 °C (see Fig. 1c), which is slightly above the decomposition of this complex. TOF values at maximum NO conversion shown in Table 1 do not support the role of copper dimers as active centers in the decomposition of NO as TOF in the over-exchanged catalyst is less than in the 100% exchanged one. The possible role of the acidity is indicated by the high TOF for the Cu-AlTS-1 catalyst, which is more acidic than Cu-ZSM-5.

3.2. Decomposition of N_2O

On all three catalysts there is a complete decomposition of N_2O into N_2 and O_2 at about 400 °C (see Fig. 2) which is just the starting temperature for NO decomposition. TPD after the N_2O decomposition is similar to the one measured after NO decomposition. The only differences are that there is a slight excess in oxygen as given in Table 1 and the O_2 peak is slightly broader than the NO one. This indicates that besides the NO_3 type complex there is some other type of oxygen present in a small amount. In this reaction the NO_3 type complex is also an active intermediate, which is proved by the isothermal transient at 406 °C given in Fig. 3a. On switching from Ar to the reaction mixture there is a complete decomposition of N_2O in the first few seconds of the reaction
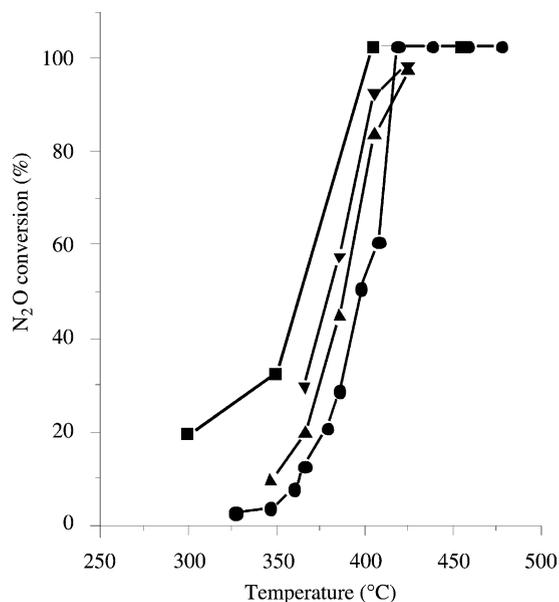
Fig. 2. N_2O decomposition in 20 ml/min 2.01% N_2O/Ar. (■) Cu-ZSM-5-24-132; (●) Cu-ZSM-5-24-88; (▲) Cu-AlTS-1-55-140; (▼) N_2O + NO, Cu-AlTS-1-55-140.

when a small amount of copper is oxidized. This is rather a stoichiometric surface reaction than a catalytic one. As copper is oxidized the N_2O decomposition slows down indicated by the increase of N_2O and decrease of N_2 signals. Simultaneously the oxygen containing surface complex builds up and stable catalytic activity develops. As the amount of the complex is sensitive to the reaction conditions any change results in a disturbance as shown in Fig. 3b. On changing the flow rate from 20 to 40 ml/min and back to 20 ml/min there are overshoot and undershoot type changes in the O_2, N_2 and N_2O signals. This sensitivity results in oscillations in the O_2 and NO gas phase concentrations at full N_2O conversion given in Fig. 4 for the Cu-AlTS-1-55-140 catalyst. In contrast to reports in the literature [4–8] in our case not the reaction rate itself but the amount of the surface complex changes as there is no oscillation in the N_2O and N_2 signals. Synchronization is via the gas phase NO concentration evidenced by the phase shift between the O_2 and NO oscillations. Even traces of NO added completely quench the oscillation [9], although it has no effect on the N_2O conversion itself (see Fig. 2).
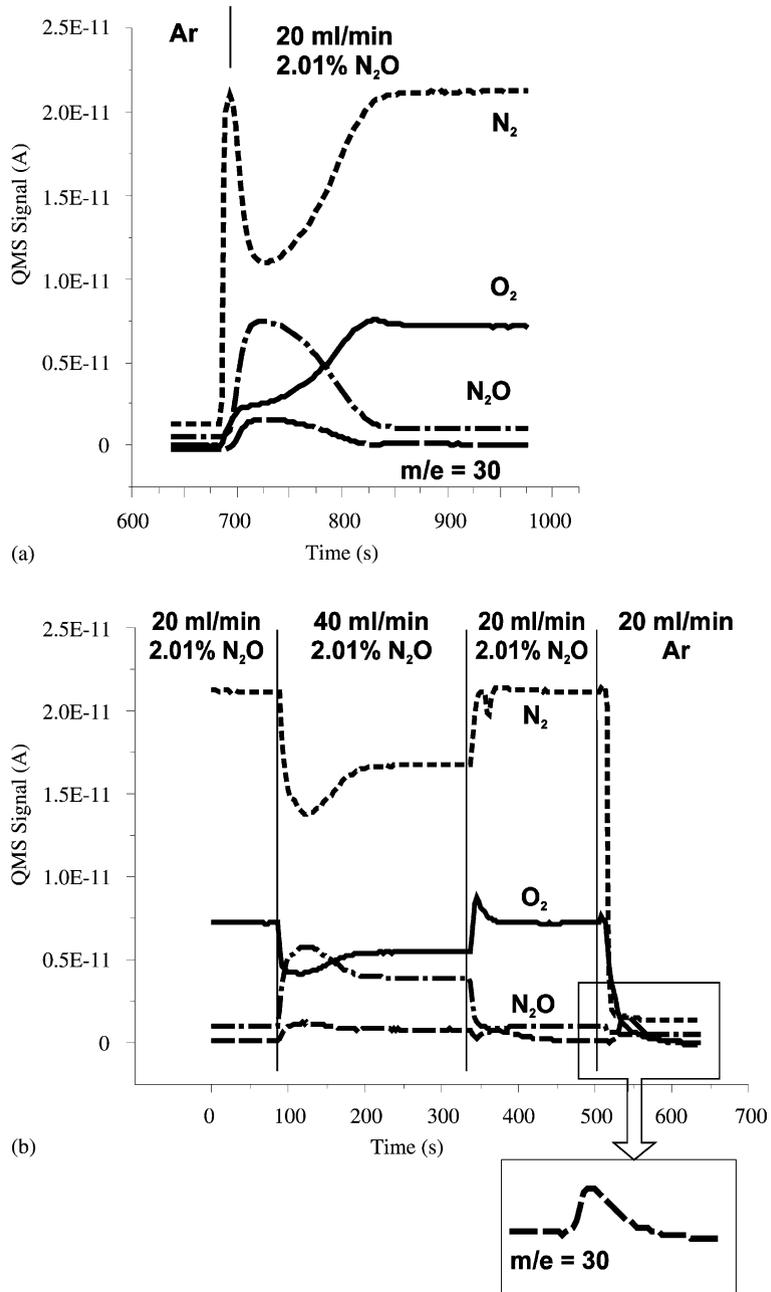
Fig. 3. Isothermal transients in N$_2$O decomposition on Cu-ZSM-5-24-88 at 406 °C: (a) change from 20 ml/min Ar to 20 ml/min 2.01% N$_2$O/Ar; (b) flow rate changes.
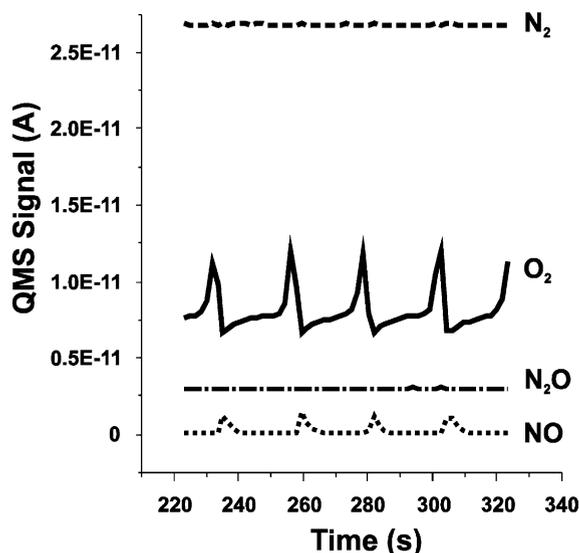
Fig. 4. Oscillations at full N_2O conversion on Cu-AlTS-1-55-140.

3.3. NO SCR by propane

Propane and NO conversions vs. temperature are shown in Fig. 5a. For all three catalysts the NO conversion shows a maximum at about 320–370 °C. The shape of the curves is similar to that already reported in the literature [10–12], but the maximum in NO conversion is 80–100%. TPD after the reaction (Fig. 5b) proves that both oxygen containing surface species and carbonaceous deposits are on the surface. Their amounts are given in Table 1. No oxygen desorption was observed and NO desorbed only from the Cu-AlTS-1-55-140 catalyst. Isothermal transients on switching from Ar to the reaction mixture showed a delay in the NO signal indicating the formation of NO containing surface complex.

3.4. NO SCR by CH4

CH$_4$ and NO conversions vs. temperature are given in Fig. 6a. Here again NO conversion has a maximum but at much higher temperature than for SCR by propane and the conversion maximum is also much lower being only about 20%. TPD after the reaction (Fig. 6b) also shows different characteristics as only NO and O$_2$ evolves without CO and CO$_2$. Amounts are given in Table 1. This clearly shows that the
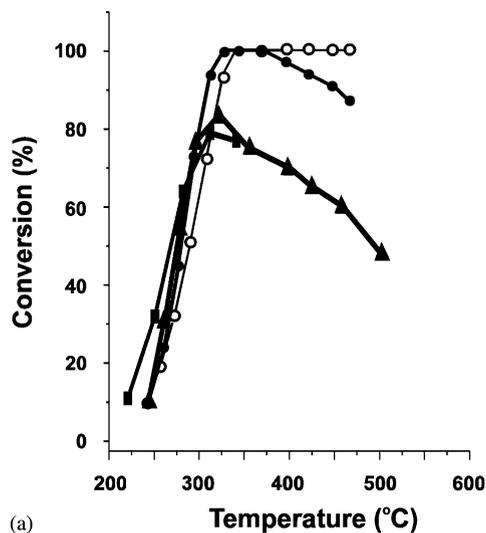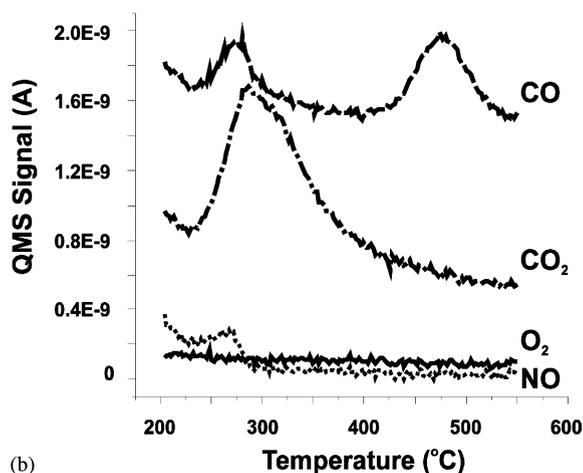
Fig. 5. NO SCR by propane: (a) NO conversion vs. temperature. (■) Cu-ZSM-5-24-132; (●) Cu-ZSM-5-24-88; (▲) Cu-AlTS-1-55-140; (○) Cu-ZSM-5-24-88, C_3H_8 conversion. Conditions: 40 ml/min flow rate, 0.9% C_3H_8 + 1% NO + 4.4% O_2 and balance Ar. (b) TPD after NO SCR by propane on Cu-ZSM-5-24-132, 20 ml/min Ar, 10 °C/min ramp.

active centers are different in the SCR by propane and methane. Their structure is probably similar to the ones active in the decomposition reactions indicated by the similar amounts of NO and O_2. The function of methane is not quite clear as the NO conversion vs. temperature curves are similar but not identical to the methane free NO decomposition. Further work is needed to clear the problem.

for the decomposition of NO and N_2O is at different temperature sides of the stability of the complex resulting in different sensitivity of the reactions to the state and amount of this complex. Oscillations in the N_2O decomposition are also explained by the stability of the complex. Most probably this complex plays a role in NO SCR by methane, whereas in NO SCR by propane NO containing carbonaceous complex is part of the active center.

Fig. 6. NO SCR by methane: (a) conversion vs. temperature. (■) NO, Cu-ZSM-5-24-88; (●) CH_4, Cu-ZSM-5-24-88; (▲) NO, Cu-AlTS-1-55-140; (▼) CH_4, Cu-AlTS-1-55-140. Conditions: 40 ml/min flow rate, 1% CH_4 + 1% NO + 2.5% O_2 and balance Ar. (b) TPD after NO SCR by methane on Cu-ZSM-5-24–88, 20 ml/min Ar, 10 °C/min ramp.

4. Conclusions

There are similarities in the decomposition of NO and N_2O as an NO_3 type surface complex is the active intermediate in both reactions. The temperature range

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