Decomposition and selective catalytic reduction of NO by propane on CuZSM-5 zeolites: a mechanistic study

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Abstract

NO decomposition and selective catalytic reduction (SCR) of NO by propane in oxygen were compared over Cu-ZSM-5 with various Si/Al ratios and extent of exchange. It was established that the turnover frequency (TOF) values referred to copper ions species characterized by NO desorption, are independent of the Si/Al ratio and the extent of exchange. The presence of propane and oxygen accelerates N_2 formation and higher conversion can be reached at lower temperature. TPD experiments indicate that the $Cu^{2+}(O)(NO)(NO_2)$ surface complex, which is formed as an intermediate in the decomposition of NO, is not the active pathway in SCR. In SCR of NO by propane in the presence of oxygen, the first step is Cu(I) to Cu(II) conversion by oxygen. NO_2 formation is facilitated by Cu(II) species, which react with propane forming a nitrito–propane compound. Its result in N_2 formation at a lower temperature than what is required for decomposition of NO. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last few years, NO decomposition over Cu-ZSM-5 zeolites have been reported in numerous papers [1–8]. In a review article, Centi and Perathoner [9] detailed all information available till 1995 on NO interactions with various catalyst systems. Still there is an uncertainty whether special Cu–O–Cu pairs [10] or individual Cu ions in a special environment are the active species [11]. Generally, it was found that by decreasing Si/Al ratio the activity increases and with the same Si/Al ratio it goes through a maximum at about Cu/Al = 0.5 exchange level. As there are still conflicting data in the nature of the reaction site, the mechanism of the reaction is also not fully understood. Notably, there are different views on the formation of dinitrogen molecules in

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high modulus zeolites in which the majority of the copper sites is separated.

NO decomposition is an attractive process but under real conditions — in large excess of O_2 and in about 10 vol.% H_2O — the activity of Cu-ZSM-5 declines. Selective catalytic reduction (SCR) of NO by hydrocarbons is another important process as the light-off temperature is 200 K lower and under this condition the hydrothermal stability of Cu-ZSM-5 is also better. It is believed that in the SCR by C_3H_8 over Fe-ZSM-5, a nitrogen containing organic deposit is formed on the catalyst and it reacts with NO_2 formed in excess O_2 [12]. The N_2 yield goes through a maximum at about 570 K.

In this work, we compare the NO decomposition and SCR of NO with propane on Cu-ZSM-5 catalysts with Cu/Al = 0.3–1 prepared by solid state ion exchange of $CuCl_2$ into H-ZSM-5 of Si/Al = 25 and 41. Our goal is to identify the possible common steps and catalytic sites in the two different reactions.

2. Experimental

2.1. Catalyst preparation

Na-ZSM-5 with 25 and 41 Si/Al ratios were prepared in the presence of propilamine template. The as-synthesized zeolites were calcined in air at 823 K to remove the template and transformed into the NH_4-ZSM-5 form. The ion exchange capacities were 0.643 and 0.396 mmol/g, respectively. The NH_4-ZSM-5 forms were decomposed in air at 773 K to obtain H-ZSM-5. Calculated amounts of $CuCl_2$ $2H_2O$ and H-ZSM-5 were homogenized in an achat mortar, heated by 10 K/min in a quartz tube in dry N_2 to 873 K and kept isothermal for 3 h. The exchange was followed by measuring the HCl in the gas flow. Finally, the samples were washed until no Cl^- ion was detected in the liquid phase. The catalysts are marked as a combination of the Si/Al ratio and the exchange level (100% exchange means Cu/Al = 0.5), e.g. 25-140 means Si/Al = 25 and 140% exchange. One sample (25-100-NH_4^+) was prepared directly from the NH_4-ZSM-5 form. The

exchange temperature for the 25-200 sample was only 823 K.

2.2. Catalytic reactions

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. The gas flow rates of 20–23 ml/min were applied. Details are described in Ref. [11]. Premixed gases of 1.96% NO/Ar, 1.78% C_3H_8 + 3.8% O_2 in Ar, 1.1% CO/Ar, and pure Ar were further mixed by mass flow controllers. Although the initial purity of the NO/Ar supplied by BOC was N4.9, during 9 years of use some N_2O formed in the cylinder at room temperature. A Spectramass PC2000 quadrupole mass spectrometer (QMS) in multiple ion detection mode was applied for analysis. It was interfaced to the reactor via a differentially pumped capillary and an orifice. This arrangement assured a linear response of the QMS signal to the gas concentration and the system was calibrated using known gas mixtures. FT-IR with a flow through gas cell was applied to analyze N_2 and CO (which can be measured at the same m/e = 28 value) and the CO_2 and N_2O (appears at m/e = 44), which are expected to form in the SCR of NO with C_3H_8.

The catalysts were first heated in Ar to 470 K at the rate of 5 K/min to avoid any disruption of the zeolite. They were further heated to 870 K at a 10 K/min rate and this rate was applied in all other cases. After 2 h at 870 K, the catalysts were cooled in Ar to 770 K and the flow was switched for 20 ml/min 1.96% NO/Ar mixture. This is called as first contact with NO. The NO conversion was measured as a function of temperature during stepwise heating and cooling. Isothermal transients were measured by switching several times from NO/Ar to pure Ar and back to NO/Ar. The catalyst was cooled in the reaction mixture to 470 K for temperature-programmed desorption (TPD) measurement. Then, the system was purged using Ar and was heated by 10 K/min ramp rate in 20 ml/min Ar to 870 K. In the SCR, a mixture of NO/Ar, C_3H_8 + O_2/Ar, and Ar was applied to give 23 ml/min total gas flow with 0.77% NO + 0.85% C_3H_8 + 1.82%
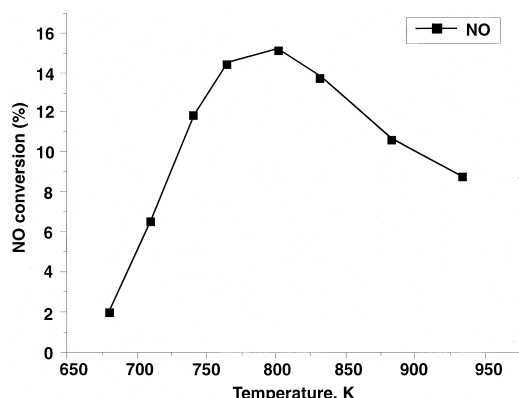
Fig. 1. NO decomposition on the 41-144 catalyst.

O_2 balance Ar composition. For the C_3H_8 oxidation, the NO/Ar stream in the above mixture was replaced for pure Ar. In both cases, the catalyst was cooled in the reaction mixture before TPD.

3. Results

3.1. NO decomposition, C_3H_8 oxidation and selective catalytic reduction (SCR) of NO with C_3H_8

In order to obtain deeper insight into the mechanism of the selective catalytic reduction of NO with propane, the reactions are investigated separately. The NO decomposition on Cu-ZSM-5 sample is studied first. The general shape of the NO conversion vs. temperature curve measured over 41-144 Cu-ZSM-5 sample is presented in Fig. 1. The H-

ZSM-5 zeolite sample without copper is inactive. Similar to earlier experiments [11], there is a maximum rate in NO conversion in the range between 790 and 820 K. The position of the maximum is independent of the Si/Al ratio and of the copper content. Above 700 K, N_2 and O_2 are the only products formed. The calculated mass balance is correct within 10%. Below 670 K, N_2O formation is also observed. In Table 1, the maximum values in NO conversions are given (see row 1). The turnover frequency (TOF) data are calculated in mol of NO reacted per second at the maximum conversion divided by the mol of Cu in the sample and are shown in Table 1 (row 2). The lowest TOF value was obtained on the samples containing copper ions exchanged to 200% extent. This is indicative of a large fraction of Cu sitting in an unfavorable position for catalysis in largely over-exchanged samples, whereas the TOF is the highest on the catalyst with the 25-100 sample prepared directly from NH_4-ZSM-5 zeolite. For other catalysts the TOF value has a slight maximum at around 100-140% exchange. In all catalysts the TOF is in the order of 10^{-3} indicating that only a fraction of the Cu ions is active in the NO decomposition.

In the next experiments, the propane oxidation in the absence of NO was studied. In Fig. 2, a typical conversion vs. temperature curve is presented for propane oxidation on the 41-144 sample. H-ZSM-5 is totally inactive in this reaction up to 700 K. Conversions of propane oxidation at 578 K for the catalysts are given in Table 2. The propane conversion at 587 K is about 30% on the 25-200, 25-140

Table 1
NO decomposition,[a] TPD and TOF[b]

Catalyst	25-200	25-140	25-100	25-100[c]	25-60	41-202	41-144	41-100
Maximum NO conversion (%)	34	29	33	46	14	7	22	9.2
TOF $\times 10^3$	0.9	1.5	1.7	2.4	1.2	0.3	1.3	0.7
TPD after NO reaction								
Peak temperature (K)	689	708	704	704	710	690	709	706
mol NO mol Cu^{-1}	0.15	0.17	0.20	0.28	0.15	0.07	0.14	0.07
mol O_2 mol Cu^{-1}	0.21	0.19	0.21	0.31	0.11	0.11	0.19	0.07
Modified TOF $\times 10^{3d}$	5.8	8.6	8.4	8.5	8.1	4.2	8.9	11.1

[a] Conditions: 160 mg catalysts in 1.96% NO/Ar at 20 ml/min flow rate.

[b] mol NO s^{-1} mol Cu^{-1} at maximum NO conversion.

[c] From NH_4-ZSM-5.

[d] mol NO s^{-1} mol NO^{-1} (desorbed in TPD) at maximum NO conversion.

Fig. 2. Propane oxidation on the 41-144 catalyst.

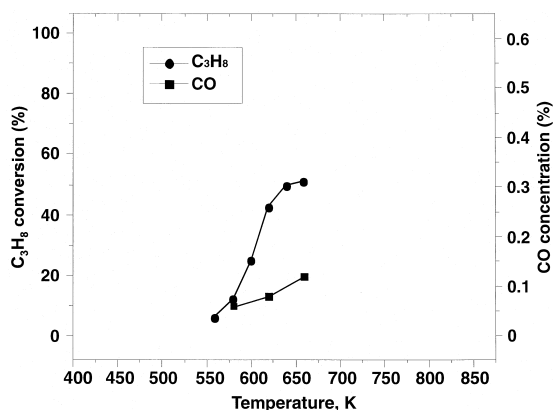Fig. 3. SCR of NO by propane on the 41-144 catalyst.

and both 25-100 catalysts, while for the other samples only about 15% conversion is measured. The CO formation starts already at low propane conversion at 580 K and its concentration increases with increasing temperature. The maximum conversion of propane is 57.2% calculated from the oxygen concentration supposing complete oxidation. When oxygen is fully consumed, the conversion of propane continues to increase slightly at the expense of CO_2.

In Fig. 3, a typical conversion vs. temperature curve is presented for the SCR of NO by propane over the 41-144 sample. The propane conversion at low temperature is independent of whether NO is in
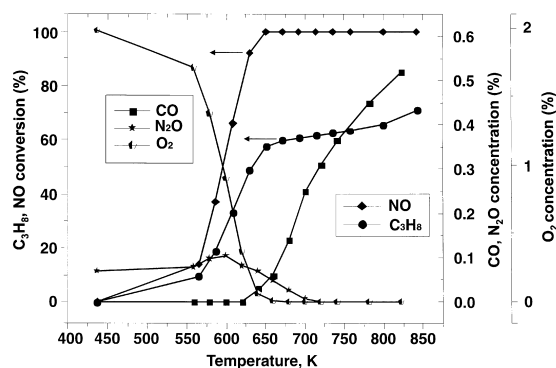
the gas mixture, whereas at a higher temperature the conversion is higher if NO is present. The formation of CO shifts by about 130 K towards higher temperature where the NO conversion is already high. These suggest that in the propane oxidation O_2 can be replaced by oxygen from NO. The NO conversion starts simultaneously with propane oxidation and reaches 100% at about 630 K when the total amount of oxygen is consumed. When the temperature is raised, there is no change in the NO conversion and neither N_2O nor NO_2 forms. This is a marked contrast to Fe-ZSM-5 catalysts [13] where NO conversion passes through a maximum rate and the selectivity to nitrogen is deteriorated. In low conver-

Table 2
SCR of NO^a and oxidation of $C_3H_8^b$ at 578 K

Catalyst	25-200	25-140	25-100	$25\text{-}100^c$	25-60	$25\text{-}0^d$	41-202	41-144	41-100
C_3H_8 *oxidation*									
C_3H_8 conversion (%)	33.6	25	29	30	14	–	16	12.4	–
NO SCR									
NO conversion (%)	56	50	48	67	44	10	32	37	43
C_3H_8 conversion (%)	33	25	24	30	19	7	20	18	23
NO TOF $\times 10^{3e}$	0.67	0.85	1.1	1.6	1.7	–	0.6	0.97	1.6
C_3H_8 TOF $\times 10^{3f}$	0.4	0.45	0.61	0.77	0.8	–	0.4	0.5	0.9
Modified TOF $\times 10^{3g}$	0.13	0.085	0.088	0.16	0.095	–	0.19	0.11	–

[a] Conditions: 160 mg of catalyst, 0.77% NO + 0.85% C_3H_8 + 1.82% O_2 at 23 ml/min flow rate.
[b] Conditions: 160 mg of catalyst, 0.85% C_3H_8 + 1.82% O_2 at 23 ml/min flow rate.
[c] From NH_4-ZSM-5.
[d] From H-ZSM-5.
[e] mol NO s^{-1} mol Cu^{-1}.
[f] mol C_3H_8 s^{-1} mol Cu^{-1}.
[g] mol NO s^{-1} mol NO^{-1} (desorbed in TPD).

sion at 600 K, some N_2O forms with a maximum concentration of about 0.05% (note that the NO/Ar gas mixture contains N_2O) but as the temperature rises further, it decreases and completely disappears above 700 K.

3.2. Temperature-programmed desorption

Typical TPD curves measured for the products formed in NO decomposition are plotted in Fig. 4a and Table 1 (rows 3–5). With the exception of the
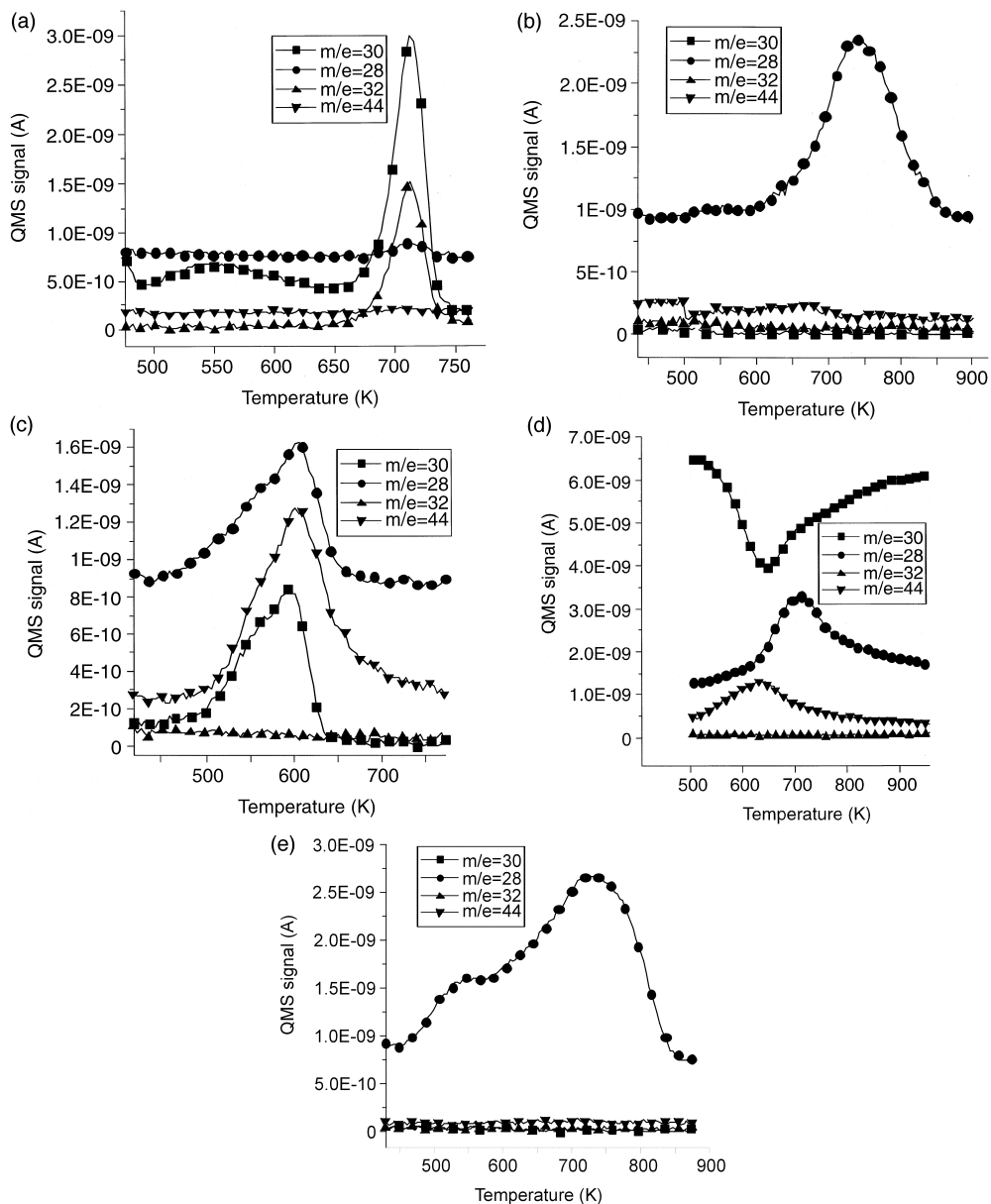

Fig. 4. TPD and temperature-programmed reaction (TPR) on the 41-144 catalyst. (a) TPD after NO decomposition; (b) TPD after propane oxidation; (c) TPD after SCR of NO by propane; (d) TPR of NO with the surface species left on the catalyst after propane oxidation; (e) CO TDP.

sample having 200% exchange, the NO and O_2 desorption peaks have the same shape and the same peak temperature at about 704–710 K. The NO/O_2 ratios are about the same — indicating the decomposition of a compound of NO_3 composition [11]. TOF is independent of the degree of exchange if instead of total Cu the amount of desorbed NO is considered as the number of active sites. This is called modified TOF in Table 1 (compare rows 2 and 6). This suggests that the surface complex to be decomposed is not a spectator species, but really an intermediate in the NO decomposition. The 200% exchanged catalysts are exceptions because the desorption peak is located at 690 K and the amount of O_2 is significantly higher than that of NO. The TOF values referred to the desorbed NO, are also lower. This again indicates that a larger part of Cu is in an hidden position.

After propane oxidation, only CO desorbs at 740 K (see Fig. 4b). In TPD measured after cooling, the catalyst in the propane/NO/O_2 mixture (SCR reaction) down to 440 K (see Fig. 4c), NO, CO, N_2O and N_2 are detected. No O_2 desorbs — suggesting that during cooling in the SCR mixture, the surface nitrito–nitrato complex disappears and NO does not react with adsorbed CO. This is further evidenced by temperature-programmed reaction with NO of the adsorbed species formed in the NO-free oxidation of propane (see Fig. 4d). On heating in 0.77% NO/Ar, N_2O forms as a mirror to NO concentration and CO appears at a temperature higher than the minimum value for NO. In the TDP after cooling, the catalyst from 600 to 450 K in 1.1% CO/Ar (see Fig. 4e), a very broad CO desorption peak is observed at about 720 K with a shoulder at about 600 K. The total amount of the CO desorbed is about 10% more than that measured in a temperature-programmed reaction. This suggests that during SCR with propane, the catalyst surface is at least partially covered by CO. The other alternative is that we need higher temperature to remove a part of the surface carbonaceous species and, due to the system's starvation for oxygen, the oxidation runs only to the stage of CO.

3.3. Transients in the NO decomposition reaction

QMS signals during the first contact with NO of the fresh 25-100 catalyst at 780 K are plotted in Fig.

5a. An overshoot in N_2, transient formation of N_2O, and a pronounced delay in the NO and O_2 signals are observed [14]. As long as N_2O is formed, there is no O_2 signal — which means that oxygen from NO decomposition is taken up by the catalyst. In other words, the catalyst is oxidized by NO. In any subsequent Ar to NO/Ar transient, there is no N_2O formation (see Fig. 5b) but the overshoot in N_2 and the delay in O_2 are still there indicating another state of the catalyst. In the transient NO/Ar to Ar, there is an overshoot in the O_2 signal, which is explained by the decomposition of NO_3 intermediate [11].
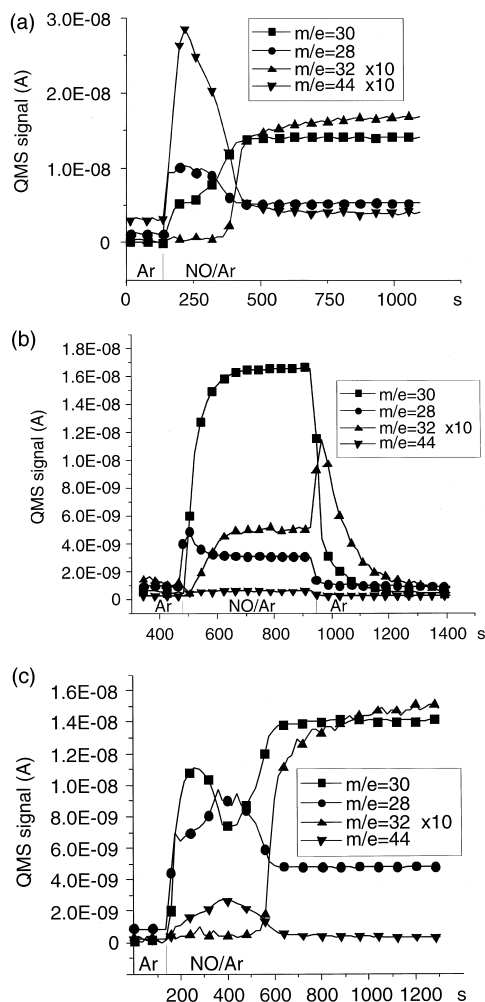

Fig. 5. Transients in the NO decomposition on the 25-100 catalyst. (a) First contact with NO of the fresh catalyst at 780 K; (b) Ar–NO/Ar–Ar transients at 680 K; (c) first Ar–NO/Ar transient after SCR of NO with propane at 780 K.

After the catalyst is used in SCR with propane, there is again N_2O formation during the first Ar to NO/Ar transient (as shown in Fig. 5c). This suggests that, in spite of the presence of O_2 during SCR, the catalyst is partially reduced, probably by CO.

4. Discussion

In our previous work [11], we suggested that a $Cu^{2+}(O)(NO)(NO_2)$ nitrito–nitrato surface complex is an intermediate in the decomposition of NO on Cu-ZSM-5 zeolite. In that work, only Cu-ZSM-5 of 25-100 composition was studied. The present study gives additional support for this assumption because, in varying the Si/Al ratio and the extent of Cu exchange, the modified TOF values in Table 1 are independent of the catalyst composition. This means that the rate of NO decomposition is proportional to the amount of the nitrito–nitrato complex.

The location of the complex is not fully understood. Based on transient kinetics and FT-IR results, we postulated that the $Cu^{2+}(O)O$ sites, formed in the reaction via oxidation of Cu^+ by NO, coordinate two NO molecules — one of them being oxidized to NO_2 resulting in an intermediate mentioned above [11]. Similar mononuclear complexes of $Cu^+(NO)$ and $Cu^{2+}(NO_3^-)$ were recently proved by Konduru and Chang [15] to be active intermediates for the decomposition of NO over Cu-ZSM-5.

Beutel et al. [10] and Moretti et al. [5,16,17] argue for oligomeric copper polyoxocations in the form of $[Cu-O-Cu]^{2+}$. In this oxocation, one of the copper atoms might be Cu(I). According to a recent density functional theory study on relatively large multiple T-site model on Cu-ZSM-5 [18], more than half of the Cu pairs had a mixed valent form and there is a wide range of Cu–Cu separations and O- and O_2-binding conformations. There are different opinions about the formation of Cu(I) — the most accepted idea being the auto-reduction of Cu(II) on heat treatment, while Dossi et al. [17,19] argue for the oxidation of carbonaceous impurities by Cu(II) inside the solid matrix.

Our results also prove the presence of Cu(I) in the activated catalysts but we suggest that most of the Cu(I) is reoxidized because the decomposition of NO

molecules yields atomic oxygen. As shown in Fig. 5a, when the activated Cu-ZSM-5 is first contacted with NO in the transient experiments, oxygen does not appear and this points to the substantial reoxidation of the Cu(I) surface species. This has already been observed in other Cu-containing zeolites [14]. After performing SCR, we found that a greater number of oxygen is missing in the repeated NO decomposition (see Fig. 5c). This is in agreement with the high reductive power of propane even in the presence of excess O_2.

In SCR, different reactions run simultaneously on Cu-ZSM-5. One of them is the oxidation of propane, which is not only catalyzed by the copper sites but also by the acid sites because in this reaction, H-ZSM-5 is also an active catalyst (see, e.g. Table 2). Furthermore, NO is oxidized to NO_2 by O_2 in the feed and the NO_2 reacts with partially oxidized propane to form organic nitrito–nitrato compounds, e.g. 2-nitrosopropane [12,20–25]. The NO also reacts with nitrito–nitrato compounds and N_2 is formed. The remaining organic part is oxidized to CO_2, and H_2O. CO is formed when there is no more O_2 or NO in the gas phase (see Fig. 3). In SCR, due to the site blocking by carbonaceous species (and also by strongly adsorbed CO as shown in Fig. 4b,c,e) and to the high reductive power of propane, the copper–nitrito–nitrato complex observed in NO decomposition in Fig. 4a cannot be formed. The full conversion of NO into nitrogen above 650 K in SCR also supports the importance of partially oxidized propane species. In our case, the O_2 concentration is less than the amount needed for the total oxidation of propane and therefore, there is always a reductive atmosphere for the NO removal. This is in contrast to other studies where O_2 is in a large excess — resulting in a temperature window for NO removal. In this case, the hydrocarbon is completely burnt at higher temperatures. Therefore, the environment changes for an oxidative one, which is unfavorable for the reduction of NO resulting in a decline in NO conversion.

Difference and similarities between NO decomposition and NO SCR by hydrocarbons over Cu-ZSM-5 are discussed by Liu and Robota [26]. While they discuss mainly the properties and formation of Cu(I), we also stress the similarities and differences in the activity of the key intermediates, namely the proper-

ties of the nitrito–nitrato complexes. We can speculate that the increase in activity in SCR, as compared to the decomposition of NO, is connected to the different pathway of the complex formation and the difference in the intermediates. Thus, in NO decomposition, the Cu(I) must be first oxidized into Cu(II), which participates in the formation of NO_2, and the copper–nitrito–nitrato complex could be created on the surface. In SCR, the first step (Cu(I) to Cu(II)) is faster due to the presence of oxygen, but after the activated propane can easily form a nitrogen-containing compound from which nitrogen is formed. The reaction cycle is concluded by the reduction of Cu(II) species, which is significantly accelerated by propane oxidation.

5. Conclusions

It was established that TOF in NO decomposition and SCR is independent of the Si/Al ratio and the extent of exchange.

TPD experiments indicate that the $Cu^{2+}(O)(NO)$-(NO_2) surface complex, which is formed as an intermediate in the NO decomposition, is not the active pathway in SCR.

In the selective catalytic reaction of NO by propane in the presence of oxygen, the first step is Cu(I) to Cu(II) conversion by oxygen. NO_2 formation is facilitated by Cu(II), which reacts with propane and thus forms a nitrito–propane compound. Its decomposition results in N_2 formation at a lower temperature than what is required for NO decomposition.

Acknowledgements

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