Dinitrogen formation over low-exchanged Cu-ZSM-5 in the selective reduction of NO by propane

E.V. Rebrov [a], A.V. Simakov [b,*], N.N. Sazonova [b] and E.S. Stoyanov [b]

[a] *Novosibirsk State University, Novosibirsk 630090, Russia*
[b] *Boreskov Institute of Catalysis, Novosibirsk 630090, Russia*
E-mail: a.v.simakov@catalysis.nsk.su

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The role of gaseous NO and C_3H_8 has been studied over low-exchanged Cu-ZSM-5 zeolite employing TPD, FTIR and pulse technique with the alternate introduction of NO or C_3H_8 onto the catalyst surface. The rate of the N_2 formation is directly proportional to the content of gaseous NO and the surface coverage with 2-nitrosopropane. There was no formation of N_2 during interaction of gaseous C_3H_8 with NO adsorbates. However, 2-nitrosopropane and its isomer acetone oxime were also formed in this reaction.

Keywords: nitrogen oxides, Cu-ZSM-5, N_2 formation, propane

1. Introduction

Copper-ion-exchanged ZSM-5 zeolites are active for the selective catalytic reduction of NO by C_3H_8 in an excess of oxygen [1]. These catalysts and their interaction with NO, hydrocarbons and oxygen have been extensively studied by several techniques. Many types of reaction mechanisms have been suggested, the majority of which are still controversial [2–8]. Note that the majority of papers contain data obtained over excessively exchanged catalysts. The peculiarities of the interaction of propane, oxygen and NO over low-exchanged Cu-ZSM-5 are in many respects similar to those over excessively exchanged ones. However, substantial differences between adsorption properties of these catalysts exist [9]. Some types of adsorbed NO were observed over excessively exchanged zeolites [6,10,11]. Meanwhile, nitrosyl and nitrite–nitrate adspecies were formed over low-exchanged ones only [12]. In contrast to the over-exchanged catalyst, a surface C–N-containing intermediate, likely nitrosopropane, was detected upon exposure of low-exchanged Cu-ZSM-5 zeolite to the mixture of $NO + C_3H_8$ as well as to the $NO + C_3H_8 + O_2$ mixture [9]. The surface coverage with this complex as a function of reagent concentrations was calculated in [12]. According to Sachtler's scheme, 2-nitrosopropane is the key intermediate in NO reduction with propane [7]. The fact that nitrosopropane is observed on the surface of low-exchanged Cu-ZSM-5 catalysts means that the rate of its following transformation is low under the chosen experimental conditions. This fact motivated a study of the transformation of nitrosopropane at the surface of a low-exchanged Cu-ZSM-5 catalyst to clarify the routes of dinitrogen formation in detail.

To study the kinetics of the formation of reaction products in the gas phase in a combination with the kinetics of the transformation of the surface adspecies, it seems appropriate to use the pulse technique with temperature-programmed desorption (TPD), which is carried out just after appropriate number of pulses are introduced on a catalyst surface. To identify the surface complexes and to obtain information on the *current* coverage with these adspecies, it seems appropriate to use FTIR *in situ*. In the present study, the routes of dinitrogen formation have been studied at the surface of low-exchanged Cu-ZSM-5 using pulse technique, TPD and FTIR *in situ*.

2. Experimental

2.1. Catalyst preparation and pretreatment

Cu-ZSM-5 was prepared by traditional ion exchange at 20 °C. A 0.07 M water solution of copper acetate complex was added dropwise to a H-ZSM-5 slurry at pH value of about 7. The slurry was stirred for 24 h before being vacuum filtered. The product was washed with deionized water. The sample obtained was air dried at 110 °C overnight and then calcined at 500 °C under atmosphere for 4 h. Elemental analysis gave the following data: $Cu/Al = 0.28$ and $Si/Al = 19.5$. BET surface area was 412 $m^2\,g^{-1}$. Prior to adsorption/desorption experiments the catalyst was treated in a flow of oxygen for 1 h, followed by a helium one for 1 h at 500 °C repeatedly (about 10 cycles). The catalyst with the particle size of 0.25–0.5 mm was used.

2.2. TPD and pulse technique

The pulse experiment was carried out on 300 mg of Cu-ZSM-5, which was mounted in a microreactor connected to a gas chromatograph. Prior to the adsorption experiment the

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[*] To whom correspondence should be addressed.

sample was pretreated to remove water and adsorbed components from the surface. Two types of sample pretreatment were used: (1) treatment in He flow (30 $cm^3\,min^{-1}$) at 500 °C for 1 h followed by cooling in He to the adsorption temperature; (2) treatment in oxygen flow (30 $cm^3\,min^{-1}$) at 500 °C for 1 h followed by cooling in the atmosphere of O_2, with subsequent purging of the sample with He flow at the adsorption temperature for 5 min to remove oxygen from the gas phase. The samples are designated as "reduced sample" and "oxidized sample", respectively. After the pretreatment, the sample was exposed to the flow of appropriate adsorption mixtures, which were prepared with helium dilution of pure gases. After adsorption equilibrium has been reached (40 min), the sample was purged with He flow of 300 $cm^3\,min^{-1}$ at adsorption temperature for 1 h to remove compounds physically adsorbed on the surface. Then the catalyst temperature was increased from 50 °C up to the required value with a heating rate of 2 °C/min. After the required temperature was reached, pulses of gases of 19.8 Ncm^3 were introduced at intervals of 12 min. Two types of pulses were used: (1) pulses of NO (666 ppm) + He, and (2) pulses of C_3H_8 (3000 ppm) + He. Helium stream of 300 $cm^3\,min^{-1}$ was employed as a carrier gas. After each pulse the analysis on N_2, N_2O and CO_2 was carried out. Just after appropriate number of pulses were introduced, the catalyst was heated from the temperature of the pulse experiment up to 500 °C at 10 °C/min heating rate in a 170 $cm^3\,min^{-1}$ He flow to evaluate the surface coverage with nitrite–nitrate and carbon-containing adspecies. The concentration of NO and NO_2 was measured by a NO–NO_2 gas analyzer "Radas-1" (Hartmann & Braun). The procedure of analysis of N_2O, N_2, O_2 and carbon-containing components was described in detail elsewhere [9].

The amount of desorbed gas was calculated based on the integral area of the corresponding TPD peak. The parameters of individual peaks in TPD profiles such as desorption order, desorption activation energy and pre-exponential factor were calculated by fitting of a simulated curve, which is a superposition of individual peaks, to an experimental one. This procedure was also described in detail in [9]. To purify He and O_2 from water vapor, a trap with molecular sieves and a trap filled with stainless steel wire were used, respectively. Both traps were maintained at -196 °C.

2.3. IR measurements

The IR cell was used to record spectra in the temperature range $20 < T < 250$ °C. Self-supporting wafers of ca. 10–12 mg/cm^2 thickness were pressed and positioned on a support between the NaCl windows of the cell. Heating was electrical and cooling was with air. The temperature was measured with a chromel–alumel thermocouple in contact with the wafer. Temperature fluctuations were within ±1.5 °C. Premixed gases were passed through the cell in a continuous flow at a rate of 100 $cm^3\,min^{-1}$ (NTP) at total pressure of 1 atm. It is known that the FTIR spectra of adsorbed NO depend on the pretreatment conditions of the sample, adsorption time, temperature and NO pressure. Therefore, the FTIR spectra were taken under similar conditions under which the TPD experiments were carried out. Prior to adsorption experiments, the wafers were pretreated in He flow for 1 h at 500 °C. Then the wafers were positioned in the IR cell and pretreated in flowing He at 200 °C.

The spectra were recorded using a BOMEM MB-102 FT-IR spectrometer (Hartmann & Braun). The spectra were taken in transmittance with 10 scans accumulated at a spectral resolution of 4 cm^{-1}. In this case, a time of 30 s was required to obtain one spectrum. The data were processed with a computer program. The spectra from the adsorbed species were obtained by subtracting the spectrum of the wafer from the spectrum recorded after adsorption. Only background-corrected spectra are discussed in the paper.

2.4. Periodic operation tests

Periodic operation tests were performed in a conventional flow system equipped with time-controlled valves shown in figure 1. This system can provide an alternative flow of three different gases (A, B1, B2) into the reactor. The outlet gas from the reactor (100 $cm^3\,min^{-1}$) was diluted with He to a flow rate of 200 $cm^3\,min^{-1}$ in order to adjust the NO_x concentration to a detectable range of the NO_x gas analyzer and to decrease the time lag of detection. The cell of a "Radas-1" gas analyzer was purged in four times faster than that of the reactor under the chosen conditions. A full-

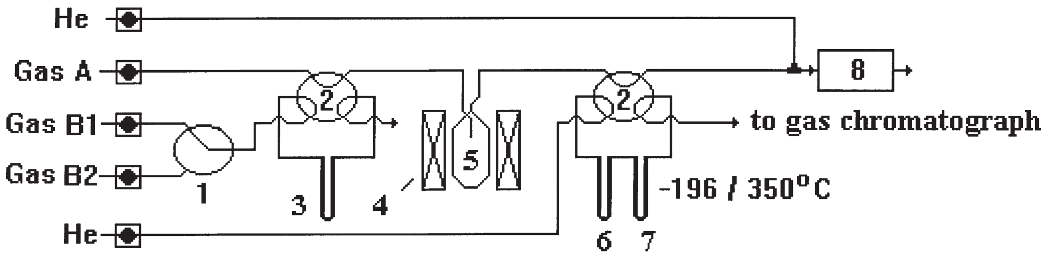

Figure 1. Schematic diagram of apparatus. (1) Three-way valve; (2) six-way valves; (3) sampling loop (40 Ncm^3); (4) reactor; (5) heater; (6) trap filled with Ni–Cr–O catalyst to remove O_2 from feed; (7) trap filled with molecular sieves. This trap was maintained at -196 °C during samplings A, B1 and B2 to collect N_2 formed. Then, the six-way valve was switched to another position and the trap was heated up to 350 °C to desorb N_2 collected; (8) NO–NO_2 gas analyzer "Radas-1". Mixture A = NO (666 ppm) + C_3H_8 (3000 ppm) + O_2 (2.0 vol%) + He; mixture B1 = NO (666 ppm) + He; mixture B2 = C_3H_8 (3000 ppm) + He.

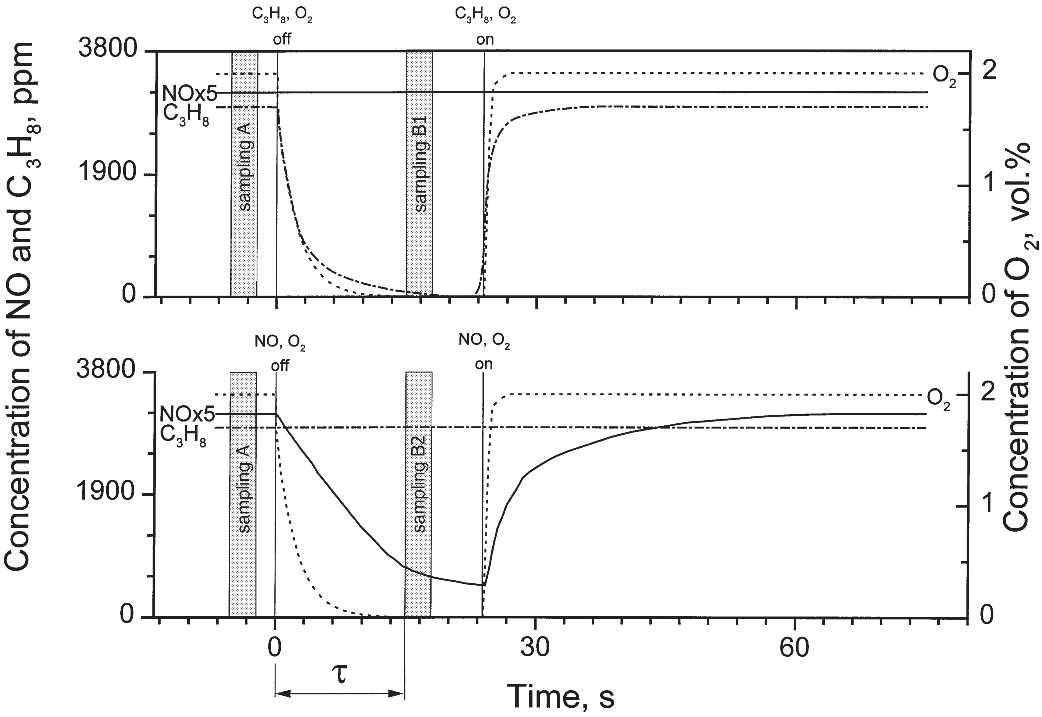

Figure 2. Periodic pattern of the feed gas composition in NO + C_3H_8 + O_2 reaction and NO, C_3H_8 and O_2 concentration change under the periodic operation. The gas composition was the same as that in figure 1.

Table 1
Change in the N_2 formation at the alternate introduction of NO or C_3H_8 with the temperature.

Temperature (°C)	NO_{in} (ppm)	NO_{out} (ppm)	NO removal rate (μmol of (NO/2)/(s g-cat))	Reaction rate (μmol of N_2/(s g-cat)) sampling A	sampling B1	sampling B2
182	665	643	0.00272	0.00249	0.00255	–
190	676	642	0.00421	0.00371	–	0.00095
	665	631	0.00421	0.00371	0.00361	–
250	676	406	0.0335	0.0299	–	0.0076
280	665	165	0.0618	0.0612	0.0492	–
	676	168	0.0627	0.0616	–	0.0159

mixed reactor with vibrofluidized catalyst bed [13] was used to study reaction kinetics on the catalyst grains with average size of 0.38 mm. The temperature was changed within 170–280 °C at constant space velocity of 16000 h^{-1} (NTP). Two types of periodic operations of NO–C_3H_8–O_2 reaction over Cu-ZSM-5 (300 mg) were conducted. In the first one, mixture A (666 ppm of NO, 3000 ppm of C_3H_8, 2.0 vol% of O_2, balance – He) was switched to mixture B1 (666 ppm of NO in He) for 24 s. In the second one, mixture A was switched to mixture B2 (3000 ppm of C_3H_8 in He) for 24 s. A periodic pattern of the gas composition in both cases and actual response curves under the periodic operations are shown in figure 2. After 15 s (unless otherwise specified) from the moment when gas A was switched to gas B1 or B2, dinitrogen was collected for 3 s. Dinitrogen was also collected from gas A for 3 s. The samplings are shown in figure 2 with gray color.

3. Results and discussion

3.1. Dinitrogen formation in the steady state and in the unsteady state of the catalyst

To determine the main reaction pathway of dinitrogen formation in NO SCR with propane over a low-exchanged Cu-ZSM-5 catalyst, the formation of dinitrogen has been studied in the steady state of the catalyst (sampling A) and in the unsteady states (samplings B1 and B2, figure 2). The scheme used made it possible to remove two components from the reaction mixture for 24 s at a constant concentration of the third component. The amounts of dinitrogen released when the feed contained all the three components and when only NO or C_3H_8 were fed are presented in table 1.

As one can see from table 1, the amount of dinitrogen formed when only NO + He was fed (mixture B1) was close to that formed when the feed contained all the

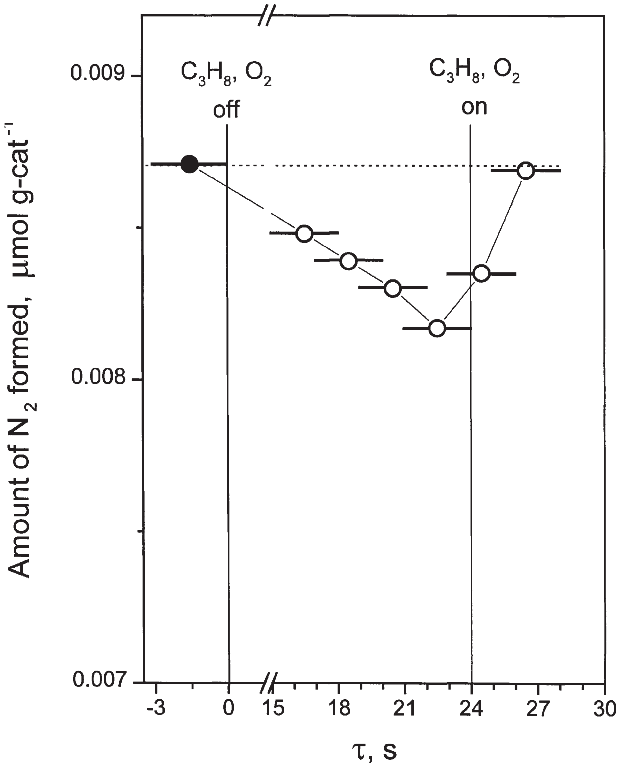

Figure 3. The effect of starting time of sampling B1 (τ) on the N_2 formation. The amount of N_2 formed during sampling A (●) is presented for comparison.

components (mixture A). Note that the amount of dinitrogen released during the passing of mixture B1 depended on the dinitrogen trapping starting time (τ) (figure 2): the later the dinitrogen trapping started, the less dinitrogen was formed (figure 3). This effect seems to be caused by the fact that the concentration of C–N-containing surface intermediates interacting with NO decreased as mixture B1 passed through the reactor, whereas it remained constant if mixture A was used. Note that the N_2 amount formed at 280 °C with the use of mixture B1 was slightly lower than in the case of mixture A. This was caused by the increase in the desorption rate of the surface complex with the temperature increase.

If only the $C_3H_8 + He$ mixture was fed (mixture B2), significantly less dinitrogen was released in the whole temperature range studied. It should be noted that NO was removed from the gas phase substantially slower than O_2 and C_3H_8 (figure 2), probably due to the NO desorption from the catalyst surface. For example, about 25% of its initial concentration remained above the catalyst surface when the N_2 concentration was measured. In this case, the N_2 formation also seems to be due to the NO interaction with the surface complexes, as the decrease in the dinitrogen formation was proportional to the decrease in the NO concentration in the gas phase by the moment τ. Thus, the experiments performed prove that the main pathway of dinitrogen formation over low-exchanged Cu-ZSM-5 zeolites below 280 °C involves the interaction of gaseous NO with complexes present on the catalyst surface.

In order to determine the complexes adsorbed on the surface of the reduced catalyst, TPD and FTIR experiments were carried out after the co-adsorption of NO and propane. It was previously shown that oxygen was not required to form C–N-containing intermediates [9].

3.2. TPD study

There are three desorption peaks in the TPD profile of NO after the co-adsorption of C_3H_8 and NO at 85 °C. The first one at 110 °C is ascribed to the decomposition of nitrosyls over Cu-ZSM-5 [14,15]. The second peak at 250 °C is ascribed to 2-nitrosopropane decomposition [9]. The third one at about 415 °C corresponds to the decomposition of nitrite–nitrate adspecies [14,16].

It should be noted that carbon-containing intermediates adsorbed on Cu-ZSM-5 are oxidized during the TPD experiments to yield CO_2. Thus, these adspecies should pick up necessary oxygen atoms to form CO_2. Based on the previous results obtained by Keulks' group [17] as well as our group [9], the nature of these oxygen atoms may be briefly described as follows: two NO molecules adsorbed on the surface to form dinitrosyl complex, which is decomposed to N_2O leaving an oxygen atom behind. During this process some of the copper cations are oxidized from Cu^+ to Cu^{2+}. This adsorbed oxygen can react with carbon-containing intermediates at higher temperature to form CO_2.

The TPD profiles of carbon-containing compounds after the co-adsorption of C_3H_8 and NO on reduced Cu-ZSM-5 catalyst at 85 °C (figure 4(a)) are in many respects similar to those obtained in [9] after the co-adsorption of these reagents at 50 °C. However, in addition to the C_3H_8 desorption peak at 130 °C (peak I-C) and the CO_2 desorption peaks at 250, 290 and 360 °C (peaks II-C, III-C and IV-C, respectively) ascribed to the decomposition of oxygenated carbon-containing products [9], there exist two new desorption peaks at about 235 (peak I-CO_2) and 335 °C (peak II-CO_2) in the TPD profile of carbon-containing products.

To ascribe CO_2 peaks within 200–400 °C to decomposition of surface adspecies, TPD of carbon-containing compounds were carried out after the adsorption of CO_2, 2-propanol and acetone on reduced Cu-ZSM-5 catalyst at 50 °C. These compounds are possible products of the C_3H_8 oxidation. Figure 4(b) shows that CO_2 peaks at 235 and 335 °C after the CO_2 adsorption coincide with peaks I-CO_2 and II-CO_2 in the TPD profile after the co-adsorption of NO and C_3H_8. A desorption peak of CO_2 at 290 °C and evolution of CO_2 above 380 °C are observed in the TPD profile after the adsorption of acetone (figure 4(c)). Note that the peak at 290 °C coincides with peak III-C after the co-adsorption of NO and C_3H_8. A peak of the CO_2 desorption at about 360 °C and evolution of CO_2 above 450 °C are also observed in the TPD profile after the adsorption of 2-propanol (figure 4(d)). In this case, the peak at 360 °C coincides with peak IV-C after the co-adsorption of NO and C_3H_8. Based on the kinetic parameters of the corresponding TPD peaks of oxygenated carbon-containing compounds,

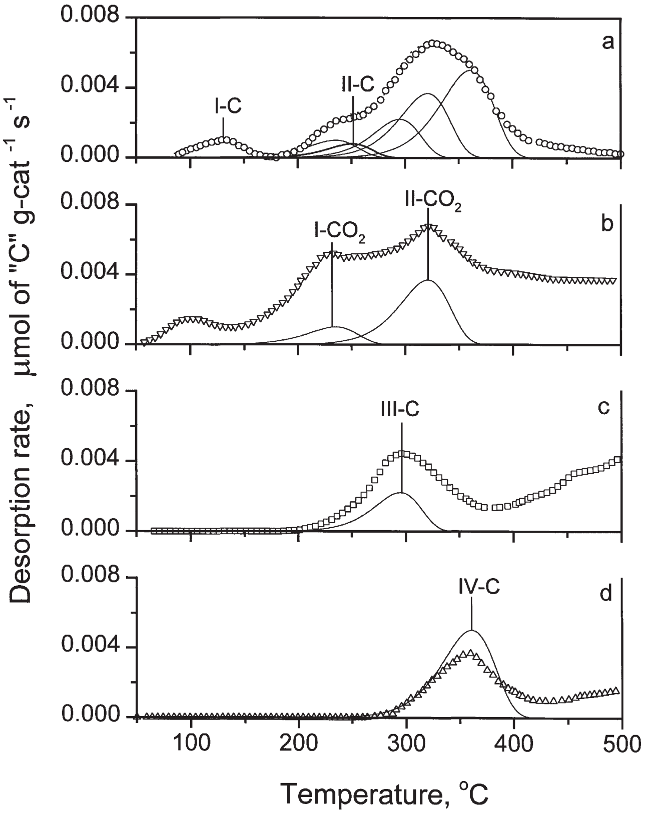

Figure 4. TPD profiles of carbon-containing products from reduced Cu-ZSM-5 after (a) co-adsorption of NO (666 ppm) and C_3H_8 (3000 ppm); (b) adsorption of CO_2: two 500 μl pulses of pure CO_2 were passed through the sample bed; (c) adsorption of acetone: two 500 μl pulses of pure CO_2 saturated acetone vapour were passed through the sample bed; (d) adsorption of 2-propanol: two 500 μl pulses of saturated propanol vapour were passed through the sample bed. Experimental TPD profiles are presented with symbols. Simulated TPD profiles of individual peaks and sums of them are plotted with solid lines. Adsorption temperature 85 °C (a) and 50 °C ((b)–(d)). Heating rate 10 °C/min.

one may conclude that peaks I-CO_2 and II-CO_2 can be ascribed to the evolution of CO_2 readsorbed, while peaks III-C and IV-C can be ascribed to the decomposition of acetone and 2-propanol, respectively. In order to obtain more straightforward evidence for our conclusions obtained from the TPD experiments, a FTIR study of surface adspecies formed during the co-adsorption of NO and C_3H_8 was performed.

3.3. FTIR study

The IR spectra of surface adspecies obtained during the co-adsorption of NO and propane on reduced Cu-ZSM-5 at 85 °C are very complex (see figure 5). These IR spectra consist of overlapping bands which can be assigned to adspecies of three types: (1) molecularly adsorbed propane and oxygenated carbon-containing products of propane oxidation; (2) N-containing adspecies adsorbed on Cu^+ and Cu^{2+}; (3) products of the interaction of NO and propane. To assign the observed bands to surface adspecies, separate adsorption of NO and propane was carried out under the same conditions.

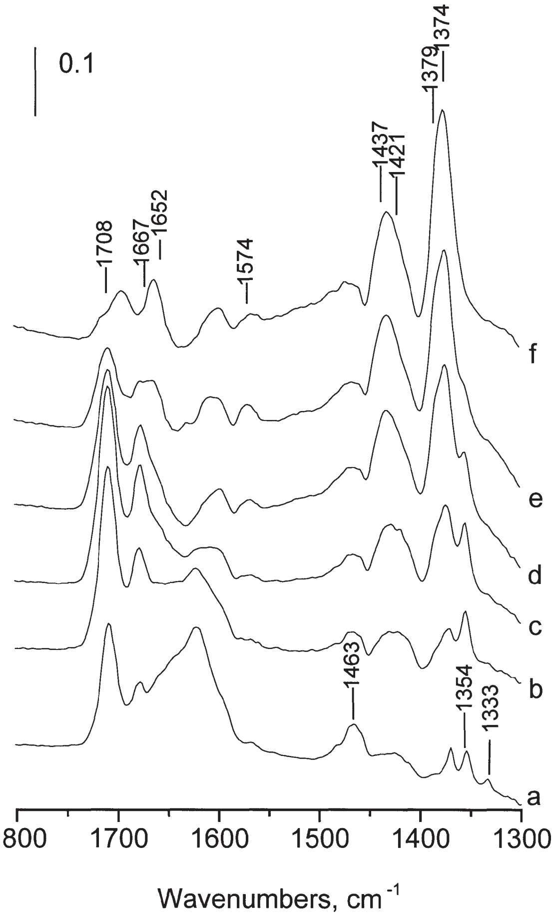

Figure 5. FTIR spectra of the surface species formed after exposure of reduced Cu-ZSM-5 catalyst to NO (666 ppm) + C_3H_8 (3000 ppm) + He mixture at 85 °C. Time of adsorption: (a) 2 min, (b) 10 min, (c) 25 min, (d) 30 min, (e) 40 min, and (f) 95 min. The spectra are background corrected.

The FTIR spectrum of propane adsorbed on reduced Cu-ZSM-5 at 85 °C is presented in figure 6. This was relatively simple and practically invariant with time. All bands may be assigned to vibrations of CH_3 and CH_2 groups based on the well-known spectrum of gaseous propane [18] due to the weak adsorption of propane on the Cu-ZSM-5 catalyst. Thus, bands at 1456, 1369 cm^{-1} and 1471, 1465, 1333 cm^{-1} have been assigned to deformation vibrations of the CH_3 and CH_2 groups in adsorbed propane, respectively. Band pairs at 2960/2896 and 2935/2871 cm^{-1} have been assigned to antisymmetric and symmetric stretching vibrations of the CH_3 and CH_2 groups, respectively. As the temperature increases, all these bands disappear around 130 °C where the propane desorption is observed in the TPD profile.

The five most intense bands were developed in the IR spectra when the reduced catalyst was contacted with NO at 85 °C for 2–25 min (figure 7). First of all, these bands may be assigned to nitrosyl adspecies. Note that two types of nitrosyl adspecies can be formed on the surface of Cu-ZSM-5:

(I) $Cu^{\oplus}-N{\equiv}O:$ (II)

$Cu^{\oplus}-\ddot{N}{=}\ddot{O}:$

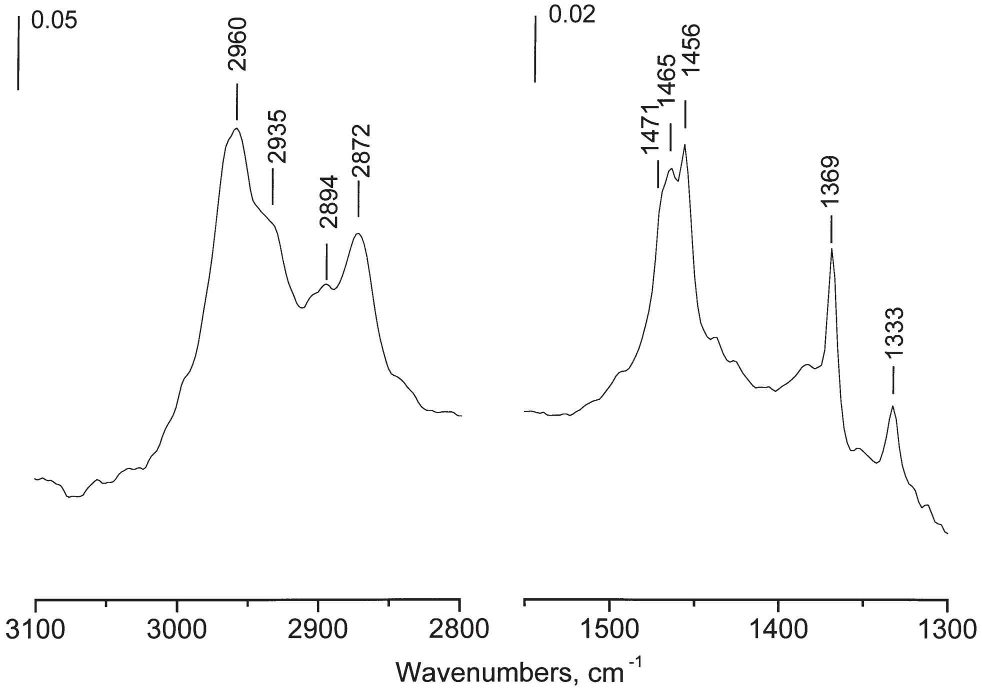

Figure 6. FTIR spectrum of the propane adsorbed on reduced Cu-ZSM-5 catalyst at 85 °C. The wafer was exposed for 10 min to C_3H_8 (3000 ppm)+He mixture. The spectrum is background corrected.

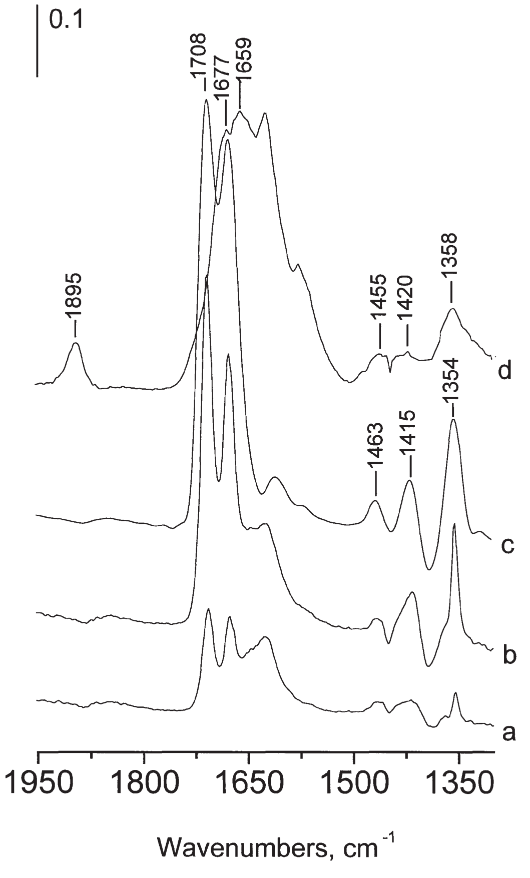

Figure 7. FTIR spectra of the surface species formed after exposure of reduced Cu-ZSM-5 catalyst to NO (666 ppm) + He mixture at 85 °C. Adsorption time: (a) 2 min, (b) 5 min, (c) 8 min and (d) 25 min. The spectra are background corrected.

A band within the 1750–1900 cm^{-1} region is observed for nitrosyl adspecies (I), while that within the 1650–1700 cm^{-1} region is characteristic for nitrosyl adspecies (II) [19,20]. Thus, the two intensive bands observed at 1708 and 1677 cm^{-1} were assigned to nitrosyl adspecies (II). The presence of two types of nitrosyl adspecies (II) means that two different types of copper cations indicated by the appearance of two bands of stretching vibrations of the NO groups in the IR spectrum exist on the surface of the catalyst. They will be named as Cu(a) and Cu(b) hereafter. The μ-NO nitrosyl adspecies are not formed, because there are no characteristic bands of these species within the 1450–1520 cm^{-1} region in the IR spectrum [21–24]. The bands of nitrito complexes (Cu–O–N=O) were not found (figure 7), whereas three bands at 1463, 1415 and 1354 cm^{-1} were observed. These bands were assigned to nitro complexes ($Cu–NO_2$). Three bands of the stretching vibrations of the NO_2 groups in the IR spectrum instead of two bands of $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$ were observed due to the presence of two different types of copper cations Cu(a) and Cu(b) on the surface of Cu-ZSM-5. If the charge of these copper cations is the same while their space environment is different, the antisymmetric stretching vibrations of the NO_2 groups of nitro complexes formed on these copper cations should be different. However, in this case the symmetric stretching vibrations of the NO_2 groups may be very close to each other. Indeed, the intensity of the $\nu_s(NO_2)$ band at 1354 cm^{-1} was about two times higher than that of the $\nu_{as}(NO_2)$ bands at 1463 or 1415 cm^{-1}. Evidently, the characteristic bands of nitrate adspecies within 1615–1550 cm^{-1} [25–29] were missing or very weak in the FTIR spectra after 8 min. At 85 °C several other adsorbed species

Table 2
IR absorption peaks and their assignment for surface species formed from NO on Cu-ZSM-5.

Freq. (cm^{-1})	Assignment	Adsorbed species
1708	ν(N=O)	Cu_a^+–N=O (bent conformation)
1677	ν(N=O)	Cu_b^+–N=O (bent conformation)
1463	$\nu_{as}(NO_2)$	Cu_a^+–NO_2
1415	$\nu_{as}(NO_2)$	Cu_b^+–NO_2
1354	$\nu_s(NO_2)$	both Cu_a^+–NO_2 and Cu_b^+–NO_2
1895	ν(N≡O)	Cu_a^{2+}–N≡O and Cu_b^{2+}–N≡O (straight conformation)
1659 (wide band)	ν(N=O)	Cu_a^{2+}–N=O and Cu_b^{2+}–N=O
1455	$\nu_{as}(NO_2)$	Cu_a^{2+}–NO_2
1420	$\nu_{as}(NO_2)$	Cu_b^{2+}–NO_2
1358	$\nu_s(NO_2)$	both Cu_a^{2+}–NO_2 and Cu_b^{2+}–NO_2

with very low concentration exist on the surface indicated by very weak IR peaks. Assignment of these bands is not available at this moment.

After 10 min, the intensity of the bands of nitrosyl complexes decreased with time with complete disappearance after 25 min. The intensity and position of the bands of nitro complexes also changed with time. After 8 min, two new bands including a well-known band of ν(N≡O) of Cu^+–NO [25,30] at 1895 cm^{-1} grew (figure 7). The intensity of the bands near 1670 cm^{-1} increased as Cu^+ was converted to Cu^{2+}, as evidenced by the changes in the intensity of the band at 1895 cm^{-1}. After 25 min, the oxidation of Cu^+ to Cu^{2+} was completed. Thus, all surface adspecies were formed on Cu^+ during the first 10 min. After 10 min, Cu^+ was converted to Cu^{2+}, but the structure of surface complexes of Cu^{2+} was the same as that of Cu^+. Note that the difference between the copper centers of Cu(a) and Cu(b) remained in the oxidized catalysts. Tentative assignments for surface species formed from NO on Cu-ZSM-5 are given in table 2.

The reaction chemistry happening on the surface during the NO adsorption for 10 min over Cu-ZSM-5 may be interpreted as follows: NO is adsorbed on Cu^+(a) and Cu^+(b) to form bent nitrosyl complexes (II). During adsorption the surface concentration of Cu_a^+–N=O increased in direct proportion to that of Cu_b^+–N=O. The coverages with both Cu_a^+–NO_2 and Cu_b^+–NO_2 complexes also increased steadily with time. It should be noted that the coverage with nitrosyl complexes is in direct proportion to that of nitro complexes just after the beginning of the NO adsorption. This means that nitro complexes are formed without induction period. This is possible if nitro complexes are formed by the adsorption of gaseous NO_2 on Cu_a^+ and Cu_b^+ rather than the nitrosyl oxidation. Indeed, small amounts of dinitrogen dioxide of ca. 2 vol% were present in the NO mixture. Thus two types of nitrosyl complexes on different Cu^+ cations were only formed during the NO adsorption on the reduced Cu-ZSM-5 catalyst for 12 min. The adsorption is not accompanied by any RedOx processes. The energies of the NO interaction with both Cu_a^+ and Cu_b^+ as well as with both Cu_a^{2+} and Cu_b^{2+} are close to each other, because the positions of bands of stretching vibrations of the NO groups in these complexes are very close to each other too (table 2).

Thus, the FTIR spectra of surface adspecies taken after the co-adsorption of C_3H_8 and NO at 85 °C within time interval of 10 min (figure 5 (a)–(b)) do not contain any other bands beside those of molecularly adsorbed propane and N-containing adspecies of Cu^+ and Cu^{2+} discussed above (figures 6 and 7). However, after 25 min, significant changes in the IR spectrum were observed. New bands developed at 1661 cm^{-1} and in the 1370–1440 cm^{-1} region (figure 5 (c)–(f)). It should be noted that the positions of the new bands were different from those of propane adsorbed. It is reasonable to assume that the bands developed are due to the interaction of C_3H_8 and NO on the surface of the Cu-ZSM-5 catalyst. According to Sachtler's scheme [9], acetone oxime (figure 8, (II)) which is formed from 2-nitrosopropane (figure 8, (I)) is the first relatively stable intermediate of the interaction of propane and NO. Indeed, all bands in the IR spectrum of products formed during the co-adsorption of reagents appeared near the characteristic positions of bands of adsorbed acetone oxime [31].

For a reliable interpretation of the IR spectra obtained after the co-adsorption of C_3H_8 and NO, the spectra of acetone oxime adsorbed on reduced Cu-ZSM-5 were obtained under the same experimental conditions. The adsorption of acetone oxime was carried out from the adsorption mixture flow, which was prepared by helium dilution of saturated vapours of acetone oxime. Two fairly strong peaks appeared in the IR spectrum at ca. 1375 and 1430 cm^{-1} corresponding to the antisymmetric and symmetric deformation vibrations of the CH_3 groups, respectively, which were very close to those in the IR spectrum obtained after the co-adsorption of C_3H_8 and NO at 85 °C (see table 3). The characteristic band of C=N bond stretching vibration at 1652 cm^{-1} [31] shifts to lower wavenumbers in comparison with its position in the IR spectrum of acetone oxime adsorbed on H-ZSM-5 (ν(C=N) = 1670 cm^{-1}). We attribute this band to the acetone oxime N-ligated to copper cation. Note that the position of the ν(C=N) band of acetone oxime ligated to Cu_a^+ and Cu_b^+ should be different. However, a wide band of C=N stretching vibration at 1652 cm^{-1} appears to consist of two overlapping bands

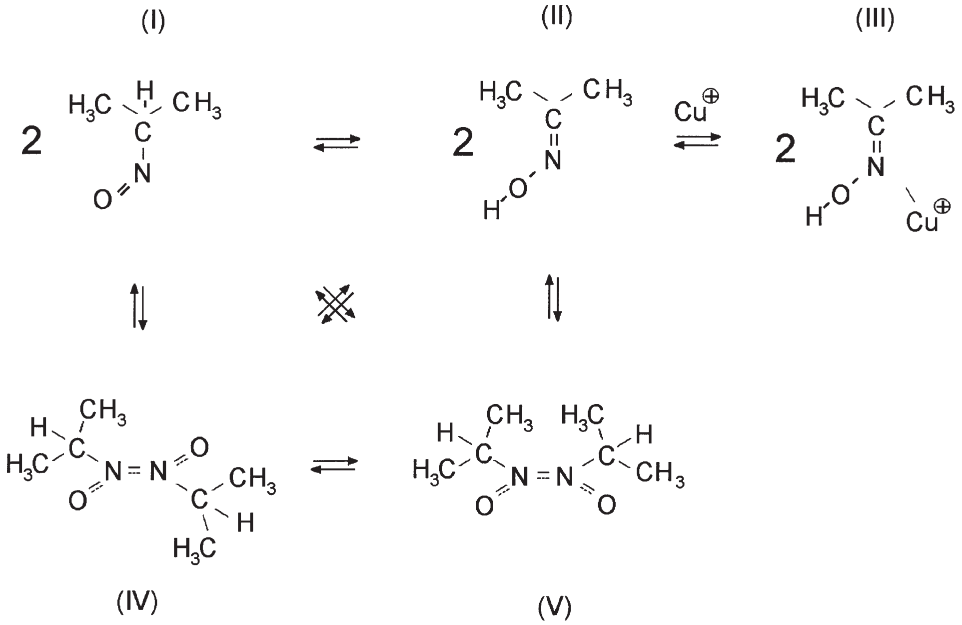

Figure 8. Scheme of transformations of 2-nitrosopropane.

Table 3

IR absorption peaks and their assignment for surface species formed from 2-nitrosopropane on Cu-ZSM-5 [32].

Freq. (cm^{-1})	Adsorbed species	Note and assignment	
1550–1530	monomer of 2-nitrosopropane (figure 8, (I))	ν(N=O)	
1410–1330	*cis*-dimer of 2-nitrosopropane (figure 8, (IV))	ν(N–O)	
1280–1170	*trans*-dimer of 2-nitrosopropane (figure 8, (V))	ν(N–O)	in Cu-ZSM-5 zeolite framework region
1670–1650	acetone oxime (figure 8, (II), (III))	ν(C=N)	
1439–1426, 1429–1421 1379–1374, 1371–1368	monomer, *cis*- and *trans*-dimers of 2-nitrosopropane	$\delta(C–CH_3)_{as}$ $\delta(C–CH_3)_s$	the position of these bands in the IR spectra is practically the same for all isomers of 2-nitrosopropane

with very small difference in wavenumbers ($\Delta\nu$(C=N)). Thus adsorbed acetone oxime (figure 8, (III)) seems to be among the key intermediates formed during the interaction of NO and C_3H_8 on the surface of the reduced Cu-ZSM-5 catalyst.

After 25 min, the bands of new surface intermediates formed after the co-adsorption of NO and C_3H_8 became the strongest ones in the IR spectrum. The intensities of the stretching vibration of C=N double bonds and the deformation vibration of the CH_3 groups varied with time. Their intensity ratio increased with time (figure 9). This means that one more N-containing intermediate was formed during the co-adsorption of the reagents. This intermediate will be named as **J** hereafter. Evidently, the bands of both stretching and deformation vibrations of the CH_3 group of intermediate **J** appeared at the same positions as those of adsorbed acetone oxime. It can be seen from the dependence of the intensity ratio ($I_{\nu(\mathrm{C=N})}/I_{\delta(\mathrm{CH_3})}$) (see figure 9) that the surface concentration of **J** grows with time, reaches a maximum after 20 min and then decreases, while the surface concentration of acetone oxime increases steadily with time and reaches a constant level after 90 min. This dependence is in agreement with Sachtler's scheme of the reaction [31]. According to Sachtler's scheme, acetone oxime is formed by isomerization of 2-nitrosopropane. The latter is not stable as monomer and tends to form dimers [32]. Secondary nitroso compounds are known to undergo spontaneous transformation to *cis*- (figure 8, (IV)) or more stable *trans*- (figure 8, (V)) dimers. Therefore, one can assume that intermediate **J** is the dimer of 2-nitrosopropane. The positions of the bands of both stretching and deformation vibrations of the CH_3 groups of 2-nitrosopropane itself as well as *cis*- and *trans*-dimers of 2-nitrosopropane reported in the literature [32] are in good agreement with the peak positions observed after the adsorption of acetone oxime (table 3). However, there is no band within 1550–1530 and 1430–1330 cm^{-1} which could be ascribed to the N–O bond stretching vibrations in the monomer and *cis*-dimer of 2-nitrosopropane, respectively (table 3). So, we attribute intermediate **J** to the *trans*-dimer of 2-nitrosopropane. By the way, the characteristic band of the NO stretching vibration in the *trans*-dimer of 2-nitrosopropane is expected to be within the 1180–1170 cm^{-1} region where it cannot be observed due to intensive absorbance from the Cu-ZSM-5 zeolite framework. So, the formation of acetone oxime via the *trans*-dimer of 2-ni-

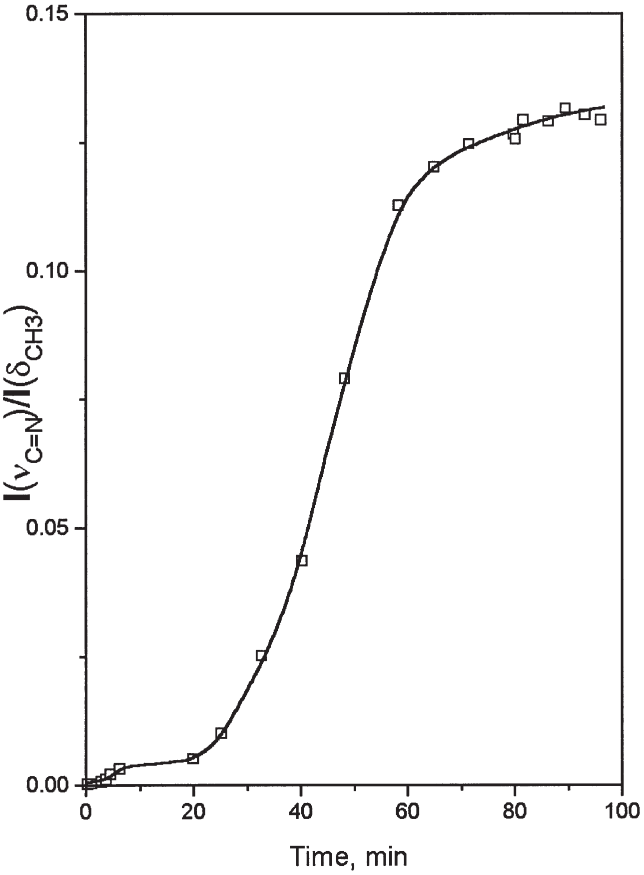

Figure 9. Relationship between intensities of the stretching vibration of C=N double bonds and the deformation vibration of the CH_3 groups for Cu-ZSM-5 catalyst as a function of time. Co-adsorption of NO and C_3H_8 was carried out at 85 °C. The other experimental conditions are the same as those in figure 5.

trosopropane appears to be in good agreement with the IR spectra.

The FTIR spectra changed with temperature. At 160 °C, a dramatic increase in band intensity is observed in the region of 1705–1667 cm^{-1}. New bands at 1700, 1687 (shoulder) and 1666 cm^{-1} appear. In the range of CH_3 deformation vibrations, new bands at 1417 and 1365 cm^{-1} appear. Band intensities at 1437/1421, 1379/1374 and 1652 cm^{-1} are depleted due to the desorption and decomposition of both acetone oxime and the *trans*-dimer of 2-nitrosopropane observed in the TPD profiles within 220–280 °C. Heating to 220 °C causes an increase in intensity within the 1705–1667 cm^{-1} region. The bands at 1417 and 1365 cm^{-1} are due to the antisymmetric and symmetric deformation vibrations of the CH_3 groups in acetone. Emerging strong absorption bands within the 1703–1667 cm^{-1} region are ascribed to C=O double bonds in acetone differently ligated to copper ions. This assignment is confirmed in separate experiments of the acetone adsorption on the reduced Cu-ZSM-5, which yielded bands at 1418, 1365 cm^{-1} and three bands within the 1700–1667 cm^{-1} region. The same bands were observed after the adsorption of acetone on the oxidized Cu-ZSM-5 catalyst. The positions of the bands within the 1700–1667 cm^{-1} region depend on the strength of the copper–oxygen bond in acetone adsorbed.

Finally, five types of oxygenated carbon-containing compounds were detected on the surface of Cu-ZSM-5 by our TPD and FTIR experiments. These compounds are 2-nitrosopropane, acetone oxime, 2-propanol, acetone and CO_2 adsorbed.

3.4. Pulse study

To explore the details of the interaction of NO and C_3H_8 with the surface complexes, two types of experiments have been conducted. In the first series of experiments, NO pulses were fed to the catalyst with preadsorbed C_3H_8 with the measurement of the evolution of gaseous products and changes in the surface coverage with the surface complexes. In the second series, C_3H_8 pulses were fed to the catalyst with preadsorbed NO.

Figure 10(a) presents the evolution of gaseous products (N_2, NO and CO_2), and figure 10(b) shows the changes in the coverage of the catalyst surface with adsorbed complexes during feeding of NO pulses to the catalyst with preadsorbed C_3H_8. The amount of the nitrite–nitrate complexes monotonously increased from the first NO pulse, while the amount of C_3H_8 in the molecular form decreased. Detectable amounts of nitrosopropane started forming only from the second NO pulse, its formation rate gradually increasing and reaching its maximum at the sixth pulse. Note that after complete removal of molecular C_3H_8 the formation rate of the nitrite–nitrate complexes grew. The surface was saturated with the nitrite–nitrate complexes only after 23 NO pulses. The first NO pulse led to the increase of the surface coverage with 2-propanol, whereas practically no N_2 or CO_2 were formed. After additional NO pulses the surface concentration of 2-propanol slightly decreased, this decrease corresponding to the increase of the surface coverage with acetone. Meanwhile, from the second NO pulse CO_2 was the main product of the propane oxidation. The surface coverage with CO_2 monotonously grew and reached the value close to its maximum before the fifth pulse. From this moment the CO_2 evolution into the gas phase was observed. The N_2 evolution into the gas phase was observed from the second NO pulse. Still, maxima in the evolution of both N_2 and CO_2 were observed after the 10th NO pulse, when the surface coverage with nitrosopropane was the highest. It is important that N_2 was the main product of the NO reduction, as the amount of N_2O formed was by two orders of magnitude lower than that of N_2.

The analysis of the data obtained during the series of experiments with the NO pulses led us to the following conclusions. First, the match of the CO_2 and N_2 evolution curves with the curve of the surface coverage with nitrosopropane indicates that the latter participates in a chain of transformations leading to the formation of the NO selective reduction products. Second, the amount of CO_2 formed was always three times higher than that of dinitrogen. Such

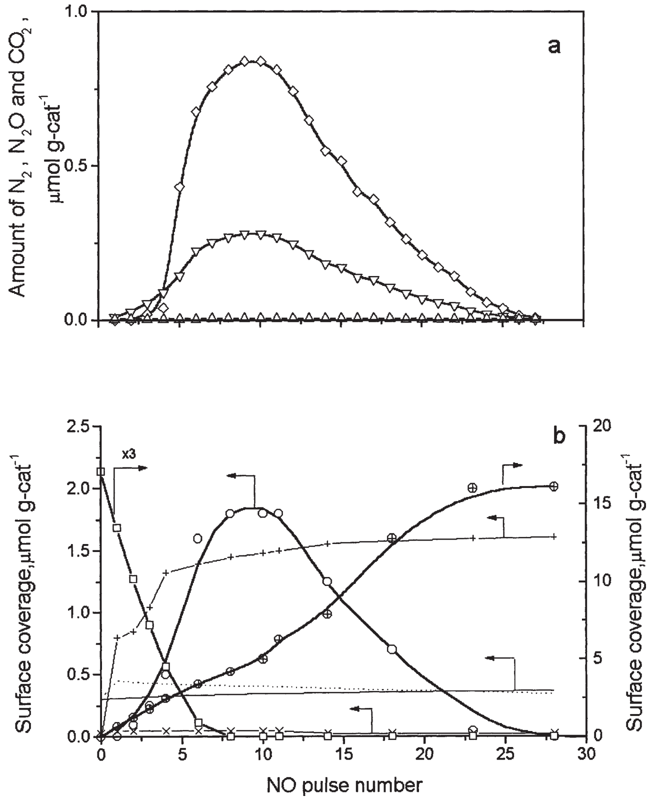

Figure 10. (a) Amount of N_2 (▽), N_2O (△) and CO_2 (◇) generated. (b) Change in surface coverage with propane (□), nitrosopropane (○), 2-propanol (···), acetone (—), nitrite–nitrate adspecies (⊕), N_2O readsorbed (⊗), and CO_2 readsorbed (+) with the number of NO pulses introduced onto the C_3H_8 preadsorbed Cu-ZSM-5 catalyst. The C_3H_8 concentration during adsorption at 50 °C was 3000 ppm. Pulse size 19.81 Ncm^3, pulse interval 12 min, temperature 85 °C.

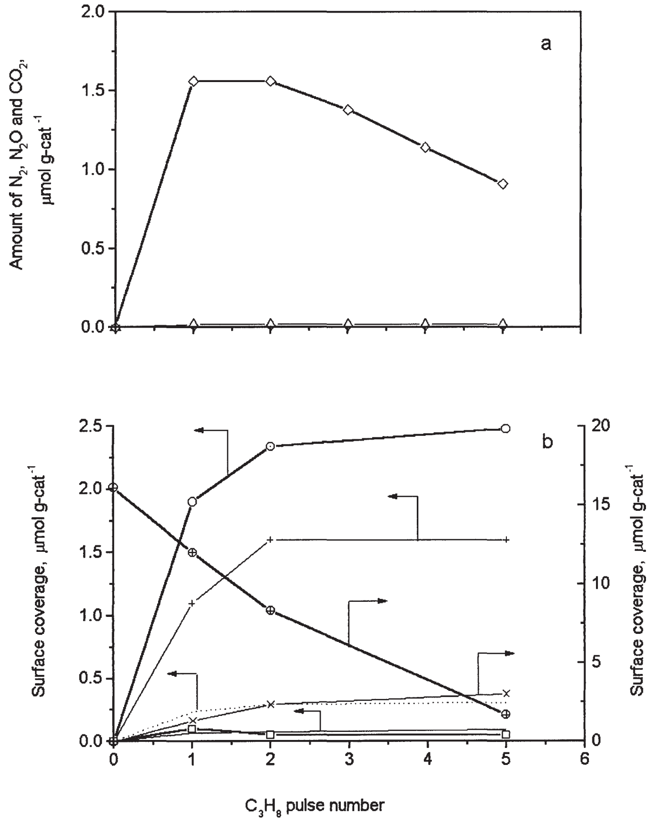

Figure 11. (a) Amount of N_2, N_2O and CO_2 generated. (b) Change in surface coverage with surface adspecies with the number of C_3H_8 pulses introduced onto the NO preadsorbed Cu-ZSM-5 catalyst. The NO concentration during adsorption at 50 °C was 666 ppm. The other experimental conditions are the same as those in figure 10. For notations, see legend of figure 10.

stoichiometry means that N_2 was formed by the selective oxidation of surface complexes consisting of three carbon atoms and one nitrogen atom, because it is known that only one N atom of nitrogen molecules originates from a surface complex [31,33–35]. Finally, the dynamics of changes in the surface coverage with the nitrite–nitrate complexes and the molecular form of C_3H_8 indicates that they interact with each other. Indeed, the rate of the nitrite–nitrates formation on the catalyst increased when the surface became free of molecular C_3H_8. It should be noted that, besides the reaction with the nitrite–nitrate complexes, desorption of molecular C_3H_8 was also observed. Indeed, an estimation of the amount of desorbed C_3H_8 based on the kinetic desorption parameters obtained in [9] has shown that 45% of the initial amount of adsorbed C_3H_8 (2.6 μmol C_3H_8 g-cat^{-1}) desorbs at 85 °C during the pulse experiment. Thus, the amount of C_3H_8 interacting with NO is 3.1 μmol C_3H_8 g-cat^{-1}. Note that after 7 NO pulses, when the surface was free from molecular C_3H_8, the total amount of C-containing compounds (3.0 μmol C_3 g-cat^{-1}) formed on the surface and released into the gas phase was in good agreement with the amount of C_3H_8 transformed.

For comparison, let us discuss the dynamics of the evolution of gaseous products (figure 11(a)) and changes in the surface coverage with nitrosopropane, nitrite–nitrate and C-containing complexes (figure 11(b)) during the introduction of the C_3H_8 pulses to the catalyst with preadsorbed NO. It is obvious that in this case nitrosopropane was formed without induction period, and its surface coverage close to maximum was reached already after the third C_3H_8 pulse when the surface concentration of the nitrite–nitrate complexes was maximal. As the C_3H_8 pulses were fed, the surface coverage with the nitrite–nitrate complexes monotonously decreased, while its coverage with nitrosopropane reached a constant value. After two C_3H_8 pulses practically maximum surface coverage with propanol and acetone was reached, and the formation of CO_2 on the catalyst surface was observed. CO_2 was also released into the gas phase, its amount monotonously decreasing as the C_3H_8 pulses were fed. In contrast to the experiments with the NO pulses, N_2O rather than N_2 was formed in this case, the former readsorbing on the catalyst surface under the experimental conditions.

Thus, the observed dynamics of the transformations of the surface forms and evolution of the gaseous products of their reactions with NO and C_3H_8 is in general agreement with a scheme [7] which implies that N_2 is formed due to the interaction of gaseous NO with surface C–N-containing complexes. The only observed deviation from this scheme is the evolution of N_2O instead of N_2 during the addition of C_3H_8 to the catalyst with preadsorbed NO. It can be explained by the fact that the NO adsorption results in the oxidation of the catalyst surface, which prevents N_2O formed from further reduction to N_2.

It is interesting to note that the formation of nitrosopropane was observed in both series of pulse experiments. It is important that the C_3H_8 desorption from the molecular form was observed during the addition of the NO pulses to preadsorbed propane at 85 °C. In turn, at the temperature at which the experiments with the propane addition were performed, NO desorbs from nitrosyl complexes. Therefore, a certain amount of a gas was present in both types of experiments. A calculation based on the kinetic desorption parameters obtained in [9] has shown that the average C_3H_8 concentration in the gas phase after the propane adsorption at 50 °C is about 10 ppm. In the case of NO, a similar evaluation gives its concentration about 5 ppm. Thus, in both types of pulse experiments, when pulses of one gas were introduced at 85 °C, the second compound was present in the gas phase in the concentration about 100 times lower than that of the fed gas.

The formation of nitrosopropane in both cases appears to follow the same mechanism involving the NO reaction with propyl radicals formed due to the propane interaction with the nitrite–nitrate complexes. Nitrosopropane adsorption on the catalyst surface seems to be the next step. Note that the kinetic desorption parameters of nitrosopropane formed in both types of pulse experiments were exactly the same.

It is known that nitrosopropane cannot interact directly with NO to give N_2. According to [7], NO can react only with its isomer – acetone oxime. The isomerization rate of nitroso compounds is known to decrease significantly after their adsorption on a surface [32]. Indeed, at 85 °C, the nitrosopropane isomerization to acetone oxime is a slow stage, as a significant amount of nitrosopropane is present on the surface. The temperature increase to 100 °C resulted in the increase of the N_2 evolution at a maximum nitrosopropane coverage, although the value of the maximum coverage itself, which was obtained from the square of the NO peak with the maximum at 250 °C, decreased.

As to the pulse experiments, it is necessary to emphasize that during the NO pulses acetone oxime reacted with NO. This reaction resulted in the decrease of the nitrosopropane concentration starting from the 12th pulse. Meanwhile, in the case of the C_3H_8 pulses, the NO concentration in the gas phase was not sufficient to lead to the decrease of the acetone oxime and, hence, nitrosopropane concentrations.

Two stages can determine the rate of the overall process [7]: the reaction of C_3H_8 with the nitrite–nitrate complexes or the reaction of NO with acetone oxime. In our case, the formation of $C_3H_7^{\bullet}$ radicals in the propane reaction with the nitrite–nitrate complexes is unlikely to determine the rate of the process as nitrosopropane resulting from the interaction of NO with $C_3H_7^{\bullet}$ is stabilized on the surface in significant amounts already at 50 °C. In order to obtain more reliable evidence on the rate-determining step in this temperature region, the kinetics of both nitrosopropane isomerization to acetone oxime and reaction of the latter with NO should be studied over low-exchanged Cu-ZSM-5 catalysts in detail. This work is already in progress.

4. Conclusion

The choice of a low-exchanged Cu-ZSM-5 catalyst in the present study made it possible to observe the active intermediates and to define their surface coverage. The reaction mechanism of NO SCR with propane in which 2-nitrosopropane is the key intermediate [7] has been proved experimentally. It was assumed that dimers of 2-nitrosopropane adsorb on the surface of the catalyst and isomerize to acetone oxime, which would give N_2 in the reaction with NO. The rate of the N_2 formation is directly proportional to the surface coverage with 2-nitrosopropane. There was no formation of N_2 during the interaction of gaseous C_3H_8 with NO adsorbates. However, 2-nitrosopropane and its isomer, acetone oxime, were also formed in this reaction. It follows that the presence of gaseous NO is essential for its selective reduction with C_3H_8 over Cu-ZSM-5. At least two types of copper sites, which are active for NO, acetone and acetone oxime adsorption on low-exchanged Cu-ZSM-5, were detected by our FTIR experiments.

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