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Journal of Catalysis 227 (2004) 164–174
JOURNAL OF CATALYSIS
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The surface chemistry of N_2O decomposition on iron-containing zeolites (II)—The effect of high-temperature pretreatments

Pijus K. Roy, Gerhard D. Pirngruber *

Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, (ETH) Zürich, Wolfgang-Pauli Str. 10, CH-8093 Zürich, Switzerland

Received 15 April 2004; revised 28 June 2004; accepted 4 July 2004

Abstract

The effect of pretreatment conditions on the N_2O-decomposition activity of Fe-ZSM-5 prepared by chemical vapor deposition (CVD) was studied by steady-state kinetics and step-response experiments. Pretreatment at 873 K in H_2 or He significantly increased the N_2O-decomposition activity of Fe-ZSM-5 CVD. In addition to the increased steady-state activity, the catalyst exhibited a very high initial activity in the step-response experiments, which slowly decayed to steady state. This “transient” activity was particularly high after pretreatment of the samples in He, whereas it vanished completely after pretreatment in O_2 or exposure to water vapor. This led to the conclusion that the transient activity is related to strongly dehydroxylated Fe^{2+} sites created by autoreduction at high temperatures. On the basis of isotope-labeling data a mechanism for N_2O decomposition is proposed. The first step is the reaction of Fe^{2+} with N_2O to give a Fe^{3+}–O^- species, which quickly transforms into a Fe^{2+}–peroxo complex. Desorption of O_2 occurs upon reaction of the Fe^{2+}–$O_2{}^{2-}$ complex with another N_2O molecule (mainly during the transient) or via the recombination of two peroxo species after their migration over the iron oxide cluster (mainly during steady state).

Keywords: Fe-ZSM-5; CVD; Isotope labeling; ^{18}O; Surface oxygen; α-Oxygen

1. Introduction

In the 1990s Panov and co-workers discovered that the interaction of N_2O with iron zeolites generates highly active surface oxygen species, called α-oxygen [1]. α-Oxygen has a high reactivity for the oxidation of CO and CH_4 as well as for oxygen isotope exchange already at moderate temperatures [2,3]. It is thought to be the active species in N_2O decomposition and in the selective oxidation of benzene to phenol over Fe-ZSM-5. The high selectivity (close to 100%) in the oxidation of benzene, which is achieved with α-oxygen, stimulated much research on iron zeolites. α-Oxygen was first detected on samples prepared by hydrothermal synthesis of [Fe]-ZSM-5, followed by calcination and/or steaming at high temperatures. It is formed by reaction of the catalyst with N_2O at temperatures around 523 K

$$* + N_2O \rightarrow N_2 + *–O_\alpha.$$

The structure of the active oxygen species on the catalyst surface is still subject to debate. A Mössbauer study suggested that α-oxygen is an O^- radical bound to a binuclear iron cluster [4]

$$Fe^{2+}–\mu\text{-(OH)}–Fe^{2+} + N_2O \\ \rightarrow O^-–Fe^{3+}–\mu\text{-(OH)}–Fe^{3+}– O^-.$$

Since a structural identification is difficult, α-oxygen is usually characterized by reactivity tests. The existence of active surface oxygen species on iron zeolites, which react with CO or $^{18}O_2$ at low temperatures, was confirmed in several publications [5,6].

A popular preparation method of iron zeolites is the chemical vapor deposition (CVD) of anhydrous $FeCl_3$. This method leads to an overexchanged iron zeolite with a high

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* Corresponding author. Fax: +41-1-632-1162.
E-mail address: pirngruber@chem.ethz.ch (G.D. Pirngruber).

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doi:10.1016/j.jcat.2004.07.004

iron loading (Fe/Al ∼ 1) [7,8]. Fe-ZSM-5 CVD has attracted attention as a very effective catalyst for the decomposition of N_2O [9–11]. It is also active in the oxidation of benzene to phenol, but its selectivity is moderate compared to the Panov-type catalysts [12,13]. CVD catalysts are quite different from those described by Panov and co-workers, due to the much higher iron loading and the different method of iron incorporation. The question arises whether α-oxygen species can also be formed on the CVD catalysts. We investigated the mechanism of N_2O-decomposition on Fe-ZSM-5 CVD catalysts in detail [14,15], but evidence for highly reactive surface oxygen species could not be found. It must be stressed that the Fe-ZSM-5 CVD catalysts used in these studies were never pretreated at temperatures higher than 673 K, except for the original calcination in O_2 at 773 K. Jia et al. reported that active surface oxygen species were only formed on Fe-ZSM-5 CVD if the catalyst was treated in H_2 or vacuum at temperatures above 873 K [16]. Zhu et al. detected a very small concentration of α-sites on Fe-ZSM-5 CVD, which increased significantly after calcinations or steaming at 973 K [12]. These results indicate that treatments at high temperatures are required to create active oxygen species on Fe-ZSM-5 CVD. We therefore decided to study the effect of such high-temperature pretreatments on the reactivity of Fe-ZSM-5 CVD toward N_2O in more detail. Step-response experiments and isotope labeling were employed to study the dynamic behavior of the surface oxygen species in the system.

2. Experimental

2.1. Preparation of catalyst

A Na-ZSM-5 sample was kindly provided by Zeochem AG (Na-ZSM-5 Zeocat PZ-2/40, Si/Al = 25). The H-ZSM-5 was obtained after threefold ion exchange with a 1 M aqueous solution of NH_4NO_3 at room temperature, followed by calcination in O_2 at 773 K. The iron exchange was carried out by CVD of anhydrous $FeCl_3$ on H-ZSM-5 in a flow of N_2 at 593 K, as described by Chen and Sachtler [7]. A U-shaped tubular quartz reactor containing the H-ZSM-5 and anhydrous $FeCl_3$, separated by a frit, was used. First the H-ZSM-5 was loaded in the reactor and calcined in a flow of O_2 at 773 K to remove the residual water adsorbed on the surface. The reactor was then closed and transferred to the glove box to load anhydrous $FeCl_3$ and subsequently heated in a furnace at 593 K (2 K/min) under N_2 flow for 3 h. The reactor was allowed to cool to ambient temperature under the same gas flow. Finally the sample was washed with deionized water until no Cl^- ions were detected using a $AgNO_3$ solution. Then the sample was dried in air and finally calcined in a flow of O_2 at 773 K (1 K/min) for 2 h. Elemental analysis by AAS revealed that the Fe/Al ratio of the catalyst was 1.1 (4.5 wt% Fe), corresponding to the exchange of one iron per Brønsted acid site [7].

2.2. Catalytic tests

N_2O decomposition was carried out in the temperature range 573 to 798 K, using a standard flow reactor. The flow over the reactor was always kept at 50 ml_{NTP}/min, corresponding to a GHSV = 40,000 h^{-1}; 2500 ppm N_2O in He was used as feed gas. An amount of 50 mg pelletized catalyst (mesh size 250–300 µm) was used for all catalytic tests. The catalyst bed was located in the middle part of a quartz tube reactor with 4 mm inner diameter and was held in place with quartz wool. The catalyst was pretreated with 10% O_2 in He for 1 h at 773 K in order to remove adsorbed hydrocarbons. Gas chromatography was used to detect N_2, N_2O, and O_2.

2.3. Step-response experiments

For the step-response experiment 50 mg of pelletized catalyst (mesh size 250–300 µm) was placed in between two pieces of quartz wool in a quartz reactor with 4 mm inner diameter. The catalyst was pretreated with 10% O_2 in He for 1 h at 773 K in order to remove adsorbed hydrocarbons and then with 20% H_2 in He, pure He, or water vapor at the desired temperature. Before changing to N_2O, the reactor was flushed with pure He for about 5 min. Then the inlet stream was changed to 5000 ppm N_2O in He by switching a 4-port electronic valve. N_2O decomposition was followed for about 45–60 min and finally the inlet stream was switched back to pure He. All the step-response measurements were done at 673 K.

For exposure to water vapor, the catalyst was pretreated at 873 K with pure He or with 20% H_2 in He for 1 h and then cooled down to 573 K in same flow. Then the catalyst was treated with 13 mbar water vapor, which was administered through a saturator, at 573 K for ∼1 h. Finally the catalyst was heated to 673 K in pure He.

The gas flow rate over the reactor was always kept at 25 ml_{NTP}/min, corresponding to GHSV = 20,000 h^{-1}. The outlet gas mixture was analyzed by using a quadrupole mass spectrometer with mass fragments $m/e = 4$ (He), 28 (N_2 and N_2O), 32 (O_2), and 44 (N_2O). He ($m/e = 4$) was used for normalization of the signals. Time resolution was 4 s.

2.4. Isotope exchange and N_2O treatment

Fifty milligrams of pelletized catalyst (mesh size 250–300 µm) was placed in a quartz reactor of 4 mm inner diameter. The catalyst was first pretreated in a mixture of 10% O_2 in He for 30 min at 673 K in order to remove adsorbed hydrocarbons. In order to incorporate ^{18}O, the catalyst was reduced with 20% H_2 in He for 1 h and subsequently reoxidized by a step from He to 1% $^{18}O_2$ in He (93% ^{18}O, Eurisotop) at 673 K. After 30 min at 673 K, the catalyst was heated to 873 K in 1% $^{18}O_2$ in He and kept in $^{18}O_2$ for 5 min and then for one more hour in He at that temperature. After cooling to 673 K a pulse of 1% CO in He was given (0.2 µmol CO, CO/Fe = 0.005). The pulse of CO served to determine the concentration of labeled oxygen on the catalyst surface [17]. Then a step to 5000 ppm N_2O in He was performed. N_2O decomposition was followed for about 1.5 h and finally the inlet stream was switched back to pure He. The gas flow rate over the reactor was kept at 25 ml_{NTP}/min, corresponding to GHSV = 20,000 h^{-1}. The reaction products were analyzed using a quadrupole mass spectrometer with mass fragments $m/e = 4$ (He), 28 (N_2 and N_2O), 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$), 36 ($^{18}O_2$), 44 ($N_2{}^{16}O$), and 46 ($N_2{}^{18}O$); $m/e = 4$ (He) was used as a reference. Time resolution was 2 s. The fraction of ^{18}O in the O_2 product during N_2O decomposition was calculated as $^{18}f = ([^{16}O^{18}O] + 2*[^{18}O_2])/(2*[O_{2,tot}])$. The value of equilibrium constant of the isotope exchange reaction $^{16}O_2 + {}^{18}O_2 \leftrightarrow 2\,{}^{16}O^{18}O$, $K_e = [^{16}O^{18}O]^2/([^{16}O_2] * [^{18}O_2])$, was also computed. If $K_e = 4$, the distribution of isotopes in O_2 is statistical; i.e., there is a complete equilibration of the oxygen atoms.

2.5. Al K-edge XANES

Al *K*-edge XANES measurements were performed at the SRS Daresbury (UK), Station 3.4. The synchrotron was operating at 2.0 GeV with an average current of 120 mA. A double-crystal scanning monochromator mounted with YB_{66} crystals was used. Self-supporting pellets of the samples were placed into a cell, which was designed for low-energy in situ X-ray absorption experiments [18–20]. No windows were used and the spectra were recorded under vacuum ($p < 10^{-5}$ mbar), using fluorescence detection via a gas proportional counter. The samples were first measured at room temperature, heated to 873 K in vacuum, exposed to air, and then measured again at room temperature.

3. Results

3.1. Effect of pretreatment for N_2O decomposition

Fig. 1 shows how the pretreatment in He or H_2 at 773 or 873 K changed the activity of the catalyst toward N_2O decomposition. The activation energy and the rate constant at 698 K for the various pretreatment of Fe-ZSM-5 catalyst are listed in Table 1. The values were determined assuming first-order kinetics with respect to N_2O. As can be seen from Fig. 1, the high-temperature pretreatment with He or H_2 led to an increase of activity toward N_2O decomposition. This is in agreement with the findings of Jia et al. [16] and Zhu et al. [12]. The activation energies were not very much affected by the pretreatment conditions.

3.2. Effect of pretreatment on the step response

In the first step-response experiment, the catalyst was first reduced at 873 K with 20% H_2 in He for 1 h and then another hour in pure He at 873 K and finally cooled down to 673 K in pure He. The step response is shown in Fig. 2. After stepping to 5000 ppm N_2O in He, immediately a large amount of N_2 was produced during reoxidation of Fe^{2+}, i.e., by the reaction $2Fe^{2+} + N_2O \rightarrow 2Fe^{3+}\text{–}O^{2-} + N_2$ [14]. The amount of N_2 formed during reoxidation was quantified by subtracting two times the O_2 curve from the N_2 curve. The resulting curve of excess N_2 exhibited a peak between 0 and 400 s and was zero (within the error of measurement) afterward. The peak area corresponded to $N_2/Fe = 0.51$, as expected for the full reoxidation of Fe^{2+} to Fe^{3+}. Reoxidation was followed by a period of high N_2O decomposition activity (the broad "plateau" of N_2 and O_2 between 500 and 2500 s in Fig. 2), which slowly decayed to steady state. This phenomenon was observed before [12,21] and is referred to as transient N_2O decomposition in the following.

Fig. 3 shows the response of the catalyst which was reduced with 20% H_2 in He at 873 K for 1 h, cooled down to 673 K in the same flow, and finally flushed with pure He for about 10 min before stepping to N_2O. Again a certain amount of N_2 ($N_2/Fe = 0.48$) was produced during reoxidation, followed by the formation of N_2 and O_2. In this case only a small amount of N_2 was produced during the transient N_2O decomposition as compared to the catalyst, which was pretreated with 20% H_2 in He and then with pure He at 873 K (Fig. 2). For comparison [22], the catalyst was also

Table 1
Activation energy (E_a) and rate constant (k_{N_2O}) for N_2O decomposition at 698 K after various pretreatments

Catalyst	Pretreatment method	k_{N_2O}[a]	E_a (kJ/mol)[b]
He-773	773 K in pure He	14	139
He-873	873 K in pure He	30	129
H_2-773	773 K in 20% H_2 in He	19	127
H_2-873	873 K in 20% H_2 in He	47	132

[a] In 10^{-5} mol s^{-1} g_{cat}^{-1} bar^{-1}.
[b] The accuracy is ±10 kJ/mol.

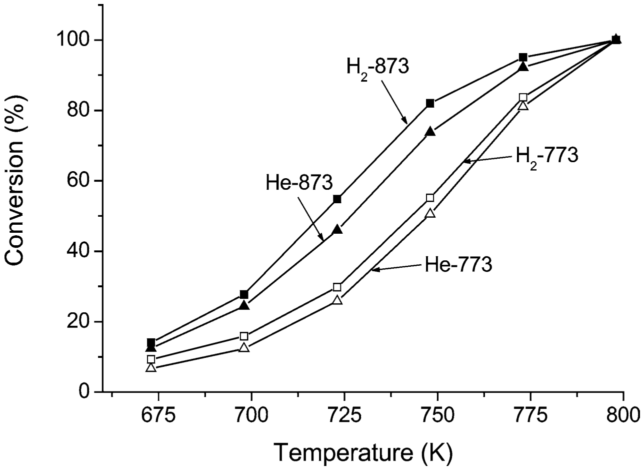


Fig. 1. N_2O decomposition over Fe-ZSM-5 catalyst after various pretreatments. The catalyst was pretreated at 773 K with He (△), at 873 K with He (▲), at 773 K with 20% H_2 in He (□), and at 873 K with 20% H_2 in He (■). Feed composition: 2500 ppm N_2O in He and GHSV = 40,000 h^{-1}.

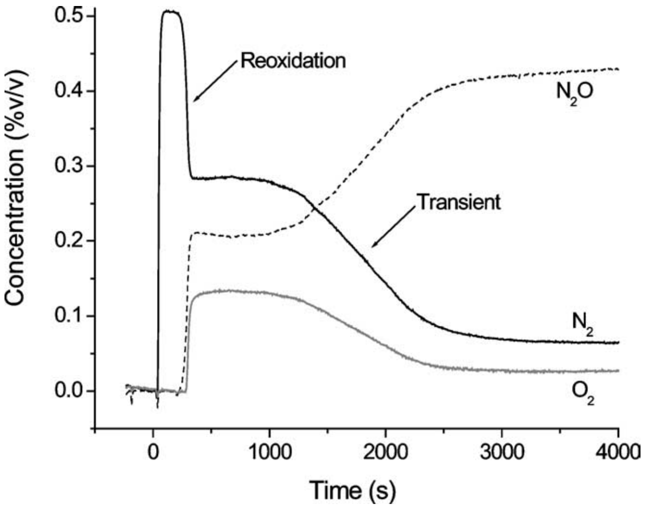


Fig. 2. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O. The catalyst was first reduced with 20% H_2 in He at 873 K then treated with pure He at 873 K and finally cooled down to 673 K with He.

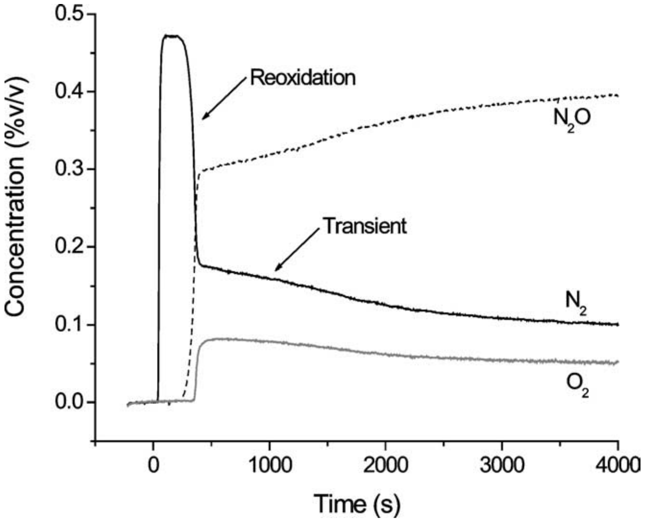
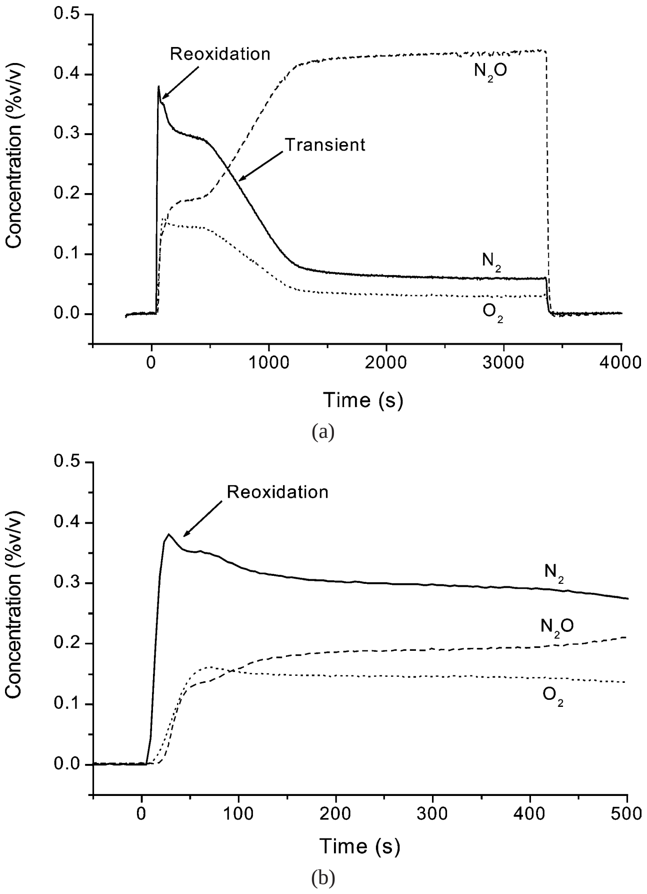


Fig. 3. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O after reduction with 20% H_2 in He at 873 K.

reduced with 4% CO in He at 873 K before the step to N_2O at 673 K. The step response after CO treatment was similar to the one after treatment in H_2 and then He at 873 K (see Fig. 2).

When the step to N_2O was performed after pretreatment in pure He at 873 K (Fig. 4) only a small amount of N_2 ($N_2/Fe = 0.025$) was formed during reoxidation. The transient activity was initially as high as after reduction at 873 K, but lasted for a shorter period. A peak of N_2 and O_2 could be distinguished after 65 s, followed by a broad shoulder (see the enlargement of the step response between 0 and 500 s in Fig. 4b). The catalyst, which was pretreated with 10% O_2 in He at 873 K (Fig. 5), gave even less N_2 ($N_2/Fe = 0.005$) during reoxidation and showed no transient activity. In both cases N_2O and O_2 evolved at the same time.



(a)

(b)

Fig. 4. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O after treatment in pure He at 873 K.

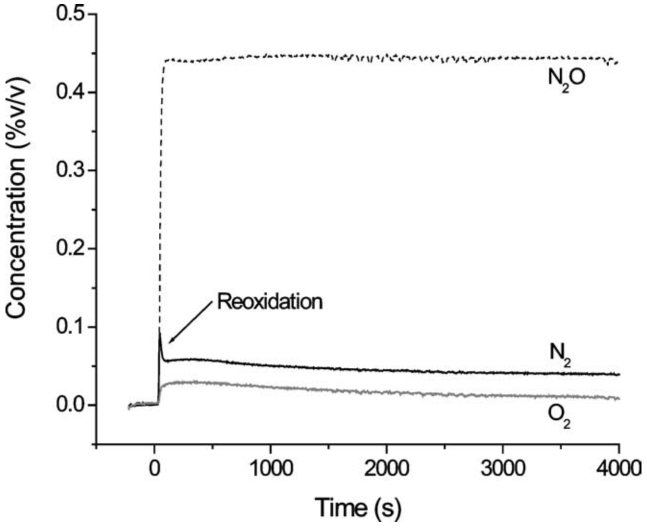


Fig. 5. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O after treatment with 10% O_2 in He at 873 K.

The effect of exposure to water vapor on the step response of the catalyst is shown in Figs. 6 and 7 after pretreatment with pure He and with 20% H_2 in He at 873 K, respectively. After the step to 5000 ppm N_2O in He, N_2 was formed

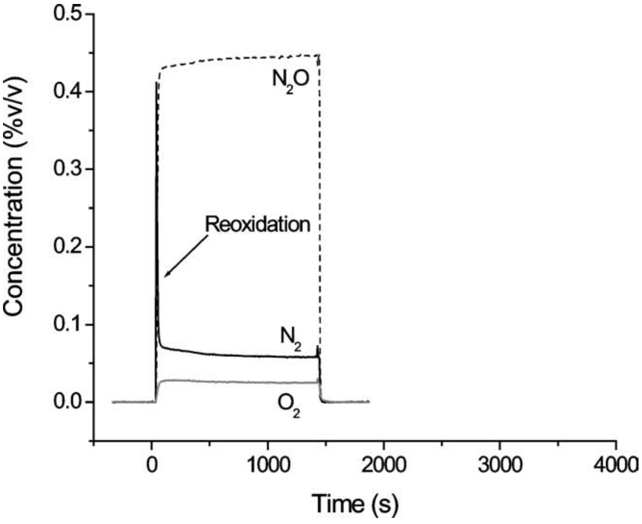


Fig. 6. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O after treatment in pure He at 873 K and then with water vapor at 573 K.

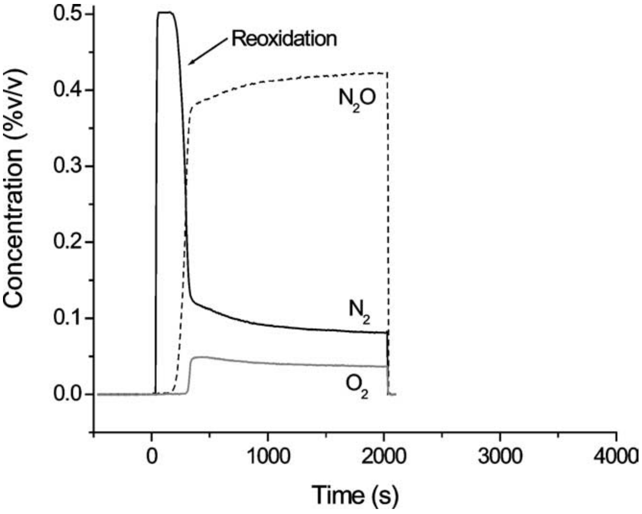


Fig. 7. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O after treatment with 20% H_2 in He at 873 K and then with water vapor at 573 K.

during reoxidation, but only very little transient N_2O decomposition was observed in either case.

The integration results for all the step-response experiments are summarized in Table 2. It shows that the amount of N_2 formed during reoxidation decreased from pretreatment in H_2 to He to O_2, as observed before [14]. Exposure to water vapor had no influence on the reoxidation. For the stoichiometric oxidation of Fe^{2+} to Fe^{3+}, the N_2/Fe ratio should be 0.5. The experimental amount of N_2/Fe ratio during reoxidation was found to be ~ 0.5 after reduction with 20% H_2 in He at 873 K. Thus, the catalyst was completely reduced to Fe^{2+} after reduction at 873 K and subsequently reoxidized with N_2O. When the catalyst was pretreated with pure He at 873 K a small amount of N_2 ($N_2/Fe = 0.025$) was formed during reoxidation, due to the autoreduction of some Fe^{3+} to Fe^{2+} at 873 K [14,21,23]. The amount of N_2 and O_2 formed during the transient reaction (steady-state activity was subtracted) decreased from the treatments H_2–He-873 K to He-873 K to H_2-873 K and was negligible for the samples, which were pretreated in O_2 or exposed to water. It must be noted that the amount of N_2 and O_2 produced during the transient reaction was not highly reproducible. The general trend described above was, however, safely established. Moreover, we note that the reaction temperature and the partial pressure of N_2O did not, in a qualitative sense, change the shape of the step-response curves.

Table 2
Amount of N_2 formed during reoxidation and transient N_2O decomposition after a step to 5000 ppm N_2O at 673 K, following various pretreatments of the catalyst

Catalyst	N_2/Fe during reoxidation (mol/mol)	Transient N_2/Fe (mol/mol)	Yield N_2 (%) steady state
H_2-He-873[a]	0.51	1.25	13
H_2-873	0.48	0.19	19
CO-873	0.43	1.52	14
He-873	0.025	0.82	10
O_2-873	0.005	< 0.01	8
He-873-H_2O[b]	0.026	< 0.01	10
H_2-873-H_2O[c]	0.49	0.01	18

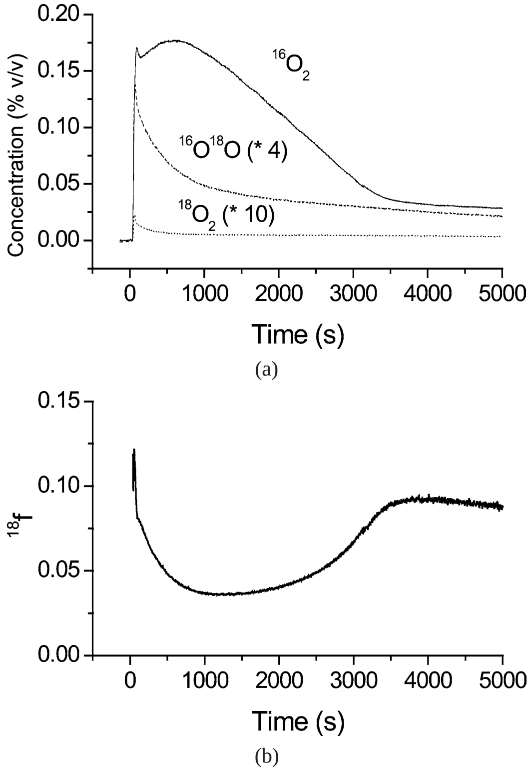
[a] The catalyst was first reduced with 20% H_2 in He at 873 K, then treated with pure He at 873 K and finally cooled down to 673 K in He.

[b] The catalyst was heated at 873 K in pure He for 1 h and cooled down to 573 K in He. Then the catalyst was treated with water vapor through a saturator at 573 K and finally heated to 673 K in He.

[c] The catalyst was reduced at 873 K with 20% H_2 in He for 1 h and cooled down to 573 K in the same flow. Then the catalyst was treated with water vapor through a saturator at 573 K and finally heated to 673 K in He.

3.3. *Isotope exchange with $^{18}O_2$ and N_2O decomposition*

Labeled oxygen was introduced into Fe-ZSM-5 by oxidation of the reduced catalyst with $^{18}O_2$, followed by a treatment in He at 873 K (see Section 2). The fraction of labeled oxygen in the catalyst at the end of the pretreatment was determined by a pulse of CO at 673 K [17]. Thirty-six percent of the CO was oxidized to CO_2, which contained all three isotopomers $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$. The distribution of isotopes in CO_2 was statistical ($K = [C^{16}O^{18}O]^2/([C^{16}O_2]*[C^{18}O_2]) = 3.85$), which means that a full equilibration of CO_2 with the surface had taken place. Under these conditions the fraction of labeled oxygen in CO_2 must be equal to the fraction of labeled oxygen on the surface. In our case a value of $^{18}f_{CO_2} = {}^{18}f_{surface} = 0.23$ was found. Only 0.002 CO/Fe had been converted in the pulse. We can therefore safely assume that the pulse of CO did not severely change the state of the catalyst surface. The response of the catalyst to the step of He to 5000 ppm N_2O, after the pulse of CO, was similar to that in Fig. 4 and is therefore not shown: Initially a peak for N_2 was formed due to the reoxidation of Fe^{2+} sites, followed by transient N_2O decomposition. The extent of transient N_2O decomposition was higher than in Fig. 4. Fig. 8 shows the evolution of the three O_2-isotopes during the step response. $^{16}O^{18}O$ and $^{18}O_2$ are amplified for



(a)

(b)

Fig. 8. Response of Fe-ZSM-5 at 673 K to a step from 0 to 5000 ppm N_2O. The catalyst was reduced with 20% H_2 in He at 673 K, reoxidized with 1% $^{18}O_2$, and subsequently treated in pure He at 873 K. (a) Concentration of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, (b) fraction of ^{18}O in O_2.

clarity. In the first peak of O_2 after ∼ 65 s all three isotopes were formed. In the broad shoulder, which followed, the concentration of $^{16}O^{18}O$ and $^{18}O_2$ decreased very quickly. $^{16}O_2$ was the dominating species during the transient reaction. This is also reflected in the evolution of ^{18}f with time, shown in Fig. 8b. ^{18}f started at a value of 0.12 and decreased to a minimum of 0.035 after ∼ 1000 s. With the decay of transient activity, an increasing fraction of labeled oxygen was again incorporated into O_2, shown by the rise of ^{18}f between 1000 and 3500 s. Once steady state was reached, ^{18}f decreased gradually, due to the slow removal of ^{18}O from the surface by O_2 desorption, as observed before [15]. The K_e value during steady state was ∼ 3, i.e., close to a statistical distribution of the isotopes. It indicates that an extensive equilibration of the surface oxygen atoms by mutual exchange reactions took place before their desorption as O_2 [15]. That only holds for the steady-state reaction, but not for the transient. During the transient the isotope distribution was far from equilibrium.

3.4. *Al K-edge XANES*

The Al K-edge XANES spectrum of the parent NH_4-ZSM-5 sample (Fig. 9) is typical for tetrahedrally coordinated aluminum atoms in framework positions [20,24]. The spectrum of Fe-ZSM-5 CVD was almost identical to that of the parent. It did not change upon treatment at 873 K in vacuum, which was supposed to simulate the treatment at 873 K in our reactor.

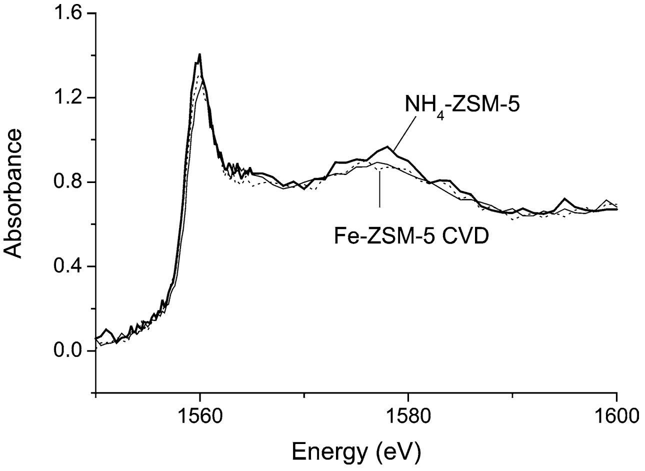


Fig. 9. XANES of the Al K-edge of NH_4-ZSM-5 (bold), Fe-ZSM-5 (solid), and Fe-ZSM-5 after treatment in vacuum at 873 K (dashed), all recorded at room temperature.

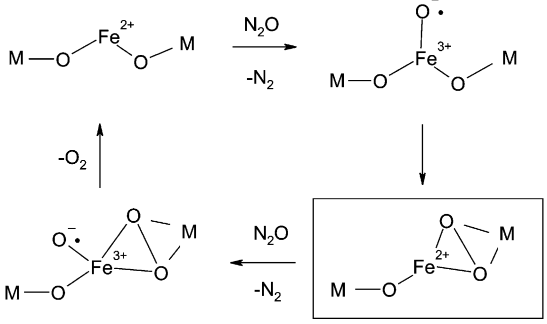
4. Discussion

4.1. *The origin of the high initial N_2O decomposition activity—The transient reaction*

Depending on the pretreatment, some of the Fe-ZSM-5 CVD catalysts exhibited a high transient N_2O decomposition activity, which slowly decayed to steady state. This phenomenon was observed before for several iron zeolites, in particular steamed samples, after pretreatment at 773 K in He [21]. Zhu et al. [12] detected transient activity after pretreatment of a steamed Fe-ZSM-5 CVD catalyst in He at 648 K. The extent of the transient reaction strongly decreased when the pretreatment was carried out in O_2. This is in line with the results presented here. It led to the conclusion that the occurrence of the transient reaction is related to Fe^{2+} sites, which are slowly reoxidized by N_2O [12].

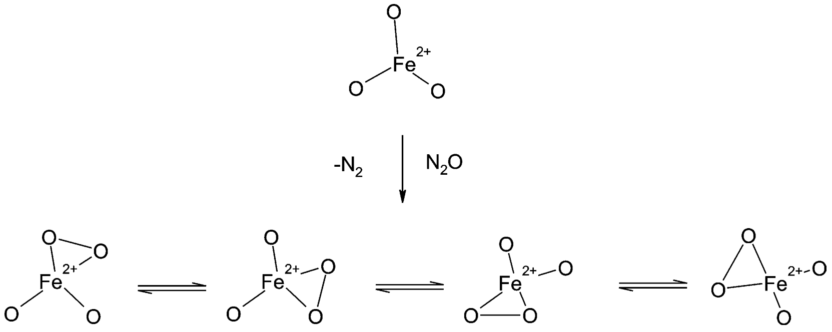
Our results show, however, that the presence of Fe^{2+} sites is not sufficient to initiate the transient reaction. After treatment in H_2-873 K and in H_2-873 K–H_2O-573 K, the Fe-ZSM-5 catalyst contained initially only Fe^{2+} sites, but showed little or no transient activity. Furthermore, reoxidation of the Fe^{2+} sites always preceded the transient reaction (see Figs. 2–4). The conclusion that the transient reaction is due to a slow reoxidation of Fe^{2+} sites, as suggested in Ref. [12], does therefore not hold. Still, the observation that pretreatment in O_2 annihilated the transient activity indicates that there is some relation between Fe^{2+} sites and the occurrence of the transient reaction. But not every Fe^{2+} site leads to transient activity. When Fe-ZSM-5 was pretreated at 673 K in H_2 or He, no transient reaction was observed [14]. Also after treatment in H_2-873 K–H_2O-573 K the sample did not show any transient activity. Pretreatment at high temperatures in inert gas was most efficient in initiating the transient reaction whereas exposure to water removed all transient activity. These results suggest that the transient reaction is related to dehydroxylated Fe^{2+} sites, which are created by (auto)reduction at high temperatures. A similar observation has been made before. Jia et al. [16] found that the reaction of N_2O with Fe-ZSM-5 CVD catalysts formed highly active oxygen species, if the catalysts were pretreated in H_2 or vacuum at high temperatures. Exposure to water poisoned these highly active sites. This result links the creation of active oxygen species to the presence of dehydroxylated Fe^{2+} sites, similar to the transient reaction.

Having identified dehydroxylated Fe^{2+} sites as the active sites for the transient reaction we now have to discuss the mechanism of the reaction. Fig. 4b shows that the majority of Fe^{2+} sites created by autoreduction were first reoxidized to Fe^{3+}, with the release of N_2 and the deposition of a surface oxygen atom. Then transient N_2O decomposition set in. The O_2 formed at the beginning of the transient contained about half the isotope fraction of the catalyst surface (${}^{18}f_{O_2} = 0.12$ vs ${}^{18}f_{surface} = 0.23$). In contrast to steady state, little mixing of the isotopes took place before desorption as O_2. The initial value of ${}^{18}f$ suggests that an oxygen atom from N_2O reacts with a surface oxygen atom to form O_2 [25]. As the transient reaction proceeded, however, the fraction of labeled oxygen in O_2 decreased and O_2 was mainly formed from oxygen atoms originating from N_2O. In order to explain these observations a mechanism, which was originally proposed for Cr_2O_3/Al_2O_3 catalysts [26], was adopted in slightly modified form (Scheme 1). The active site is pictured as a dehydroxylated Fe^{2+} ion, which is bound via bridging oxygen atoms to Al or Fe neighbors (M). The two $(M–O)^-$ ligands are the minimum number of ligands required for charge balancing the Fe^{2+} ion. In a more realistic picture, additional oxygen atoms from the zeolite lattice should be added, which also coordinate to the Fe^{2+} ion. We want to stress, however, that a high coordinative unsaturation of Fe^{2+} is a prerequisite for the mechanism proposed below. Recent in situ EXAFS studies showed that the Fe–O coordination number of samples, which were treated at high temperatures, is indeed low, i.e., between 2.0 and 3.0 [27]. Reaction of N_2O with the dehydroxylated Fe^{2+} site creates a $Fe^{3+}–O^-$ species [4,26]. The formation of O^- species upon reaction with N_2O was proved for CoO/MgO catalysts, but their stability is not very high [28]. It is therefore assumed that they are quickly transformed into a peroxo species. The $Fe^{2+}–O_2{}^{2-}$ complex still has free coordination sites, due to the strong dehydroxylation, and can easily react with another N_2O molecule to form $O^-–Fe^{3+}–O_2{}^{2-}$. The peroxo group desorbs from this intermediate as O_2 and is replaced by O^-, which receives one electron from Fe and becomes O^{2-}. With this the catalytic cycle is closed. The feasibility of such a reaction path was proven by DFT calculations [29]. According to this mechanism, the first desorbing O_2 molecules should contain one oxygen atom from the iron cluster and one oxygen atom from N_2O. This agrees with the experimental observation that the initial isotope concentration of O_2 was $\sim 0.5 {}^{*18}f_{surface}$. As the reaction proceeds, the iron cluster is depleted of ${}^{18}O$ and replaced with unlabeled oxygen atoms from N_2O. Hence, ${}^{18}f_{O_2}$ goes down, as observed experimentally: ${}^{18}f$ decreased very quickly during the initial period of the transient reaction.

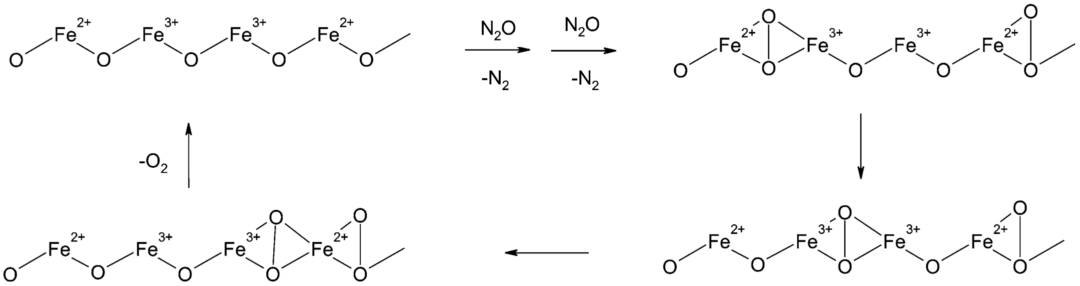


Scheme 1. Mechanism of N_2O decomposition on a dehydroxylated Fe^{2+} site during the transient reaction.

After a certain time the very fast N_2O decomposition pathway shown in Scheme 1 is blocked and the transient reaction decays. Probably the reaction of a N_2O molecule with the $Fe^{2+}–O_2{}^{2-}$ complex becomes inhibited (we will discuss possible reasons in the next paragraph). The peroxo species has now time to exchange with the neighboring oxygen atoms, as shown in Scheme 2, before the slow reaction with a second N_2O molecule provokes the desorption of the peroxo group as O_2. The mechanism is the same as during the transient, but due to the randomization of the oxygen atoms (Scheme 2) a high K_e value is expected for the desorbed O_2, as observed experimentally ($K_e = 3$). The model can, however, not explain why ${}^{18}f$ increases when the transient activity decays, i.e., between 1000 and 3500 s in Fig. 8b. The increase of ${}^{18}f$ indicates that not only the oxygen atoms, which are directly attached to the active Fe^{2+} site, contribute to O_2 formation, but that other oxygen atoms begin to mix in as the transient reaction loses importance. It was reported before that an extensive exchange of the surface oxygen atoms takes place during steady-state N_2O decomposition at 673 K, which involves all the iron atoms of the catalyst [15]. The exchange of the surface oxygen atoms can take place via the migration of the peroxo species over the iron oxide cluster, as depicted in Scheme 3, combined with a randomization of the peroxo bond at each iron center (Scheme 2). O_2 desorbs when two peroxo species meet each other. In this model all oxygen atoms of the iron oxide cluster are involved in O_2 desorption. It explains why ${}^{18}f$ increases when steady state is approached, but it also predicts a complete randomization of the oxygen atoms during steady state; i.e., $K_e = 4$. Since a significantly lower K_e value was measured ($K_e = 3$) we infer that part of the O_2 still desorbs via the mechanism shown in Scheme 1, i.e., without migration of surface oxygen atoms over the whole cluster. The existence of two O_2 desorption mechanisms was also derived from pulse response experiments where a rather fast and di-



Scheme 2. Randomization of the peroxo bond.



Scheme 3. Model for the desorption of O_2 on larger clusters: The peroxo group formed on one site migrates over the iron cluster to a second Fe^{2+}–O_2^{2-} complex where it provokes desorption of O_2. The representation of the iron cluster is only schematic. Additional coordinating oxygen atoms are missing.

rect O_2 formation and a more gradual O_2 desorption were distinguished [21]. They can be associated with the mechanisms in Schemes 1 and 3, respectively. A quantification of their contributions is not possible with the data at hand.

The mechanisms proposed above are based on the existence of Fe^{2+} sites, which keep the catalytic cycle running. The important role of Fe^{2+} has been invoked by other authors [4,5,31] and is also supported by the observation that the autoreduction of the iron catalyst correlates strongly with its catalytic activity [14,21]. We had observed, however, that the first step of the reaction of N_2O with Fe-ZSM-5 CVD was always the reoxidation of Fe^{2+} sites by N_2O (see Figs. 2–7). That is only a seeming contradiction. It was shown that the concentration of Fe^{2+} sites on a working catalyst must be extremely small, i.e., $< 5\%$ [21,31]. To be precise one should say that a large majority of the Fe^{2+} sites are initially reoxidized during the reaction with N_2O whereas a small minority maintains the catalytic activity.

The reaction pathways shown in Schemes 1 and 3 give a model for O_2 desorption during transient and steady state, which is consistent with the experimental results. Yet, we did not answer the question what caused the transition from the fast transient reaction to the slow O_2 desorption in steady state. The most obvious explanation for the decay of the transient is that the dehydroxylated Fe^{2+} sites are slowly rehydroxylated by traces of H_2O in the feed. Once the Fe^{2+} ions are hydroxylated they lose open coordination sites and the reaction of a N_2O molecule with the Fe^{2+}–O_2^{2-} complex becomes more difficult. In order to prove that hypothesis, pulses of 10–20 mbar H_2O vapor were given during transient N_2O decomposition. After the water pulses transient activity steeply decayed to steady state within a few minutes. The rate of decay increased with the partial pressure of H_2O. Also a pulse of CH_4 abruptly stopped the transient reaction. In the reaction of CH_4 with N_2O, H_2O is produced directly on the iron sites, which explains why its impact is even stronger than during adsorption of water from the gas phase:

$$CH_4 + 4N_2O \rightarrow CO_2 + 4N_2 + 2H_2O,$$

$$CH_4 + 3N_2O \rightarrow CO + 3N_2 + 2H_2O.$$

Conversely, a pulse of CO did not affect the transient reaction because the oxidation of CO does not produce any water:

$$CO + N_2O \rightarrow CO_2 + N_2.$$

The relatively low transient activity of the catalyst, which was pretreated in H_2 at 873 K (see Table 2), is attributed to small amounts of H_2O, which remained adsorbed on the iron clusters during the cooling in H_2. This is supported by the observation that reduction in CO, which does not produce H_2O, did lead to a large transient activity, even without a subsequent treatment in He at 873 K.

4.2. *Effect of pretreatment on steady-state activity*

The pretreatment at high temperatures had an effect not only on the transient reaction but also on the steady-state activity. The two effects were not directly related to each other [21]. Table 1 and Fig. 1 show that the steady-state N_2O decomposition activity increased in parallel with the transient activity when the samples were pretreated at 873 K instead of 773 K. However, pretreatment in H_2 led to a higher activity than pretreatment in He whereas the opposite was the case for the transient. Hydroxylation of a reduced catalyst did not affect its steady-state activity, but removed the transient (Table 2). We can conclude that the presence of Fe^{2+} after pretreatment leads to a high steady-state activity irrespective of the degree of dehydroxylation. The positive effect of a reductive pretreatment was already observed before and ascribed to the high concentration of oxygen atoms from N_2O, which are incorporated into the reduced catalyst during reoxidation [14]. On the basis of the mechanisms sketched in Schemes 1–3 we can explain why the oxygen atoms, which N_2O incorporates into the iron oxide clusters, are more reactive than "normal" oxygen atoms [30]. Reaction of a reduced Fe-ZSM-5 with N_2O leads first to a stoichiometric oxidation of Fe^{2+}, according to $2Fe^{2+} + N_2O \rightarrow Fe^{3+}–O^{2-}–Fe^{3+} + N_2$. The oxygen atom is incorporated in the iron cluster as O^{2-}, which does not have any particular catalytic activity. This agrees with the observation that a large fraction of the oxygen atoms, which were deposited during reoxidation, was inactive. Table 2 shows, for example, that after the H_2-873 K treatment 100 times more oxygen atoms from N_2O were incorporated than after O_2-873 K treatment, but the steady-state activity of the H_2-873 K sample was only a factor of 2 higher. Incorporation of the oxygen atom as an inactive O^{2-} species requires that two Fe^{2+} cations be in close vicinity to each other, so that the oxygen atom can serve as a bridge between them. On single Fe^{2+} sites this reaction is not possible. A $Fe^{3+}–O^{-}$ species will be formed instead, which has to migrate over the surface to get rid of the excess electron, and thereby forms an active site for N_2O decomposition. Reductive pretreatment maximizes the concentration of these sites since it assures that all potentially active Fe^{2+} sites are created.

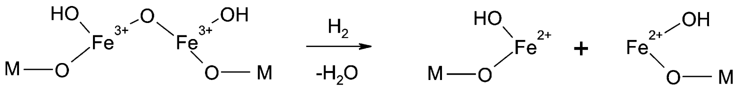
Fig. 1 shows that the pretreatment temperature had an even larger effect on the steady-state activity than H_2. A positive effect of pretreatment at high temperatures was also observed by others. Hensen et al. ascribed the increased activity to the formation of an extraframework iron–aluminum mixed oxide upon dealumination of the zeolite framework at high temperatures [31,32]. In our case Al *K*-edge XANES did not provide evidence for a dealumination of the samples at 873 K. The XANES spectrum of Fe-ZSM-5 CVD, which was treated in vacuum at 873 K, was almost identical to that of the parent material (see Fig. 9) and did not show any of the typical features attributed to octahedrally coordinated extraframework aluminum [20,24]. That means that the treatments at high temperatures do not lead to dealumination of the samples and the formation of extraframework Fe–O–Al clusters (higher temperatures than 873 K are probably required for that), but change the structure of the iron sites in some other way. We propose the following explanation: During the treatment at 873 K in He or H_2 the iron species undergo spontaneous autoreduction and/or are actively reduced by H_2. A parallel in situ XAS study [27] showed that the reduction breaks the iron oxide clusters apart by removing bridging oxygen atoms (see Scheme 4). In this way isolated Fe^{2+} sites can be created. Due to the strong dehydroxylation of the catalyst at high temperatures, the Fe^{2+} sites stabilize themselves by forming strong bonds to the oxygen atoms of the zeolite matrix. As a result, the broken clusters do not heal during reoxidation by N_2O [27]. The isolated Fe^{2+} sites are stabilized. Investigations of the N_2O-decomposition activity of transition metal cations in matrices like MgO, Al_2O_3 and $MgAl_2O_4$ showed that isolated metal ions have the highest activity [26,33–36]. The high N_2O-decomposition activity of the samples, which were pretreated at 873 K, is therefore tentatively attributed to the creation of such isolated Fe^{2+} cations, which do not agglomerate during reoxidation, due to their strong bonds to the zeolite matrix. Further experimental proof for that hypothesis is, however, required.

Note that the isolated Fe^{2+} sites, which lead to a high steady-state activity, are also active sites for the transient reaction. The mechanism shown in Scheme 1 operates during the transient as well as during steady state, the difference being that during the transient the Fe^{2+} site is dehydroxylated and the addition of the second oxygen atom from N_2O is very fast. In steady state the coordination sphere of the Fe^{2+} site is less open (due to its rehydroxylation) and the reaction with a second N_2O molecule is slow. We can state that the creation of isolated Fe^{2+} ions always increases the steady-state activity, but transient reaction on these sites is only observed if they were dehydroxylated at high temperatures.

4.3. Relation to other work

The mechanism of N_2O decomposition on hydroxylated or dehydroxylated iron sites was discussed on a theoretical basis by Yakovlev et al. [37]. Unfortunately they did not calculate the transition states of the proposed catalytic cycles so that predictions about the rate of N_2O decomposition on hydroxylated and dehydroxylated iron sites were not possible.

Kiwi-Minsker and co-workers recently described transient response experiments, which are (approach wise) similar to those presented here [5,38]. Fe-ZSM-5 samples with very low iron content were studied, which were steamed and treated at high temperatures in He. Although samples and experimental conditions are different (lower reaction temperatures of 523–653 K) many analogies to our results can be found. Like here, the formation of a peak of N_2 immediately after the step to N_2O was observed. Oxygen was deposited on the catalyst surface and only N_2 was released, i.e., $N_2O + * \rightarrow N_2 + O–*$. The reactivity of the deposited oxygen atoms was probed by CO. Not all the deposited oxygen atoms reacted with CO [5]. Following the arguments of the preceding section, the nonreactive oxygen atoms can be ascribed to oxygen atoms, which were used for stoichiometric reoxidation whereas the reactive oxygen atoms were deposited on isolated Fe^{2+} sites. The fraction of these isolated sites must, however, be much higher than in our samples, due to the lower iron content and/or the higher pretreatment



Scheme 4. Reduction of a binuclear iron cluster.

temperature. Moreover, we suspect that the unusually high N_2O-decomposition activity of the samples reported in Refs. [5,38] is a long-lasting transient reaction, which was mistaken for steady-state activity. This suspicion is corroborated by the observation that the activity completely disappeared after exposure to H_2O [38], as described here for the transient. Further comparison of the two types of samples could give interesting insights into the reaction mechanism on catalysts with high and low iron loadings.

5. Conclusions

Pretreatment of Fe-ZSM-5 CVD at a high temperature (873 K) in He or H_2 significantly increases the N_2O-decomposition activity of the catalyst. Unlike in steamed samples, this effect cannot be related to the formation of extraframework Fe–O–Al species. As a tentative explanation we suggest that the (auto)reduction at high temperature breaks the iron oxide clusters apart and creates isolated Fe^{2+} species, which stabilize themselves by forming strong bonds to the zeolite matrix. The isolated Fe^{2+} sites have a high-turnover frequency in N_2O decomposition and increase the overall reaction rate, but they are not the only sites, which are responsible for catalytic activity. Larger clusters also contribute to N_2O decomposition. On the larger iron oxide clusters, migration and exchange of the surface oxygen atoms precede O_2 desorption. The fraction of Fe^{2+} sites, which maintains catalytic activity, is very small. Most of the Fe^{2+} sites are stoichiometrically reoxidized by N_2O and do not exhibit a significant catalytic activity afterward. The difference between active and inactive Fe^{2+} sites is attributed to the fact that Fe^{2+} pairs can incorporate the oxygen atom from N_2O as an inactive O^{2-} species, whereas single Fe^{2+} sites can only transfer one electron to the oxygen atom and form Fe^{3+}–O^-, which then carries the catalytic cycle.

The high-temperature treatment in He and H_2 not only increase the steady-state rate of N_2O decomposition but also leads to a very high initial decomposition activity, which lasts for less than 1 h and then slowly decays to steady state. This phenomenon, called transient activity, is related to the presence of strongly dehydroxylated Fe^{2+} sites, which were created by autoreduction at high temperatures. Due to the coordinative unsaturation of these sites, they can rapidly pick up a second oxygen atom from N_2O, once the Fe^{2+}–peroxo complex was formed with the first oxygen atom from N_2O. Then rapid O_2 desorption occurs. This very fast catalytic cycle decays as the iron sites are rehydroxylated by traces of water.

Acknowledgments

The Swiss National Science Foundation is acknowledged for financial support, Prof. Prins for very fruitful comments and discussions as well as the critical reading of the manuscript, and Dr. van Bokhoven for the Al XANES measurements. SRS Daresbury (UK) is thanked for providing beamtime (beam time award No. 40203).

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