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The surface chemistry of N_2O decomposition on iron containing zeolites (I)

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Abstract

The reaction of Fe-zeolites prepared by sublimation of $FeCl_3$ with N_2O was studied by step- and pulse-response experiments. Steps from 0 to 5000 ppm N_2O were performed at 673 K, after pretreatment of the catalyst in H_2, He, or O_2. When the catalysts were prereduced in H_2, N_2O was first consumed for the reoxidation of the catalyst, before steady-state N_2O decomposition started. Also pretreatment in He reduced the catalyst. This autoreduction was not spontaneous, but caused by a small amount of hydrocarbons adsorbed on the catalyst. Prereduced catalysts had a higher steady-state activity, indicating that the incorporation of oxygen from N_2O changed the structure of the active sites. Pulse responses proved that O_2 desorption is the rate-limiting step of N_2O decomposition. O_2 desorption was relatively fast from a small fraction of sites, while a second oxygen pool desorbed only slowly from the catalyst. Only the former is responsible for catalytic activity.

Keywords: N_2O decomposition; Fe-ZSM-5; Alpha-oxygen; Step response

1. Introduction

Some years ago Panov and co-workers discovered that Fe-ZSM-5 catalysts contain active sites with remarkable redox properties [1–3]. Upon interaction with N_2O at moderate temperatures (473–523 K) these active sites, called α-sites, create a highly active surface oxygen, which readily exchanges with O_2 and oxidizes CO and CH_4 already at room temperature. The creation of α-oxygen occurs only when the catalysts are treated with N_2O. O_2 treatment leaves the catalyst unchanged. Before being loaded with α-oxygen, the α-sites are inert toward molecular oxygen. A recent Mössbauer study suggests that the α-sites are binuclear Fe^{2+} clusters [4]. It was proposed that they react with N_2O as follows:

$$\begin{aligned}&Fe^{2+}\text{–}\mu\text{–(OH)–}Fe^{2+} + 2N_2O\\&\to O^-\text{–}Fe^{3+}\text{–}\mu\text{–(OH)–}Fe^{3+}\text{–}O^-.\end{aligned}$$

The classical α-site catalysts are prepared by direct incorporation of iron into the framework of ZSM-5 during the synthesis, followed by extraction of iron from the framework by high-temperature treatment, in particular using steam. Only upon extraction from the framework positions, the iron sites are converted to α-sites. Dubkov et al. showed that the generation of α-sites is not tied to this particular preparation method [4]. α-Sites were also detected on Fe-ZSM-5, in which iron was introduced by postsynthetic impregnation with $FeCl_3$, after it was subjected to a high temperature treatment. The results indicate that the method of iron incorporation is of secondary importance for the creation of α-sites. Treatment of high temperature, on the other hand, seems to be a prerequisite. In confirmation, Jia et al. [5] recently showed that Fe-ZSM-5 catalysts prepared by sublimation of $FeCl_3$ exhibit α-site-like behavior if they are reduced at temperatures above 873 K. Sublimed Fe-ZSM-5 catalysts, which were reduced only at 773 K, behaved “normally”: interaction with N_2O did not create oxygen species, which underwent isotopic exchange with $^{18}O_2$ at low temperatures. Still, these catalysts are good catalysts in N_2O decomposition. They are less active than the Panov-type catalysts on the basis of turnover frequency, but more active on a per gram basis [6]. What is the nature and role of the oxygen species on these “conventional” iron zeolites? Does interaction with N_2O create a special surface oxygen species, which is different from the oxygen present in the original iron oxide cluster, also on this type of catalysts? N_2O decomposition proceeds

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Table 1
Elemental composition of the samples as determined by AAS

Sample	Si/Al	Fe (wt%)	Fe/Al
Fe-ZSM-5	20	3.6	1.0
Fe-ZSM-12	27	2.7	1.1
Fe-BEA	11	2.6	0.4

according to the following mechanism [7],

$$^{*} + N_2O \rightarrow N_2 + {}^{*}\text{–}O, \qquad (1)$$

$$^{*}\text{–}O + N_2O \rightarrow N_2 + O_2, \qquad (2)$$

$$2^{*}\text{–}O \rightarrow O_2 + 2^{*}, \qquad (3)$$

where * stands for an active (iron) site on the surface. Steady-state experiments only show the global kinetics of the reaction and are not very informative about the reaction mechanism and the surface species involved. In step-response experiments, however, where the concentration of N_2O is abruptly changed from zero to a finite value or vice versa, the buildup (Eq. (1)) or the consumption (Eq. (3)) of the oxygen species on the surface can be observed. We therefore decided to use that technique to learn more about the surface chemistry of iron zeolites prepared by postsynthetic ion exchange. High temperature treatments of the catalysts were deliberately avoided. Their effects on the behavior of the catalyst will be dealt with in a separate paper.

2. Experimental

2.1. Sublimation of $FeCl_3$

An ammonium-exchanged zeolite was loaded into a U-tube and first treated in a flow of O_2 at 773 K for 3 h to remove adsorbed water and other impurities. The reactor was then closed and transferred to the glovebox where $FeCl_3$ was loaded. Subsequently, the reactor was heated in a flow of N_2 to 593 K (heating rate 2 K/min) where sublimation of $FeCl_3$ onto the zeolite was performed for 3 h. The reactor was cooled to room temperature, and the $FeCl_3$-loaded zeolite was recovered and immediately washed with water, until no Cl^- ions could be detected in the washing water. The zeolite was dried in air and finally calcined in a flow of O_2 at 773 K for 2 h (heating rate 1 K/min).

As parent zeolites ZSM-5 (MFI-P 46, Südchemie), BEA (PB3, Zeolyst), and ZSM-12 (provided by the University of Cincinnati) [8] were used. The composition of the samples after sublimation, washing, and calcination was determined by AAS (see Table 1).

2.2. Step-response experiments

In a standard step-response experiment 50 mg of pelletized material (mesh size 250–300 µm) was placed between two pieces of quartz wool in a quartz reactor of 4 mm ID. The catalyst was pretreated in H_2/He, O_2/He, or He at 673 K for 60 min. The reactor was brought to reaction temperature and flushed with pure He. After stabilization, the inlet stream was changed to 5000 ppm N_2O in He by switching an electronic valve. N_2O decomposition was followed for about 45 min. Then the inlet stream was switched back to pure He and the catalyst was flushed for a time t (5 to 90 min) before performing a second step up to 5000 ppm N_2O. In several cases other gas mixtures than 5000 ppm N_2O in He were used for the steps, e.g., O_2 in He or a mixture of O_2 and N_2O in He.

The gas flow rate before and after the step was kept at 25 $\text{ml}_{\text{NTP}}/\text{min}$, corresponding to GHSV = 20,000 h^{-1}. All experiments were performed at atmospheric pressure. The reactor effluent was analyzed using a quadrupole mass spectrometer. Usually, the mass fragments $m/e = 4$, 28, 32, and 44 were recorded. $m/e = 4$ (He) was used for the normalization of the signals. Time resolution was 2 s. In some experiments, Ar was added as a tracer gas.

Blank experiments showed that the dead time of the system was 40 s. N_2O reached 95% of its final concentration within 30 s in a step up and it took the same time to go down to 5% of its original concentration in a step down. The graphs presented hereafter are not corrected for the dead time of the system. Time zero is the time when the valve was switched.

2.3. Pulse-response experiments

A 6-port valve was installed between the 4-port switching valve and the reactor, which allowed a combination of pulse and step experiments. In a standard step-pulse experiment the catalyst was preconditioned in He and N_2O. Then a step from pure He to 1000 ppm N_2O in He was performed. After reaching steady state, six pulses of 5000 ppm N_2O in He were administered (pulse volume 500 µl) at an interval of 2 min. Ar was added as a tracer to the pulse mixture in some of the experiments. After the series of pulses, a step down to He was performed. One minute after the step down a new series of six (or more) pulses was given.

3. Results

3.1. Characterization

The Fe/Al ratio (see Table 1) of Fe-ZSM-5 and Fe-ZSM-12 was close to 1, corresponding to the exchange of one iron per Brønsted acid site [9]. For Fe-BEA, however, the ratio was much lower. We attribute this to the high concentration of defects in BEA, where not every Al atom corresponds to a Brønsted acid site. UV–vis and EXAFS spectra of all three catalysts (not shown) were similar to those reported before [10,11] for Fe-ZSM-5. This suggests that the same iron oxide clusters are formed in all iron zeolites prepared by sublimation.

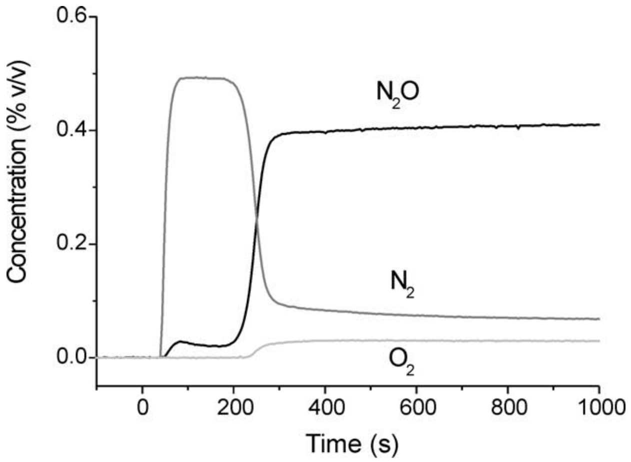

Fig. 1. Response of Fe-ZSM-5 to a step from 0 to 5000 ppm N_2O after reduction in 35% H_2 in He at 673 K for 1 h, at 673 K, GHSV = 20,000 h^{-1}, and 1 bar.

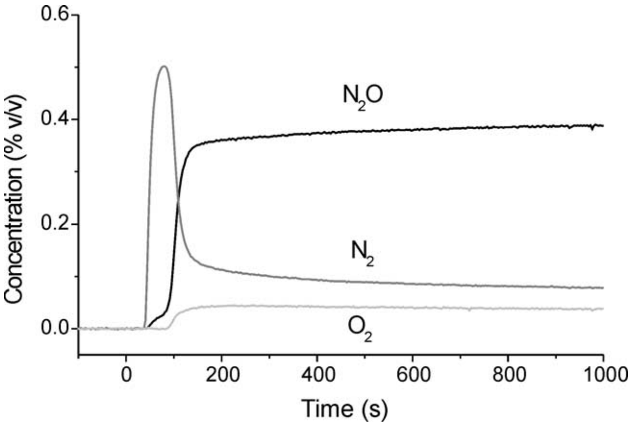

Fig. 2. Response of Fe-ZSM-5 to a step from 0 to 5000 ppm N_2O after treatment in He at 673 K for 1 h, at 673 K, GHSV = 20,000 h^{-1}, and 1 bar.

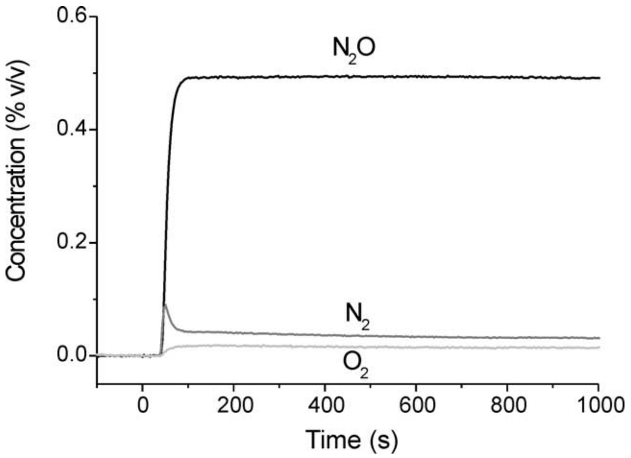

Fig. 3. Response of Fe-ZSM-5 to a step from 0 to 5000 ppm N_2O after treatment in 2000 ppm O_2 in He at 673 K for 1 h, at 673 K, GHSV = 20,000 h^{-1}, and 1 bar.

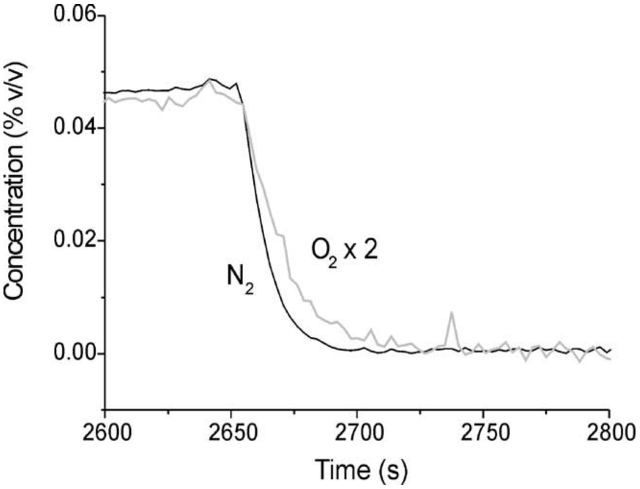

Fig. 4. Response of Fe-ZSM-5 to a step from 5000 ppm N_2O to pure He at 673 K, GHSV = 20,000 h^{-1}, and 1 bar.

3.2. *Effect of pretreatment on the step response*

In a first experiment, Fe-ZSM-5 was reduced in a stream of 35% H_2 in He and then subjected to the step to N_2O. The step response is shown in Fig. 1. A fast evolution of N_2 was observed, which reached a steady-state level after about 300 s. Simultaneous with the decay of the N_2 peak, O_2 started to evolve and the N_2O concentration increased to its steady-state level. The small peak in the N_2O concentration after 40 s disappeared when the catalyst was reduced a second time in H_2 and the step to N_2O was repeated. In that case the N_2O concentration remained zero till to the simultaneous increase of N_2O and O_2 and the decay of the N_2 peak (not shown).

Fig. 2 shows the response of the catalyst to a step of N_2O after pretreatment in pure He for 1 h. As in Fig. 1, a fast initial formation of N_2 was observed, followed by an increase of the N_2O and O_2 concentrations and a simultaneous decay of the N_2 formation. After the initial N_2 peak the catalyst gradually approached steady state, which was reached after about 1000 s. In comparison to the step response after reduction in H_2, the amount of N_2 formed in the initial peak was smaller and the rise of the N_2O and the O_2 concentration occurred earlier. When the step was performed after pretreatment in 2000 ppm O_2 (Fig. 3), N_2O and O_2 evolved without delay and only a small peak in the N_2 concentration was detected.

Fig. 4 shows a typical response to the step down from 5000 ppm N_2O back to pure He. The O_2 concentration decreased slower than the N_2 concentration, i.e., O_2 desorption from the catalyst was slow. The tailing of the O_2 concentration was even stronger when the experiment was performed at 623 K. When a second step up was performed after flushing the catalyst for 15 min in He (as described in the experimental section), the response resembled the one shown in Fig. 3, irrespective of the original pretreatment.

The amount of excess N_2 formed in the N_2 peak following the step up to N_2O was quantified by subtracting two times the O_2 curve from the N_2 curve. The integration results are compiled in Table 2.

Table 2
Step response of Fe-ZSM-5 after pretreatment at 673 K in 35% H_2, He, 2000 ppm O_2, or 10% O_2

	Pretreatment					
	H_2	H_2[a]	He	O_2 0.2%	O_2 10%	He[b]
	Excess N_2/Fe (mol/mol)					
First step	0.62	0.53	0.19	0.01	0.005	0.19
Second step	0.012	0.011	0.008	n.d.	0.004	0.010
	Yield N_2/O_2 (%)					
First step	12.5	13.8	13.1	6.1	6.8	11.8
Second step	12.4	13.2	12.4	n.d.	6.7	10.0

Reported are the amount of excess N_2/Fe formed after the step to 5000 ppm N_2O and the steady-state yields of N_2 and O_2, as well as the values for a second step to 5000 ppm N_2O after flushing for 15 min in He.

[a] After second reduction in H_2.

[b] Step to 4500 ppm $N_2O + 4500$ ppm O_2.

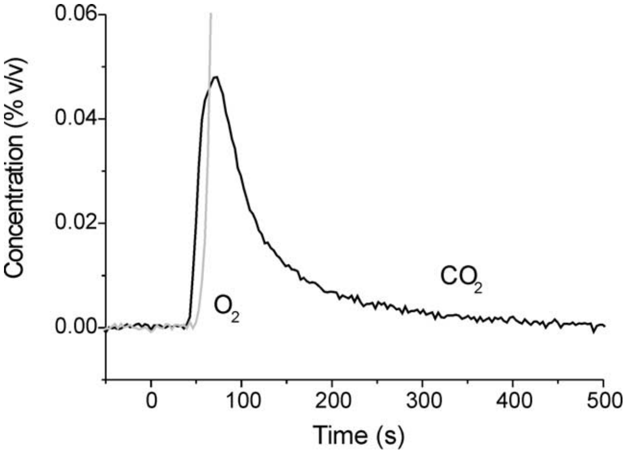

Fig. 5. Response of Fe-ZSM-5 to a step from 0 to 4500 ppm O_2 after treatment in He at 673 K for 1 h, at 673 K, GHSV = 20,000 h^{-1}, and 1 bar.

For comparison, we also probed the step response of the catalyst toward 4500 ppm O_2 (cf. Fig. 5). Immediately after the step to O_2, a peak of mass 44 was detected. Since the peak cannot originate from N_2O, it was ascribed to the formation of CO_2 by oxidation of a small amount of hydrocarbons adsorbed on the catalyst. The amount of CO_2 formed was 0.01 mmol/g catalyst. The oxidation of adsorbed hydrocarbons also explains the small peaks or shoulders observed in the N_2O-response curves of fresh catalysts, which were not pretreated in O_2 (as seen, for example, in Fig. 1). The peaks and shoulders are an artifact caused by CO_2, which cannot be distinguished from N_2O in the mass spectrometer.

In a step to a mixture of 4500 ppm N_2O with 4500 ppm O_2 (cf. Fig. 6) a large amount of excess N_2 was formed, but also the O_2 response was delayed by about 20 s. Quantitative analysis showed that 0.19 mol excess N_2/Fe was formed. At the same time 0.06 mol O_2/Fe was consumed by oxidation of the catalyst. The amount of O_2 consumed was calculated by comparison with a blank experiment.

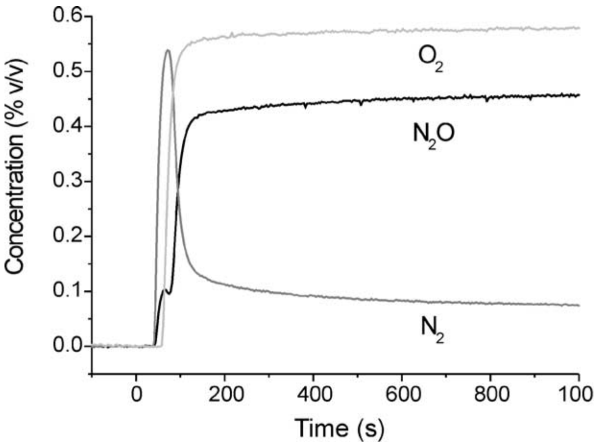

Fig. 6. Response of Fe-ZSM-5 to a step from pure He to 4500 ppm $N_2O + 4500$ ppm O_2 after treatment in pure He at 673 K for 1 h, at 673 K, GHSV = 20,000 h^{-1}, and 1 bar.

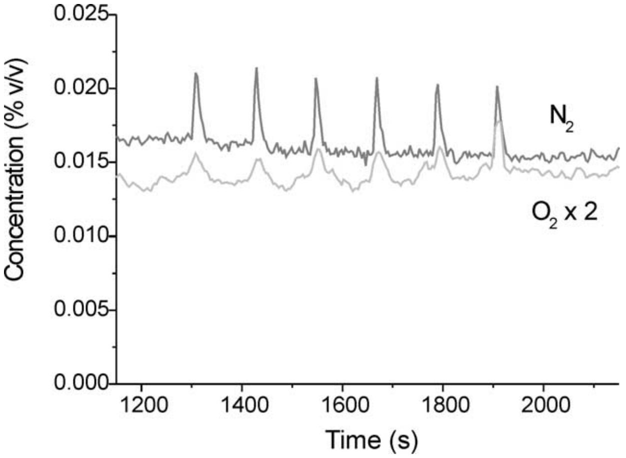

Fig. 7. Six pulses (500 µl) of 5000 ppm N_2O in He were given while flowing 1000 ppm N_2O over Fe-ZSM-5 at 673 K, which had been pretreated in He. The graph shows the N_2 and O_2 (×2) concentration. The O_2 line was smoothed (5 point adjacent averaging) to reduce the noise.

3.3. *Combined step-pulse experiments*

The goal of the pulse experiments was to get information on the reactivity of the catalyst toward N_2O during and after steady-state N_2O decomposition. For this purpose the N_2O concentration in the steady-state decomposition was reduced to 1000 ppm and pulses of a higher concentration (5000 ppm) were given during N_2O decomposition. Fig. 7 shows the result of such an experiment at 673 K. Fourteen percent of the N_2O in the pulse was converted to N_2. The steady-state yield of N_2 was 16%, i.e., practically identical. The N_2 peaks formed in the pulses followed the shape of the Ar tracer peaks. The O_2 peaks were more diffuse. The curve of excess N_2 ($c_{N_2} - 2^*c_{O_2}$) did not show any peaks, which raised clearly above noise level.

One minute after switching the reactor inlet stream from 1000 ppm N_2O to pure He, another series of six pulses of 5000 ppm N_2O was administered (Fig. 8). A comparison with Fig. 7 shows that a lot more N_2 was produced (41%

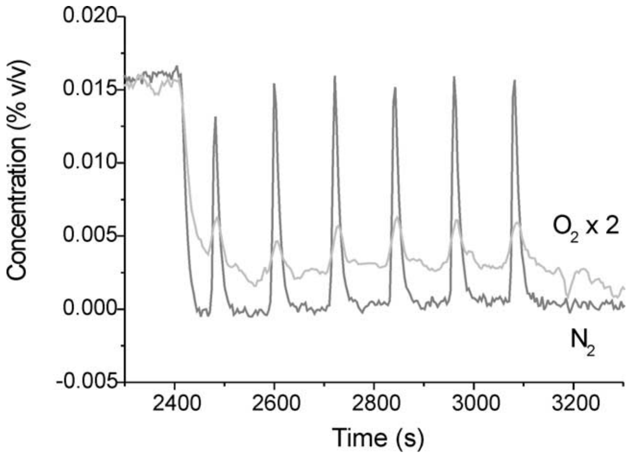

Fig. 8. Six pulses of N_2O given 1 min after the step down from 1000 ppm N_2O to He, at 673 K. The graph shows the N_2 and the smoothed O_2 (×2) concentration.

conversion of N_2O to N_2), but the O_2 formation remained about the same. About 0.001 mol N_2/Fe was formed in excess per pulse. The N_2 yield in the first pulse, which was given during the tail of the O_2-desorption curve following the step down, was significantly lower than in five subsequent pulses. Two minutes after the last pulse injection the feed was switched back to 1000 ppm N_2O. A 0.005 mol excess N_2/Fe was formed during the step up. The catalyst reached the same steady state as before.

Since the amount of N_2O converted in six pulses may be too small to affect the state of the catalyst, the experiment was repeated giving a series of 15 pulses after the step down. As in the experiment with six pulses, the pulse response was stable except for the first pulse, which produced less N_2. In the subsequent step up to 1000 ppm N_2O the same amount of excess N_2 was formed (0.005 mol N_2/Fe).

The same experiment was carried out at 623 K. At this temperature steady-state conversion was very low (3–4%). The conversion of N_2O to N_2 in the pulses during steady-state decomposition was higher (approximately 7%), but could be overestimated due to the high noise level. O_2 formation during the pulses almost disappeared in the noise. After the step down to He, the conversion of N_2O to N_2 in the pulses increased to 10%. O_2 formation remained low, i.e., hardly above noise level. In contrast to the experiment at 673 K, the N_2 yield in the first pulse was not significantly lower than in the following pulses. When a step up to 1000 ppm N_2O was performed 2 min after the last pulse injection, only 0.0015 mol excess N_2/Fe was produced. Table 3 compiles the results described above, including data at 648 K.

4. Discussion

4.1. Origin of the initial N_2 formation

Irrespective of the pretreatment of the catalyst in H_2, He, or O_2, a peak of N_2 was found at the beginning of the step response. The amount of excess N_2 formed decreased from pretreatment in H_2 to He to O_2 (cf. Table 1). This indicates that the N_2 formation is related to a reoxidation of reduced sites according to

$$2Fe^{2+} + N_2O \rightarrow 2Fe^{3+}\text{–}O^{2-} + N_2. \qquad (4)$$

For a stoichiometric oxidation of Fe^{2+} to Fe^{3+}, a N_2/Fe ratio of 0.5 is expected. The experimental ratio found after reduction of the catalyst in H_2 was close to this value. Thus, Fe-ZSM-5 was completely reduced to Fe^{2+} by the H_2 treatment at 673 K and subsequently fully reoxidized by N_2O. Only after initial reoxidation, steady-state N_2O decomposition set in (see Fig. 1).

Also the He-treated catalyst produced a large amount of excess N_2, which suggests that part of the iron sites autoreduce in He. The control experiment with O_2 showed, however, that adsorbed hydrocarbons are largely responsible for this autoreduction. Already 2000 ppm O_2 reduced the excess N_2/Fe to 0.01, i.e., the “autoreduction” to 2% (see Fig. 3). This is in agreement with the results of Voskoboinikov et al., who found that O_2 desorption from sublimed Fe-ZSM-5 starts above 673 K [12]. Hence, spontaneous autoreduction,

Table 3
Conversion of N_2O in the combined step-pulse experiments

	673 K		648 K		623 K	
Steady-state conversion N_2O to N_2 (%)	16		6		3	
Conversion N_2O to N_2 in pulse (%)						
During N_2O decomposition	14		9		7	
After N_2O decomposition						
First pulse	38		16		10	
Average of the other pulses	43		18		10	
Amount of N_2/O_2 produced in a pulse (10^{-3} mol/mol Fe)	N_2	O_2	N_2	O_2	N_2	O_2
During N_2O decomposition	0.4	0.15	0.25	n.d.	0.2	n.d.
After N_2O decomposition	1.5	0.25	0.65	0.15	0.35	n.d.
Excess N_2/Fe in second step up, after the pulses	5		2.5		1.5	

Fe-ZSM-5 was pretreated in He at 673 K for 1 h, cooled to reaction temperature, and exposed to 1000 ppm N_2O. Six pulses of 5000 ppm N_2O were given at an interval of 2 min. One minute after the step down to pure He another series of pulses was administered, followed by a second step up to 1000 ppm N_2O, 2 min after the last pulse.

which is not caused by reaction with adsorbed hydrocarbons, is not expected to take place to a significant extent at 673 K.

Pretreatment in 10% O_2 at 673 K reduced the formation of excess N_2 further ($N_2/Fe = 0.005$), but not completely to zero. Note that this behavior resembles the behavior of α-sites. α-Sites produce N_2 according to the reaction

$$^* + N_2O \rightarrow {}^*\text{–}O + N_2 \qquad (5)$$

and they are inert toward O_2. The inertness of α-sites toward O_2 distinguishes the deposition of α-oxygen from a simple reoxidation of the catalyst, i.e., Eq. (4). To make sure that our catalyst was completely oxidized before the step to N_2O, we treated it at 673 K in 10% O_2 in He and cooled down in the same gas mixture before performing the step to N_2O at 523 K. No excess N_2 was formed. This proves that the small amount of excess N_2 observed at 673 K was due to an equilibrium concentration of Fe^{2+}, which is quickly formed by flushing with He at this temperature, and has nothing to do with α-site chemistry.

4.2. Mechanism of N_2O decomposition

In all step-response experiments the formation of N_2 occurred immediately, i.e., without any delay with respect to the tracer. That shows that reaction (1) is a fast step in the N_2O decomposition cycle. This is a generally accepted opinion. The removal of surface oxygen via scavenging with a second N_2O molecule Eq. (2) or via recombination Eq. (3) is the rate-determining step of the reaction. Since oxygen does not have an inhibiting effect on N_2O decomposition over iron catalysts, it was long believed that recombination of surface oxygen cannot be the mechanism of O_2 formation. If O_2 formation is irreversible, i.e., its reverse reaction very slow, this argument does not hold. Indeed, Mul et al. showed with pulse experiments that recombination of surface oxygen is the mechanism of O_2 formation over Fe-ZSM-5 prepared by hydrothermal synthesis followed by steaming [13]. The low recombination rate was explained by a slow migration of oxygen atoms originally adsorbed on spatially separated sites toward each other [14]. The iron loading of our catalyst is much higher, which should facilitate the recombination of adsorbed oxygen atoms. Yet the O_2 concentration strongly tailed after a step down from N_2O to He, which indicates that O_2 desorption was also rate determining on our catalyst.

In order to obtain more detailed information on the mechanism of O_2 formation pulse experiments similar to the ones of Mul et al. [13] were performed. Pulse experiments are most suited to distinguish reaction (2) from reaction (3). If reaction (2) is taking place, then O_2 must be formed simultaneously with N_2 in the pulse. For reaction (3) a broadened and/or delayed O_2 response can be expected. One has to bear in mind, however, that reaction (2) might escape detection in pulse experiments performed on a resting catalyst if a surface oxygen atom, which has a short lifetime, i.e., a hot atom, catalyzes it. Therefore we pulsed N_2O *during and after* steady-state N_2O decomposition.

In none of the pulses given during N_2O decomposition a sharp O_2 peak was evolved simultaneously with the N_2 peak. O_2 always desorbed as a broad feature, which could hardly be distinguished from the noise of the spectrometer. Hence it can be ruled out that surface oxygen species react directly with N_2O according to reaction (2). O_2 must be formed by a slow recombination/desorption of surface oxygen atoms.

During steady-state N_2O decomposition the conversion in the pulse was comparable to the steady-state conversion. In the pulses given after N_2O decomposition the N_2O conversion was significantly higher. The difference between the two values increased with temperature. Moreover, the conversion of the first pulse, which was given at a moment when O_2 desorption from the catalyst was not yet completed, was always lower than in the subsequent pulses. Also this difference increased with temperature. Both effects indicate that the N_2O conversion increases with the concentration of oxygen vacancies on the catalyst. At 673 K oxygen desorption from the catalyst is relatively fast (although still rate determining). When the inlet stream was switched back to He a large number of oxygen vacancies was created, which could react with N_2O in the pulses. Mainly N_2 was produced in the reaction and only a small amount of O_2. That suggests that N_2O was actually reoxidizing the catalyst and that the oxygen from N_2O remained bound to the surface, as described in Eq. (4). But if oxygen indeed accumulated on the surface, the conversion in the pulse should decrease during a long series of pulses. In the series of 15 pulses a large amount of oxygen atoms should have accumulated on the surface (0.015 mol O/Fe), but the pulse response did not change throughout the series (with the exception of the first pulse). Moreover, the amount of excess N_2 formed in a step up following the pulses was the same after 6 and after 15 pulses. This clearly shows that the catalyst had reached a steady state and was not further oxidized by the pulses. Hence, all the oxygen deposited from N_2O must have desorbed from the catalyst. But only one-third of the stoichiometrically expected amount of O_2 was detected at 673 K. This suggests that two desorption processes are going on, one relatively fast and, thus, detectable, the other slow and undetectable by our mass spectrometer.

The amount of excess N_2 produced in the step-up response can be identified with the number of oxygen vacancies, or in other words the degree of autoreduction of the catalyst (see Eq. (4)). We determined the number of oxygen vacancies created by flushing in He at 673 K for different times t in a cycle N_2O–He (t)–N_2O. The result is shown in Fig. 9, including the point after 2 min determined in the pulse experiments. The shape of the curve confirms that some of the oxygen atoms desorb very fast from the iron sites and a second pool desorbs very slowly. One can speculate that the fast desorbing oxygen atoms adsorb on iron clusters in close vicinity to each other or even on the same iron cluster, while the second oxygen pool has to recombine via slow migration over the surface.

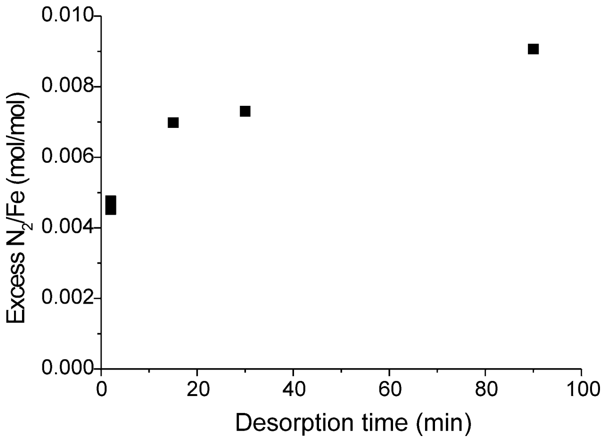

Fig. 9. Amount of excess N_2 formed in the second step up to N_2O of a cycle N_2O–He (t)–N_2O as a function of the time t, at 673 K, GHSV $= 20{,}000$ h^{-1}, and 1 bar.

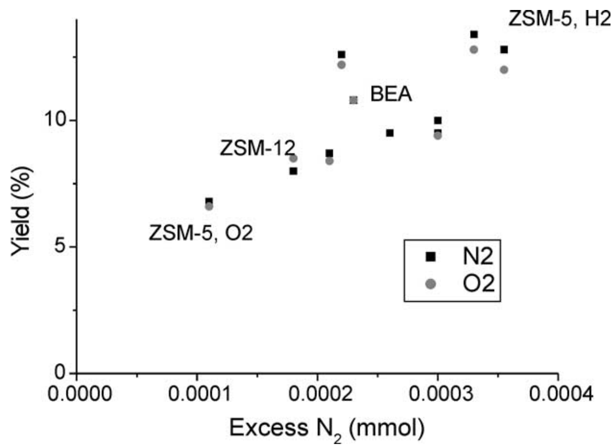

Fig. 10. Steady-state yield of N_2 and O_2 obtained during N_2O decomposition vs the concentration of oxygen vacancies. The concentration of oxygen vacancies (the degree of autoreduction) is equal to the amount of excess N_2 produced in the second step to N_2O of a cylce N_2O–He (15 min)–N_2O.

At 623 K O_2 desorption was much slower than at 673 K. Flushing in He did not create many vacancies and therefore the conversion in the pulses after N_2O decomposition was not much higher than the steady-state conversion. The experiments at 648 K showed an intermediate situation.

If O_2 desorption is rate determining, the degree of autoreduction of the catalyst, i.e., the fraction of sites from which O_2 can desorb easily, should be correlated with the rate of N_2O decomposition. The degree of autoreduction was determined in step-up/step-down cycle N_2O–He (15 min)–N_2O, for different catalyst and different pretreatments. The concentration of oxygen vacancies created by autoreduction correlated fairly well with the steady-state yields of N_2 and O_2 (see Fig. 10). The line does not pass through the origin because both the fast and the slow O_2 desorption contribute to the autoreduction after 15 min, whereas only the fast O_2 desorption process governs catalytic activity. A better correlation can be expected if the degree of autoreduction is measured after a shorter time.

4.3. The nature of the surface oxygen

Table 2 and Fig. 10 show that the steady-state yield of N_2 and O_2 depended on the pretreatment of the catalyst. A small, but significant increase was observed from pretreatment in O_2 to He to H_2. In the reduced catalyst all the iron clusters were reoxidized with oxygen originating from N_2O. This catalyst had a significantly higher activity than the catalyst pretreated with O_2, for which only a limited incorporation of oxygen from N_2O was possible. That indicates that the structure of iron clusters changes when they are oxidized by N_2O. Moreover, catalysts oxidized by O_2 showed a higher degree of autoreduction than catalysts exposed to N_2O (0.02 vs 0.006 mol excess N_2/Fe), which confirms that the reactivity of the iron clusters changed during their reaction with N_2O.

5. Conclusions

O_2 desorption is the rate-limiting step in N_2O decomposition over Fe-zeolites prepared by sublimation of $FeCl_3$. Fast oxygen desorption increases the number of oxygen vacancies and leads to a higher conversion of N_2O. The rate of oxygen desorption is reflected in the degree of autoreduction of the catalyst, which correlates fairly well with catalytic activity. However, only oxygen vacancies created by spontaneous desorption of oxygen contribute to the steady-state activity in N_2O decomposition. If the catalysts are artificially reduced in H_2, N_2O first reoxidizes them before a steady state is reached. Yet, iron oxide clusters, which were reoxidized by N_2O, seem to have a higher steady-state activity than those who were treated in O_2. That suggests that the oxygen from N_2O is bound in a different way to the iron cluster. Despite of the higher reactivity of iron clusters, in which oxygen from N_2O was built in, analogies to α-oxygen species cannot be drawn. The iron oxide clusters of the sublimed Fe-ZSM-5 are not inert toward O_2.

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