NO-assisted N_2O decomposition over *ex*-framework FeZSM-5: mechanistic aspects

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The decomposition of N_2O over an *ex*-framework FeZSM-5 catalyst is strongly promoted by NO. Activity data show that the promoting effect of NO is catalytic, and that besides NO_2, O_2 is formed much more extensively in the presence, than in the absence of NO. Transient *in situ* FT-IR/MS measurements indicate that NO is strongly adsorbed on the catalyst surface up to at least 650 K, showing absorption frequencies at 1884 and 1876 cm^{-1}. A change in gas phase composition from NO to N_2O results in the formation of adsorbed NO_2, identified by a sharp IR band at 1635 cm^{-1}. Switching back to the original NO gas phase induces a rapid desorption of NO_2, restoring the original NO absorption frequencies. During the IR measurements, bands typical of nitro- or nitrate groups were not observed. Multi-Track (a TAP-like technique) experiments show that the presence of NO or NO_2 on the catalyst surface significantly enhances the rate of oxygen desorption at the time of N_2O exposure to the catalyst. The spectral changes and transient experiments are discussed and catalytic cycles are proposed, to explain the formation of NO_2 and the (enhanced) formation of oxygen. The latter can be either explained by an indirect effect (electronic, steric) of NO adsorbed on sites neighboring the active sites, or by a direct effect involving reaction of adsorbed NO_2 groups with neighboring oxidized sites yielding O_2.

KEY WORDS: FeZSM-5; *ex*-framework; NO; N_2O decomposition; promotion; mechanism; transient kinetics; FT-IR; Multi-Track

1. Introduction

Fe-based zeolite catalysts are currently extensively studied, because of high activity in (i) deNOx-SCR [1–5], (ii) N_2O-mediated selective oxidation of benzene to phenol [6,7], and (iii) catalytic N_2O decomposition [8–11]. Recently we reported an extraordinary performance of a specific FeZSM-5 catalyst prepared *via* an *ex*-framework method in the latter reaction [10]. The *ex*-framework catalyst (on a *per* Fe-site basis) shows a significantly higher activity than catalysts prepared *via* other procedures, such as liquid (aqueous)- or solid-ion exchange. Also the stability of this particular catalyst in simulated tail-gas mixtures from nitric acid plants and fluid-bed combustors is excellent [10].

An intriguing general feature of FeZSM-5 catalysts in N_2O decomposition is that NO significantly enhances the activity, while the opposite effect is usually observed for other catalytic systems, *e.g.*, based on noble metals (Ru or Rh) [12,13]. This peculiar behavior of FeZSM-5 makes it very attractive to use in applications where both N_2O and NO are present, such as in tail-gas of nitric acid plants. The positive effect of NO on the N_2O conversion was first reported by some of us in 1996, using a FeZSM-5 prepared by liquid (aqueous) ion exchange with Fe(II) sulfate [14]. At that moment it was proposed that NO in the gas phase scavenged adsorbed oxygen (deposited by N_2O during the oxidation of active sites, equation (1)), leading to the formation of NO_2, and regeneration of the active site (equation (2)).

$$N_2O + * \rightarrow N_2 + O* \qquad (1)$$

$$NO + O* \rightarrow NO_2 + * \qquad (2)$$

Reduction of an oxidized site by NO as represented in equation (2) should lead to a stoichiometric process in which NO and N_2O react to form N_2 and NO_2:

$$N_2O + NO \rightarrow N_2 + NO_2 \qquad (3)$$

Recently Sang and Lund [8] further discussed the mechanism of NO-assisted N_2O decomposition. These authors propose a mechanism involving a nitrite/nitrate redox cycle by reaction with N_2O, yielding O_2 and N_2. It was also proposed that nitrites and nitrates play a role in N_2O decomposition in the absence of NO, based on spectroscopic results of Sachtler and coworkers [3,15] and O_2 exchange experiments performed in the early eighties by Hall and coworkers [16]. Further experimental evidence was not provided by Sang and Lund [8].

To further clarify the NO-assisted N_2O decomposition over highly active *ex*-framework FeZSM-5, in this paper activity data and transient experiments using FT-IR/MS (Fourier transform infrared/mass spectrometry) will be presented. Multi-Track (multiple time resolved analysis of catalytic kinetics) was used to analyze the effect of NO on the formation of oxygen in NO-assisted N_2O decomposition. The possible catalytic pathways will be discussed based on the experimental observations.

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2. Experimental

2.1. Catalysts and materials

Isomorphously substituted FeZSM-5 was synthesized hydrothermally using tetrapropylammonium hydroxide as the template. A solution of the silica source (tetraethylorthosilicate, TEOS, Acros, 98%) and the template (tetrapropylammonium hydroxide, TPAOH, Fluka, 20% in water) was added to a mixture of aluminum(III) nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Merck, 99%) and iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck, 98.5%). The molar ratios between components were $H_2O/Si = 45$, $TPAOH/Si = 0.3$, $Si/Al = 36$, and $Si/Fe = 152$. The solution was transferred to a stainless-steel autoclave lined with Teflon and kept in a static air oven at 448 K for 5 days. The crystalline material was filtered and washed with deionized water. The as-synthesized sample, in which Fe(III) is isomorphously substituted in the zeolite framework, was calcined in air at 823 K for 10 h and was then converted into the H-form by three consecutive exchanges with an ammonium nitrate solution (0.1 M) overnight and subsequent calcination at 823 K for 5 h. Finally, the catalyst was treated in flowing steam at ambient pressure (water partial pressure of 300 mbar and 30 ml min^{-1} of N_2 flow) at 873 K during 5 h, yielding *ex*-FeZSM-5. In the following description of the various experiments, N_2O, NO (5 vol% NO in He, or 15% NO in Ar (Multi-Track)), He, and Ar were of UHP grade and used as received.

2.2. Activity tests

Activity measurements were carried out in a fixed-bed flow reactor system [17], using 50 mg of catalyst (125–200 μm) and a total flow rate of 50 ml min^{-1} (space velocity, GHSV = 60000 h^{-1}) at atmospheric pressure. The feed compositions used were (i) 1.5 mbar N_2O in He, (ii) 1.5 mbar N_2O and 0.2 mbar NO in He, and (iii) 1.5 mbar N_2O and 0.4 mbar NO in He. Before reaction, the catalysts were pretreated in N_2O (1.5 mbar N_2O in He) at 723 K for 1 h. N_2O, N_2, and O_2 were analyzed with a GC equipped with a thermal conductivity detector, using a Poraplot Q column (for N_2O separation) and a Molsieve 5A column (for N_2 and O_2 separation). NO and NO_2 concentrations were determined with a chemiluminescence NO_x analyzer (Ecophysics CLD 700 EL).

2.3. FT-IR/MS experiments

The FT-IR measurements were performed using an *in situ* infrared cell with CaF_2 windows. This cell was designed and built at the University of Amsterdam [18]. Gas could be fed to the cell using a four-way valve (Valco), which was configured to select two separate gas feeds. Using a flow of 30 ml min^{-1}, the cell was completely refreshed in about 30 s after switching the valve. For the infrared measurements, the catalyst was pressed in the form of a self-supporting wafer ($\sim$70 mg cm^{-2}) at a pressure of 3 ton cm^{-2}. Pretreatment of the wafer consisted of drying at 573 K in He for 1 h. Spectra were recorded using a Nicolet Magna infrared 860 spectrometer equipped with a nitrogen cooled MCT detector and a rapid scan interferometer. Unless stated otherwise, spectra were recorded against a background of the sample at the reaction temperature under He at 4 cm^{-1} resolution, using co-addition of 48 scans. Transient experiments were performed using a rapid scan collection mode. Again 48 scans were co-added for each spectrum using scan length minimization, leading to a complete spectrum collection time of 7.7 s.

The infrared measurements were performed using a 3 vol% N_2O in He mixture, and a 5 vol% NO in He mixture. The transients in gas phase composition were followed using a quadrupole mass spectrometer (Pfeiffer Thermostarr) connected on line to the outlet of the *in situ* infrared cell.

2.4. Multi-Track experiments

A detailed description of the Multi-Track system is presented elsewhere [19]. Briefly, a catalytic reactor is located in an ultrahigh vacuum system operating at a pressure of 3 Pa. The catalyst bed (100 mg, pellet size 125–200 μm) packed between two layers of SiC particles (each containing 200 mg particles of 230 μm in size), is exposed to a gas pulse with a width of 100 μs and a size of 10^{17} molecules. In the reactor, the shape and composition of the gas pulse change due to processes such as diffusion, adsorption, and reaction. At the reactor exit the reaction products are analyzed by four quadrupole mass spectrometers. All four mass spectrometers are able to analyze one of the components in the exit gas stream with a maximum sample frequency of 1 MHz. As the signal-to-noise ratio in this system is excellent, no averaging of pulses is necessary to obtain good peak signals. This is an important aspect, as transient phenomena may remain unobserved when the peaks have to be averaged.

Before the measurements, the *ex*-framework FeZSM-5 catalyst was evacuated in the Multi-Track reactor at 723 K for 3 h. The mechanistic studies of N_2O decomposition were performed by pulsing pure N_2O at different temperatures in the range of 623–973 K. The effect of NO on the reaction was studied using so-called pump–probe experiments. A time interval of 1 s between the NO and N_2O pulse was typically applied.

3. Results

3.1. Activity measurements

The performance of *ex*-FeZSM-5 in different feed mixtures is presented in figure 1. In a N_2O/He feed, the catalyst only shows a substantial N_2O conversion above 700 K. Addition of NO (0.2 mbar; molar N_2O/NO ratio of 7.5) enhances the reaction rate considerably; the N_2O conversion curve is shifted to about 100 K lower temperatures. Higher amounts of NO in the feed gas (0.4 mbar; molar N_2O/NO ratio of 3.75) only lead to a slight further improvement, suggesting that a relatively small amount of NO (compared to N_2O in the feed) is sufficient to induce a dramatic change in N_2O decomposition activity.

Analysis of the NO, NO_2, and NO_x profiles provides further information on the effect of NO on the catalytic performance. In a N_2O + NO/He feed, the formation of NO_2 increases as a function of reaction temperature (figure 2 (a) and (b)), reaching a maximum at 650–675 K, *i.e.*, in the slope of the N_2O decomposition activity curve. Above this temperature, NO_2 formation decreases, and completely disappears at 775 K. The NO_x level is constant in the temperature range investigated, indicating that NO_x is not converted to N_2 or N_2O. The conversion of NO to NO_2 should be related to the performance of the *ex*-framework FeZSM-5 catalyst, since NO_2 formation was not observed over an inert material (SiC, not shown). Furthermore, reaction of NO with N_2O to NO_2 and N_2 is not thermodynamically limited above 675 K, since less active catalysts show a maximum of similar intensity at significantly higher temperatures, as will be reported in an upcoming publication [20].

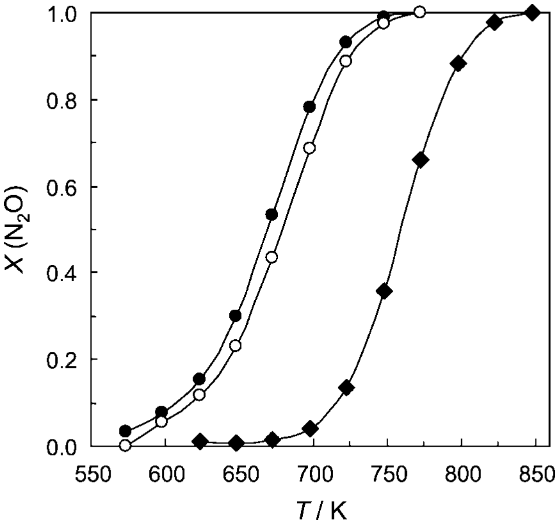


Figure 1. N_2O conversion *vs.* temperature over *ex*-FeZSM-5 in different feed compositions: (◆) 1.5 mbar N_2O in He, (○) 1.5 mbar N_2O and 0.2 mbar NO in He, (●) 1.5 mbar N_2O and 0.4 mbar NO in He. Space velocity 60000 h^{-1}.

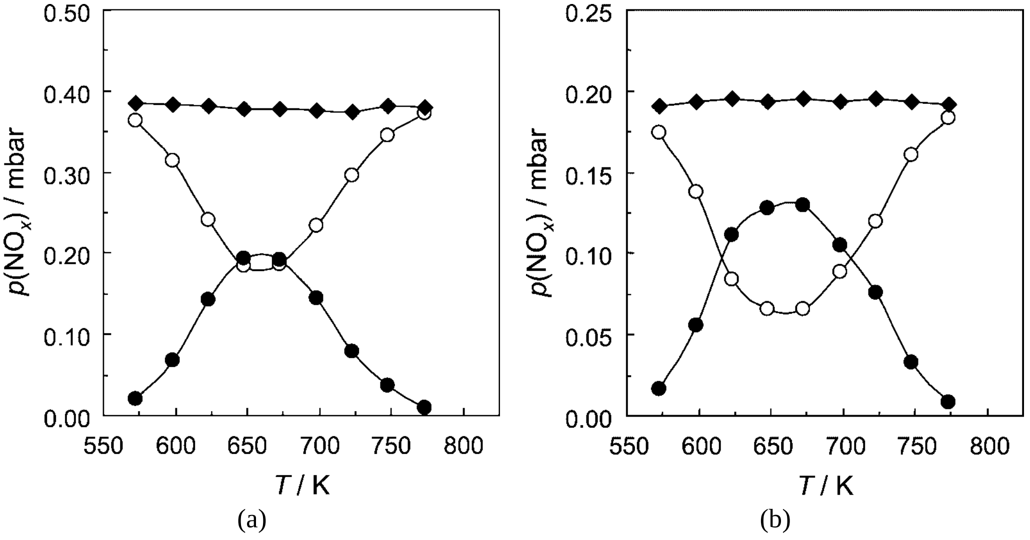
Mass balance calculations at different temperatures clearly show that the stoichiometric reaction of N_2O with NO to NO_2 and N_2 (equation (3) in section 1) cannot explain the observed effects in figures 1 and 2. Table 1 shows the result at 700 K. It can be concluded that besides inducing the formation of NO_2, the presence of NO in the N_2O containing feed also significantly enhances the production of O_2.

3.2. FT-IR/MS experiments

To verify whether N_2O could be decomposed into (adsorbed) NO/NO_2 or nitrites and nitrates, the catalyst pellet was exposed to a flow of 30 ml min^{-1} 3 vol% N_2O in He for 2 h at 373 and 573 K, respectively. Besides the features of gas phase N_2O, adsorbed species could not be observed, indicating a weak interaction of N_2O with the catalyst. Apparently the reactions leading to adsorbed NO or NO_2 species reported by others for ion-exchanged FeZSM-5 catalysts [11], and catalysts prepared *via* sublimation of $FeCl_3$ in the zeolite pores [15] are absent for the *ex*-framework catalyst. A spectrum of NO adsorbed on the *ex*-framework cat-

Table 1
Mass balance data at 700 K, as calculated from the activity measurements.

Feed composition	Partial pressure (mbar)		
	N_2O disappeared	NO_2 formed	O_2 formed
1.5 mbar N_2O in He	0.075	–	0.035
1.5 mbar N_2O + 0.2 mbar NO in He	0.955	0.105	0.460
1.5 mbar N_2O + 0.4 mbar NO in He	1.170	0.145	0.505



(a) (b)

Figure 2. Partial pressure of (○) NO, (●) NO_2, and (◆) NO_x *vs.* temperature over *ex*-FeZSM-5 during catalytic decomposition of N_2O in 1.5 mbar N_2O and (a) 0.4 mbar of NO and (b) 0.2 mbar NO. Space velocity 60000 h^{-1}.

alyst at 353 K is presented in figure 3, showing absorption frequencies at 2133, 1886 and 1874 cm^{-1}. The origin of the 2133 cm^{-1} band has recently been discussed extensively, and has been assigned to positively charged NO, occupying cationic positions in the zeolite structure [21]. Bands in the range of 1750–1920 cm^{-1} have often been observed in the spectra of NO adsorbed on zeolite and oxide supported Fe catalysts, but the assignment is ambiguous. Hadjiivanov *et al.* [1], Lobree *et al.* [2,22], and Lezcano *et al.* [23] recently discussed the origin of these bands. Both the 1874 and 1886 cm^{-1} bands are assigned to mono-nitrosylic species associated with Fe in the 2+ state (Fe^{II}–NO). The species causing the 1874 cm^{-1} absorption was assigned by Lobree *et al.* to Fe sites in little accessible β exchange positions [2]. The 1886 cm^{-1} band was observed by Lezcano *et al.* [23] including bands at slightly lower wavenumbers (1873 and 1867 cm^{-1}), but unfortunately the origin of the multiplet was not discussed, and the major 1886 cm^{-1} band assigned to Fe^{II}–NO on the basis of the assignments of the 1874 cm^{-1} band by others. At present the origin of the doublet at 1874 and 1886 cm^{-1} is not clear. A detailed IR study of Fe in *ex*-framework materials (Silcalite and ZSM-5), before and after steaming, is currently conducted to explain these spectral features.

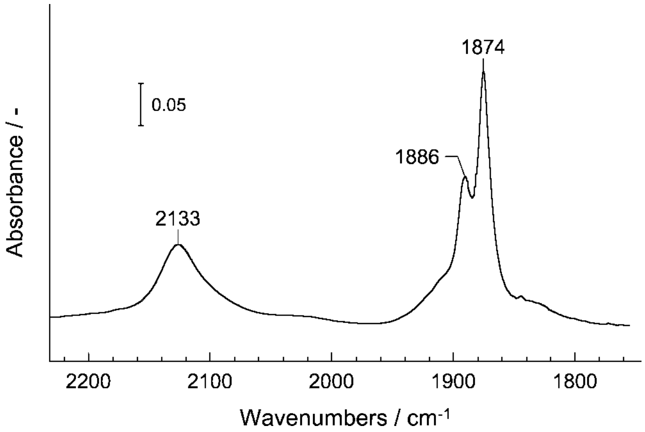


Figure 3. Infrared spectrum of NO adsorbed on *ex*-framework FeZSM-5 at 353 K in continuous flow of (30 ml min^{-1}) 5% NO in He against a background of the catalyst at 353 K in He.

The transients occurring when NO adsorbed on *ex*-framework FeZSM-5 is exposed to N_2O are shown in figure 4. The gas phase composition was changed from 5 vol% NO in He to 3 vol% N_2O in He and back to 5 vol% NO in He at 523 K. Upon the introduction of N_2O in the cell, bands assigned to gas phase N_2O appear at around 2225 cm^{-1}. A continuous decrease of the bands assigned to adsorbed NO can be observed. After an induction period of 30 s, a new band is developed around 1632 cm^{-1} which continuously grows in intensity and can be assigned to adsorbed NO_2 [1,2,22]. The corresponding gas phase product evolution is shown in figure 5. A time delay is observed between the time of switching the gas from NO to N_2O, and the formation of N_2, which corresponds to the infrared observations. The formation of NO_2 was not detected. Upon switching the gas phase composition back to NO, a rapid transition of the 1635 cm^{-1} to the original bands at 1886 and 1874 cm^{-1} was observed (not shown). At the same time the MS analysis shows that NO_2 is formed instantaneously (figure 5), as well as some N_2.

3.3. Multi-Track experiments

According to the activity measurements, the positive effect of NO on the N_2O decomposition does not only lead to formation of NO_2, but also to large amounts of O_2. In order to further investigate the effect of NO on O_2 formation, Multi-Track experiments were performed. N_2O was

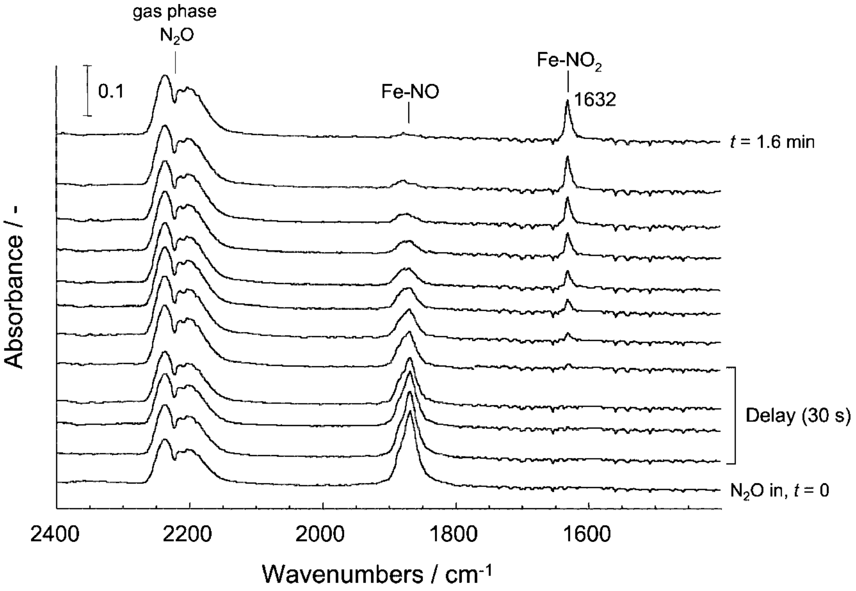


Figure 4. Transient infrared spectra of NO adsorbed on *ex*-framework FeZSM-5 at 523 K upon switching a flow of (30 ml min^{-1}) 5% NO in He to (30 ml min^{-1}) 3% N_2O in He. Spectra recorded against a background of the catalyst at 523 K in He.

pulsed through the catalyst bed at 673 K. The O_2 response is shown in figure 6. Only a slight increase of the base-line (figure 6(a)) is present, indicating very slow desorption of O_2. In pump–probe experiments, in which NO was introduced 1 s after the N_2O pulse, a remarkable effect on the O_2 response can be observed. As is shown in figure 6, curve (b), the O_2 response at the time of the N_2O pulse sharens, indicating a significantly faster O_2 desorption in N_2O–NO alternating cycles, than in the experiment with N_2O only. Switching the pulse of NO off results in desorption of NO and transition to the original catalyst behavior, with a very broad O_2 response (curves (c)–(e)). NO desorption is complete after about 20 s. At high temperatures (>800 K) the effect of NO on the oxygen desorption behavior is negligible, as shown in figure 7. The O_2 profiles obtained by pulsing N_2O only, or N_2O and NO alternately, are very similar, indicating that at this high temperature O_2 desorption is fast, and hardly affected by NO.

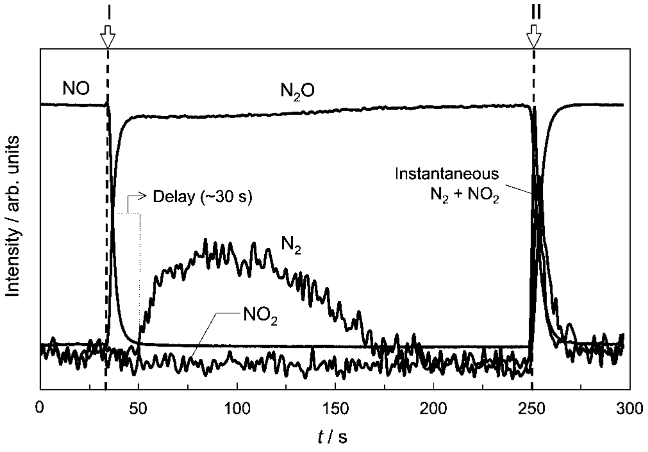


Figure 5. Transient in gas composition upon switching a (30 ml min^{-1}) flow of 5% NO in He to (30 ml min^{-1}) 3% N_2O in He at time 0 s, and back to a (30 ml min^{-1}) flow of 5% NO in He at time 250 s. MS profiles of NO, N_2O, NO, and N_2 are shown.

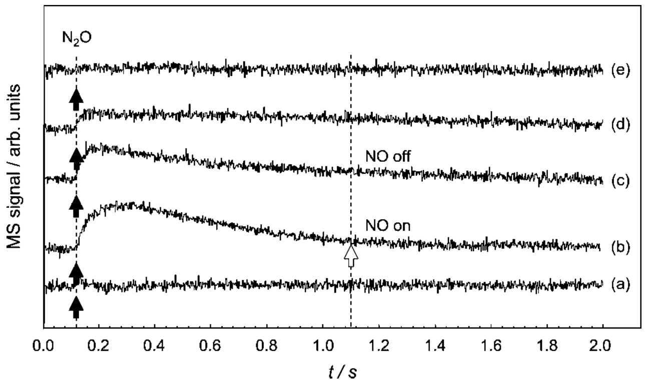


Figure 6. O_2 profiles measured by Multi-Track during catalytic decomposition of N_2O over *ex*-FeZSM-5 at 698 K: (a) pulsing N_2O at 0.1 s, (b) pulsing N_2O and NO at 0.1 and 1.1 s, respectively, (c) pulsing N_2O at 0.1 s, 10 s after switching off the NO valve, (d) pulsing N_2O at 0.1 s, 20 s after switching off the NO valve, and (e) pulsing N_2O at 0.1 s, 40 s after switching off the NO valve.

4. Discussion

The nature of the active site in FeZSM-5 catalysts prepared by various methods, has already been discussed extensively in the literature, *e.g.*, in [2,4,6,24,25]. Isolated ions in framework positions, or in various *ex*-framework positions in the zeolite channels, dinuclear or polynuclear (Fe_4O_4) species, and iron oxide particles (1–2 nm) have been identified in various samples. Based on an apparent correlation between the activity in N_2O decomposition and the size of the iron oxide particles presented elsewhere [10], the active species in the following discussion of the catalytic cycles of N_2O decomposition will be represented as Fe oxide. A detailed discussion of the nature of the active sites will be presented elsewhere [20]. Whatever the exact structure of the active site, in any case two neighboring Fe sites need to be present to account for the activity [10] and NO-assisted N_2O decomposition.

The kinetics of N_2O decomposition over Fe-based catalysts have been previously discussed [8,9]. Two alternative pathways to explain the formation of oxygen have been proposed. This is illustrated in figure 8. First, a free site is oxidized by reaction with N_2O. If this process occurs on two neighboring sites, recombination of the oxygen deposited on these sites leads to O_2 formation (pathway 1). If the second N_2O molecule reacts with the oxidized site, this also results in the regeneration of the site, according to pathway 2 in figure 8. In view of the very slow oxygen desorption (figure 6), the recombination of two oxygen atoms (located on two different sites) appears the most likely explanation for O_2 formation. Sang and Lund [8] recently proposed an alternative mechanism in which cycling between surface nitrites and nitrates plays a role (equations (4) and (5)).

$$N_2O + NO_3^-{*} \rightarrow N_2 + O_2 + NO_2^-{*} \tag{4}$$

$$N_2O + NO_2^-{*} \rightarrow N_2 + NO_3^-{*} \tag{5}$$

However, for the *ex*-framework FeZSM-5 catalyst, formation of adsorbed NO or NO_2 was never observed in IR ex-

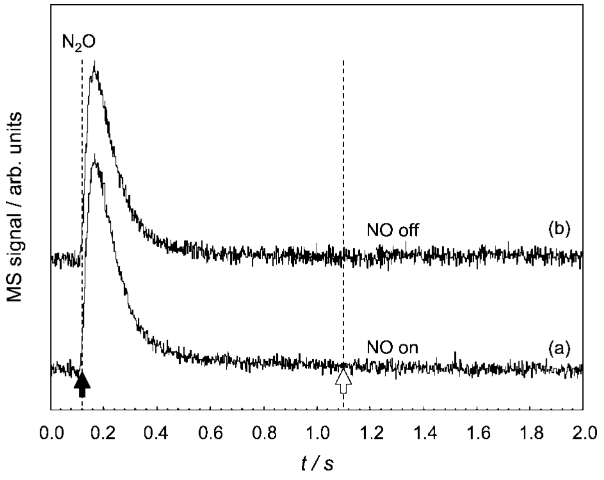


Figure 7. O_2 profiles measured by Multi-Track during catalytic decomposition of N_2O over *ex*-FeZSM-5 at 973 K: (a) pulsing N_2O at 0.1 s and (b) pulsing N_2O and NO at 0.1 and 1.1 s, respectively.

periments in which the catalyst was exposed to N_2O only, suggesting that this pathway does not occur over our catalytic system.

The beneficial effect of NO on the activity of the FeZSM-5 catalysts has been assigned by Kapteijn *et al.* to scavenging of adsorbed O, regenerating the active site (equation (2)) [9,14]. Sang and Lund [8] use the interconversion of nitrates and nitrites to explain the enhancement of N_2O conversion by the presence of NO (equations (4) and (5)). The theories of neither Kapteijn *et al.* nor Sang and Lund appear to explain the experimental data presented in this paper. If scavenging of adsorbed $O*$ by NO was the only mechanism of promotion, the enhanced production (table 1) and desorption rate of oxygen (figure 6, curve (b)) are hard to explain. The mechanism of Sang and Lund appears neither in agreement with the data presented here, since nitrate bands (in the range of 1500–1600 cm^{-1} [3,15]) have not been observed in any of the infrared spectra.

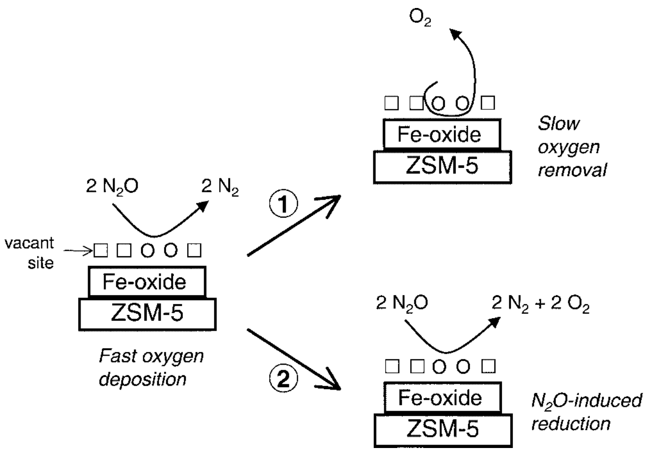


Figure 8. Schematic representation of the catalytic N_2O decomposition over FeZSM-5 catalysts in the absence of NO.

Apparently alternative pathway(s) are needed to explain the NO-assisted N_2O decomposition. The IR spectra indicate a strong adsorption of NO on the catalyst surface and in view of the intensities, a high occupancy of the available sites by NO. This is schematically shown in figure 9. A time delay between the formation of N_2 and the exposure of the catalyst to N_2O can be observed (figure 5). This suggests that some NO needs to desorb to allow N_2O to be activated, converting N_2O into N_2 and an oxidized site. This is shown as a first step in figure 9. The IR spectra (figure 4) show a similar time delay in the conversion of Fe^{II}–NO to Fe^{II}–NO_2 (decreasing 1874 and 1886 cm^{-1} bands and the increasing 1632 cm^{-1} band (figure 4)), suggesting that the oxidized site subsequently oxidizes adsorbed NO to NO_2. This is schematically shown in pathway 3. Switching back to the original NO gas phase, results in a rapid desorption of NO_2 (figure 5) and restores the original NO absorption frequencies. This is shown in pathway 4, which suggests that NO_2 adsorption on the catalyst surface is weaker than that of NO. It should be mentioned that this is apparently a specific feature of the *ex*-framework catalyst, since other authors have suggested the opposite, *i.e.*, NO_2 is more strongly adsorbed on FeZSM-5 catalysts than NO [2,5]. Step 4 is the process to close the catalytic cycle in the conversion of N_2O and NO to N_2 and NO_2. The N_2 produced in the switch from N_2O to NO in the MS profiles (figure 5) is related to the limited time that both NO and N_2O are present in the IR cell.

In our view, different steps can explain the enhanced desorption of oxygen as observed in the Multi-Track experiments, and oxygen formation in the activity measurements. Similar to the pathway in the absence of NO (figure 8, pathway 2), pathway 2 in figure 9 involves reaction of the oxidized site with N_2O, yielding O_2 and N_2. The enhanced oxygen desorption from the active site is then explained by a reduced stability of adsorbed O_2, induced by either elec-

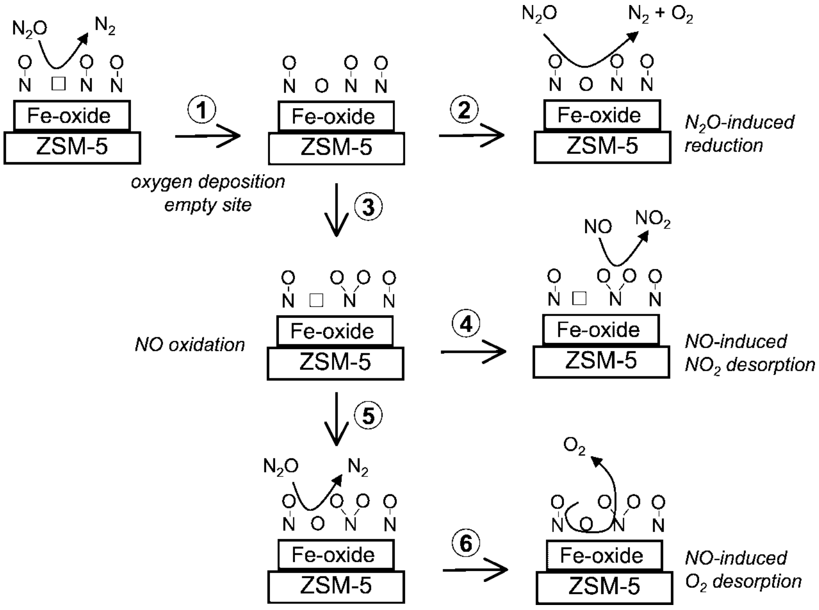


Figure 9. Schematic representation of the catalytic N_2O decomposition over FeZSM-5 catalysts in the presence of NO.

tronic or steric effects of the NO adsorbed on neighboring sites. An alternative explanation for the enhanced oxygen desorption is depicted in figure 9 as steps 5 and 6. In fact this cycle is a modification of that proposed by Sang and Lund [8], and involves the recombination of oxygen present in adsorbed NO_2 and oxygen species deposited by N_2O on a neighboring site. However, this cycle can only be justified if a nitrate-like intermediate is not involved in the recombination, since nitrates were never observed in the transient IR experiments. To gain further insight in the enhanced formation of oxygen, ^{18}O labeled N_2O should be applied. If the catalyst is "pre-loaded" with $N^{16}O$, exposure to $N_2{}^{18}O$ should lead to $^{18}O_2$ if pathway 2 occurs, and to $^{16}O^{18}O$ if pathways 5 and 6 dominate the catalytic cycle. These types of experiments are planned in the near future.

5. Conclusions

Experimental evidence for two parallel pathways to explain the promotion of catalytic N_2O decomposition over *ex*-FeZSM-5 by NO is provided, one involving NO_2 formation and the other O_2 formation. The steps explaining NO_2 formation include (i) strong adsorption of NO on the *ex*-framework FeZSM-5 catalyst, (ii) interaction of adsorbed NO with N_2O yielding adsorbed NO_2, and (iii) NO-induced NO_2 desorption. Two alternative explanations are proposed for the enhanced formation of O_2. One involves electronic and/or steric effects of NO adsorbed on sites neighboring the N_2O decomposition sites, and the other a catalytic cycle in which recombination of oxygen from adsorbed NO_2 and an oxidized active site plays a role.

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