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A look into the surface chemistry of N_2O decomposition on iron zeolites by transient response experiments

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Abstract

The mechanism of decomposition of N_2O on Fe-ZSM-5 prepared by chemical vapor deposition was studied by step and pulse response experiments and by isotope labeling. The results show that only a very small fraction of the iron sites is taking part in the catalytic cycle. N_2O deposits its oxygen atoms on these sites, the deposited oxygen atoms migrate over the iron cluster, exchange with other oxygen atoms and then desorb by recombination to O_2. On strongly dehydroxylated iron sites also a direct recombination of two oxygen atoms, which were deposited from N_2O, is possible. The concentration of these sites increases after treatment of the samples at high temperatures in inert gas. The relation between the sites involved in N_2O decomposition and the α-sites, which were first described by the group of Panov, is discussed. We can conclude that the deposition of N_2O on Fe-ZSM-5 CVD catalysts creates active oxygen species on the catalyst surface (in particular, after pretreatments at high temperature), but their properties are different from those of α-oxygen.

Keywords: Fe-ZSM-5; CVD; α-Oxygen; Step response; Isotope labeling

1. Introduction

In the 1990s, the group of Panov discovered that Fe-ZSM-5 catalysts can generate highly active oxygen species upon interaction with N_2O [1–4]. The sites where these highly active oxygen species are created were called α-sites and the oxygen species themselves α-oxygen. α-Oxygen is created when Fe-ZSM-5 reacts with N_2O at ~523 K. At this temperature, the oxygen atom of N_2O is deposited on the catalyst surface in the form of α-oxygen, while N_2 is released into the gas phase [4,5]. The catalytic properties of α-oxygen are remarkable [1] and the discovery kindled an enormous interest in the scientific community. α-Oxygen rapidly exchanges with $^{18}O_2$ at 523 K, whereas Fe-ZSM-5 that was not treated with N_2O is completely inactive for the isotope exchange at that temperature. α-Oxygen also lowers the light-off temperature for the oxidation of CO and CH_4 by ~150 K. The most interesting property of α-oxygen is that it can insert into a C–H bond. It selectively oxidizes benzene to phenol [3,6], and it even converts methane to methanol [5,7]. Latter reaction proceeds at ambient temperature, but it is stoichiometric rather than catalytic. The methanol product remains adsorbed on the catalyst surface and has to be extracted.

The structure of the α-sites has been much debated. They are Fe^{2+} sites, but they do not react with O_2 [1]. Only N_2O can oxidize them to Fe^{3+} upon formation of α-oxygen. Very early one proposal was made that α-sites are binuclear iron clusters [4,8]. The proposal was partly based on the observation that the ratio of O_α/Fe was close to 0.5, i.e. one oxygen atom bound to two iron atoms. An O_α/Fe ratio of 0.5 is, however, no proof for binuclearity. It simply follows from the stoichiometry of oxidation of Fe^{2+} to Fe^{3+}, i.e.

$$2Fe^{2+} + N_2O \rightarrow 2Fe^{3+} + O^{2-} + N_2$$

and is, therefore, not specific for binuclear iron clusters.

A second argument made the notion of a binuclear iron cluster popular. Due to the capability of α-oxygen to insert into C–H bonds, analogies to the enzyme methane monooxygenase (MMO) were drawn. MMO oxidizes methane and other alkanes to the corresponding alcohols. The active site of MMO consists of a binuclear iron core. Granted that α-sites are binuclear, they have a similar structure as the active site in MMO and a similar reactivity.

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For a long time, no spectroscopic evidence on the true nature of the α-sites could be given. Since the iron loadings of the Fe-ZSM-5 samples described by the group of Panov is very low an exact structural characterization is extremely difficult. Support for the binuclear nature of the iron sites in Fe-ZSM-5 was, however, given for a different type of sample, i.e. Fe-ZSM-5 prepared by chemical vapor deposition of $FeCl_3$. Let us briefly compare the two preparation methods. In the original recipes described by the group of Panov, an iron salt was added to the synthesis solution of ZSM-5. Iron was incorporated into the zeolite framework and had to be extracted to extraframework positions by calcination at high temperatures to make the sample active [9]. The iron loading of these samples is less than 0.5 wt%. In the CVD method [10,11], on the other hand, iron is incorporated after the synthesis of ZSM-5. $FeCl_3$ reacts in the gas phase with the Brønsted acid sites of ZSM-5 in a ratio of 1:1. Hydrolysis and calcination lead to small iron oxide clusters bound to the ion-exchange positions of the zeolite. The samples have a very high iron loading (3–5 wt%, depending on the Si/Al ratio of the zeolite) and are more easily accessible to characterization methods. EXAFS studies on Fe-ZSM-5 CVD detected a Fe–Fe coordination number of 1.0 [12–14], indicating that iron was present in the form of pairs. The Fe–Fe distance was similar to the one found in MMO. Both observations were regarded as proof for the binuclear nature of the α-sites and similarity of this system to the enzyme MMO. It should be noted, however, that at that time the existence of α-sites in CVD catalysts had not been proven. One could say that there was a mismatch in the available information. The reactivity of the catalysts prepared by hydrothermal synthesis and steaming had been described in great detail, but little was known about the structure of the active sites. For the CVD catalysts, a structural model had been proposed, but the reactivity of the oxygen species in these materials had scarcely been studied. In order to fill that gap, we decided to study the reactivity of the oxygen species that N_2O deposits on Fe-ZSM-5 CVD in detail. N_2O decomposition was chosen as a test reaction. It is a fairly simple reaction, which proceeds exclusively on the iron sites. In contrast to benzene oxidation [15], the acidity of the zeolite matrix plays, if at all, only a minor role and deactivation due to coke formation cannot mask the intrinsic activity of the iron sites. Two mechanisms have been proposed for N_2O decomposition [16,17]. In both, the first step is the deposition of the oxygen atom of N_2O on the catalyst surface (Reaction (1)). This step is fast. The slow step is the formation of O_2, either by recombination of two surface oxygen atoms (Reaction (3)) or by reaction of a surface oxygen atom with N_2O (Reaction (2)):

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

$$*-O + N_2O \rightarrow N_2 + O_2 + * \qquad (2)$$

$$2*-O \rightarrow O_2 + 2* \qquad (3)$$

Highly reactive surface oxygen species might be expected to react according to Eq. (2). Reaction (2) was also favored by many authors because of the observation that the presence of O_2 in the gas phase does not strongly inhibit N_2O decomposition over Fe-ZSM-5 [16,18,19]. Such an inhibition would be expected if oxygen was formed according to Eq. (2). We will address that issue in more detail during the discussion.

Since our goal was to perform mechanistic studies of the behavior of the surface oxygen species simple steady state kinetic measurements were not very helpful. They tell us something about the rate of O_2 formation, but nothing about the build-up and consumption of the surface oxygen atoms. Therefore, transient response experiments were employed. We constructed a reactor system that allowed fast switching from one gas mixture into another as well as pulsing of one gas mixture into another. In addition, isotope labeling was used to trace the origin of the oxygen atoms in O_2.

It should be noted that physico-chemical studies of the CVD catalyst, which were performed in recent years showed that the material is not the ideal model for catalyst containing binuclear iron clusters, as originally believed, but a very complex and heterogeneous material.

2. Experimental

2.1. Catalyst preparation

Two different parent zeolites were used for our experiment: MFI-P 46 from Südchemie and PZ2–40 from Zeochem. Both have a Si/Al ratio of 24. They contain an iron impurity level of 0.04 wt% (Südchemie) and 0.02 wt% Fe (Zeochem). The samples were received in the Na(H) form and were transformed into the ammonium form by three-fold ion-exchange with 1 M NH_4NO_3. Subsequently, they were calcined at 773 K in O_2 before sublimation (CVD) of $FeCl_3$ was carried out in a flow of N_2 at 593 K. The samples were extensively washed and calcined in O_2 at 773 K for 5 h. The details of the synthetic procedure can be found, for example, in Ref. [20]. Chlorine-free materials with Fe/Al $\sim$ 1 and an iron loading of 4–4.5 wt% were obtained. The physico-chemical properties and also the reactivity of the catalysts prepared from the two parent zeolites were very similar. Their characterization by IR, UV–vis and EXAFS is described in Refs. [12,13,20,21]. New EXAFS results [20–23] as well as Mössbauer data [22,23] indicate that the dominating iron species in Fe-ZSM-5 CVD are small iron oxide clusters, which consist of a few (from two to four) iron atoms. The original picture of a catalyst containing only binuclear iron clusters is, therefore, not entirely correct.

2.2. Transient response experiments

50 mg of pelletized catalyst were placed in quartz reactor of 4 mm inner diameter. The catalyst was held in place by two pieces of quartz wool. An electronic four-port valve allowed for fast switching between two gas streams, one leading the reactor, the other to the vent (Fig. 1). A third gas mixture could be injected into the feed stream of the reactor via a loop. Only

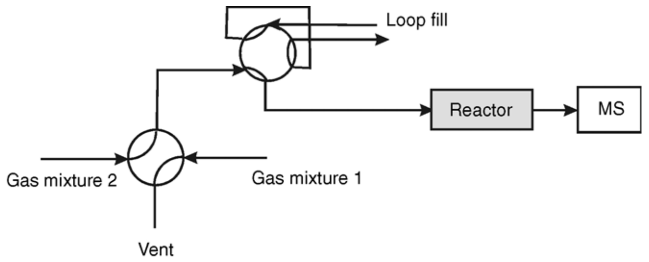


Fig. 1. Scheme of the setup used for the transient response measurements.

diluted gases were used. Standard concentrations were 5000 ppm N_2O, 1% CO and 1% $^{18}O_2$ in He.

Early tests showed that treating the catalyst in He before the experiment led to a substantial reduction of Fe^{3+} to Fe^{2+} [24]. Similar effects were also observed in in situ EXAFS experiments of others [25,26]. The reduction is caused by impurities adsorbed on the zeolite. In order to burn off these impurities, we always performed an initial oxidative treatment of the sample in the reactor (at 673 or 773 K) followed, if desired, by consecutive treatments in He, H_2, CO, etc.

The gas flow rate in the transient experiments was kept at 25 ml_{NTP}/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. We recorded the mass fragments $m/e = 4$ (He), 28 (N_2, N_2O, CO), 30 (N_2O), 32 (O_2) and 44 (N_2O, CO_2) and converted the signals into concentrations via calibration factors. When more than one component contributed to a mass fragment, a second mass was used to distinguish these two components. The N_2 concentration, for example, was determined from the signal of $m/e = 28$, after subtracting the contribution of N_2O, known from $m/e = 30$ or 44. Similarly, CO_2 was determined from $m/e = 44$ after subtracting the contribution of N_2O, known from $m/e = 30$. The subtraction leads to errors of ±50 ppm and makes it difficult to detect very low concentration precisely. As a compromise between good S/N ratio and high time resolution, we chose a scanning time of 0.2–0.5 s per mass. With that setting, one data point could be measured each 2–4 s. Our reactor is not an ideal plug flow reactor. When stepping from one gas mixture to another, a non-reacting and non-adsorbing component takes about 30 s to reach 95% of the final concentration. The half width of pulses was ∼15 s. In view of these response times, a time resolution of 2–4 s in the mass spectrometric analysis was sufficient. A TAP reactor can achieve much higher time resolutions (on the millisecond scale), but one has to keep in mind that a TAP reactor operates in high vacuum. The state of the surface may be different than under atmospheric conditions. Our setup has the disadvantage that it cannot resolve very fast reactions, but it has the advantage of being a ‘‘real’’ reactor.

2.3. NO adsorption

Infrared spectra of self-supporting wafers were recorded at room temperature. About 3–4 mg catalysts were first heated to 573 K in vacuum. Then, the sample was pretreated in situ in 20 mbar O_2 at 673 or 873 K for 1 h, evacuated and cooled down to room temperature in vacuum, followed by room temperature exposure to 5 mbar NO for 30 min. Finally, the sample was evacuated and a spectrum was recorded at room temperature.

3. Results and discussion

3.1. Oxidative or reductive pretreatment

It was shown that the active sites for N_2O decomposition (written as * in Reaction (1)) are Fe^{2+} sites [27,28]. The catalytic cycle should run faster when more Fe^{2+} sites are available. We, therefore, compared the behavior of the catalyst after oxidative and reductive pretreatment. Fe-ZSM-5 CVD was treated either in 35% H_2 or in 2000 ppm O_2 at 673 K, followed by a brief flushing in He before stepping to 5000 ppm N_2O. In both cases, a peak of N_2 was formed right after the step (Fig. 2) [24]. The peak was very intense and broad after pretreatment in H_2. O_2 formation was not detected before N_2 decayed to its steady state level. The area under the N_2 peak corresponded to 0.5 mol of N_2 per mol of Fe in the catalyst, as expected from the stoichiometry of Reaction (4):

$$2Fe^{2+} + N_2O \rightarrow Fe^{3+}{-}O{-}Fe^{3+} + N_2 \quad (4)$$

It means that all iron atoms in the catalyst were reduced to Fe^{2+} by the treatment in H_2 and then reoxidized by N_2O. Only after completing the reoxidation, steady state N_2O decomposition set in, yielding N_2 and O_2 in the stoichiometric ratio of 2:1. The same phenomenon was already reported by the group of Hall [18].

After pretreatment in 2000 ppm O_2, the peak of N_2 was significantly smaller. After subtracting the steady state level the area corresponded to $N_2/Fe = 0.01$. The N_2 formation is

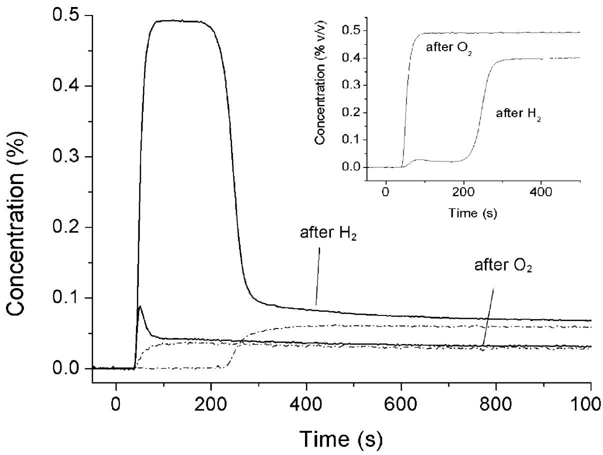


Fig. 2. Step from He to 5000 ppm N_2O in He over Fe-ZSM-5 CVD, after pretreatment in 35% H_2 in He or in 2000 ppm O_2 in He at 673 K. N_2 concentration (solid) and 2× O_2 concentration (dash-dot). N_2O concentration is shown in inset.

ascribed to the reoxidation of Fe^{2+} sites, which are created by autoreduction of the catalyst during the brief flushing in He. The steady state activity after pretreatment in O_2 was about a factor of two lower than after pretreatment in H_2. It shows that increasing the initial concentration of Fe^{2+} sites (and thereby, the concentration of deposited oxygen atoms) indeed increases the activity in N_2O decomposition, but the increase is not proportional; 50 times more oxygen atoms from N_2O were deposited on the H_2-treated catalyst, but the catalytic activity increased only by factor of two. Only a small fraction of the Fe^{2+} sites created by reduction in H_2 participates in the catalytic cycle. Most of them are simply reoxidized to Fe^{3+} by reaction with N_2O.

How can we determine the number of Fe^{2+} sites that take part in the catalytic cycle? The characteristic of these sites is that they can take up an oxygen atom from N_2O, upon oxidation to Fe^{3+} and release it again, upon reduction to Fe^{2+}. If we step back to He after reaching steady state in N_2O decomposition all sites participating in the catalytic cycle should release their oxygen atoms and return to the oxidation state +II. We can probe these sites by performing a second step to N_2O and measuring the amount of N_2 formed during the initial reoxidation of Fe^{2+}. For Fe-ZSM-5 CVD that was treated in He at 773 K before N_2O decomposition, this number was $N_2/Fe = 0.0035$ [20]. In other words, 0.35% of the iron sites can take up and release oxygen from N_2O. A comparison of different catalysts showed that the concentration of oxygen vacancies determined by this method strictly correlates with catalytic activity [20,24]. The concentration of active sites increases after reductive pretreatment of the catalyst and decreases after oxidative pretreatment.

One might be tempted to think that a very low fraction of the iron sites is active because most of the iron atoms are buried in the bulk of iron oxide clusters and not accessible to N_2O. This is not the case. According to EXAFS and Mössbauer data, the iron oxide clusters contain only a few iron atoms, i.e. there is no bulk phase. All iron atoms are on the surface. We will address the question why only a very fraction of the iron sites is active in a later section.

Having determined the concentration of iron sites taking part in the catalytic cycle, we can calculate the turnover frequency of the reaction based on these sites only, instead of normalizing by the total concentration of iron sites. At 673 K and 5000 ppm N_2O, this yields a turnover frequency of 0.07 s^{-1}. We can see that N_2O decomposition is an extremely slow reaction. Only each 13 s one turnover takes place.

The discussion above is based on the assumption that N_2O decomposition is associated with a Fe^{2+}/Fe^{3+} redox cycle. Strictly speaking, the possibility that N_2O can also dissociate on a Fe^{3+} ion upon formation of a surface peroxide cannot be ruled out. In that case, the catalytic cycle would be carried by a small concentration of Fe^{3+} sites that allow the formation of a surface peroxide. However, the observation that the activity increases from pretreatment in O_2 to He to H_2, i.e. with increasing the concentration of reduced sites, strongly speaks in favor of the redox mechanism, i.e. the involvement of Fe^{2+}.

3.2. The mechanism of O_2 formation

TAP experiments [29,30] gave convincing proof that Fe-ZSM-5 prepared by hydrothermal treatment and steaming forms O_2 by recombination of two surface oxygen atoms (Reaction (3)). For a catalyst prepared by wet ion-exchange, however, isotope-labeling experiments indicated that O_2 was formed by reaction of a surface oxygen atom with the oxygen atom from N_2O (Reaction (2)) [31]. The conflicting results show that the mechanism of O_2 formation may depend on the conditions and on the type of iron sites.

For our CVD catalysts, we obtained strong evidence that O_2 desorption in steady state takes place by recombination of two surface oxygen atoms, i.e. by Reaction (3) and not by Reaction (2). When we step-down from N_2O to He, after having reached steady state in N_2O decomposition, the O_2 concentration decreases much slower to zero than the N_2 concentration (Fig. 3). Due to the high reaction temperature (673 K), that effect cannot be ascribed to the adsorption of molecular O_2 on the catalyst. The O_2 desorption after the step-down must be due to the slow and retarded recombination of adsorbed oxygen atoms to O_2, i.e. Reaction (3), which continues for several minutes after switching from N_2O to inert gas.

The second, even more convincing evidence comes from isotope-labeling experiments. They were carried out in order to find out whether the oxygen atoms in O_2 originate only from N_2O or whether other oxygen atoms of the iron oxide cluster or the zeolite lattice are also involved [32]. In order to incorporate a high concentration of ^{18}O into the catalyst, Fe-ZSM-5 CVD was first reduced in H_2 at 673 K and then reoxidized by pulsing or flowing 1% $^{18}O_2$ (93% ^{18}O) in He. After that, a step to 5000 ppm N_2O was performed. All three isotopomers ($^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$) were found in the O_2 produced by N_2O decomposition (Fig. 4) [33]. The initial fraction of labeled oxygen atoms (^{18}f) was 0.09 and the isotope distribution within O_2 was statistical. Latter statement can be inferred from the value of the equilibrium constant of isotope exchange, which is defined as:

$$K_e = \frac{[^{16}O^{18}O]^2}{[^{16}O_2]^2[^{18}O_2]^2}$$

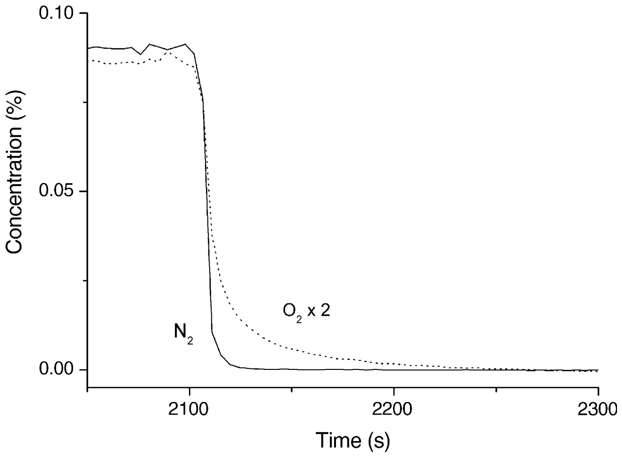


Fig. 3. Step from 5000 ppm N_2O to He at 673 K.

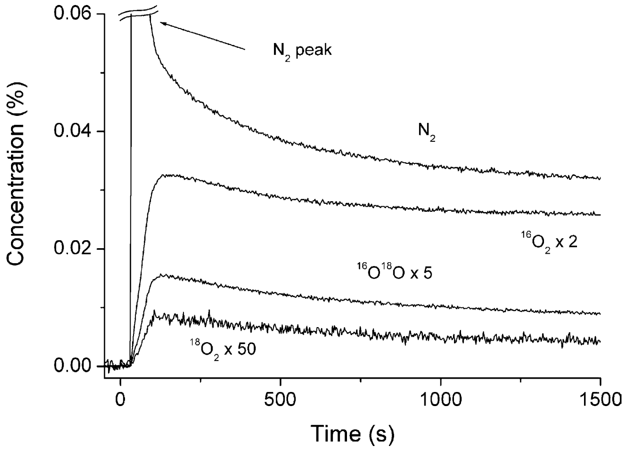


Fig. 4. Step from He to 5000 ppm N_2O over an ^{18}O-labeled Fe-ZSM-5 CVD at 673 K.

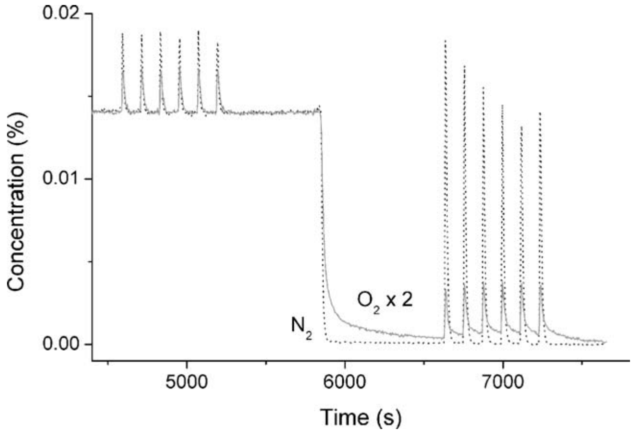


Fig. 5. Pulses of 5000 ppm N_2O into a flow of 1000 ppm N_2O in He, followed by step to He and a new series of pulses of 5000 ppm N_2O, at 673 K. Fe-ZSM-5 CVD was pretreated at 773 K in He.

When the distribution of ^{18}O over the three possible isotopomers $^{16}O_2$, $^{18}O^{16}O$ and $^{18}O_2$ is statistical, K_e has the value 4.

$$K_e = \frac{[2 \cdot {}^{18}f \cdot (1 - {}^{18}f)]^2}{{}^{18}f^2 \cdot (1 - {}^{18}f)^2} = 4$$

Our experiments yielded a K_e very close to 4.

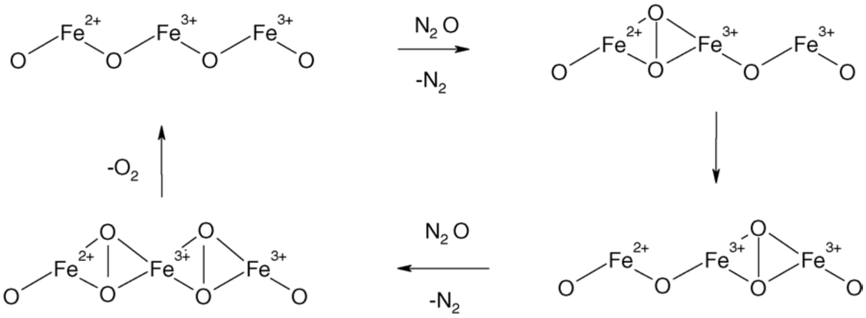
Two processes can lead to a statistical distribution of the isotopes within O_2: (i) a fast isotope exchange of gas phase O_2 with the surface, which leads to a complete scrambling of the oxygen atoms or (ii) a fast exchange of the deposited oxygen atoms on the surface *before* they recombine to form gas phase O_2. When $^{18}O_2$ was pulsed over the catalyst during N_2O decomposition no exchange reaction with the surface was observed. Option (i) can, therefore, be ruled out and the following picture emerges. When N_2O deposits an oxygen atom on the catalyst it undergoes a fast exchange with the other oxygen atoms of the iron oxide cluster. These oxygen atoms form an equilibrated pool from which O_2 desorption occurs by recombination and desorption. The size of this pool was estimated to be $O_{pool}/Fe \sim 1$ [33]. Does that mean that, in contrast to our statement above, all iron sites are involved in N_2O decomposition? The answer is no. All iron sites may take part in exchange reactions of the oxygen atoms on the surface, but only a few sites are capable of releasing O_2 into the gas phase and taking up new oxygen atoms from N_2O. Only these sites keep the catalytic cycle running. The isotope experiment shows, however, that the mobility of the oxygen atoms is very high and that they migrate over the surface before desorption as O_2. The rate of O_2 desorption may be limited by the migration or by the actual recombination and desorption as O_2.

In order to extract additional information on the mechanism of O_2 formation also pulse experiments were carried out. We administered pulses of 5000 ppm N_2O into a flow of 1000 ppm N_2O in He at 673 K (Fig. 5). The idea behind this experiment was to probe the number of sites that are free to react with N_2O under the conditions of the steady state reaction. The conversion of N_2O to N_2 in the pulses of higher concentration was similar to the steady state conversion of the 1000 ppm N_2O, which flowed continuously over the catalyst. Peaks of N_2 and O_2 were formed, roughly in the stoichiometric ratio of 2:1. The peaks of O_2 were broader and slightly tailed with respect to the peaks of N_2 and N_2O [20], but most of the O_2 desorbed simultaneously with N_2 (within the time resolution of the experiment). That result was unexpected in the light of our earlier conclusion that O_2 is formed by Reaction (3) and should be strongly delayed with respect to N_2 formation.

Strikingly, the same amount of O_2 was formed in pulses of N_2O administered after the step back to He. The area of the N_2 peak, however, increased by a factor of four. The result indicates that the catalyst contains a certain number of sites that allow rapid O_2 desorption, while the rest of the deposited oxygen atoms desorbs in slow process that is smeared out in the baseline. The number of these rapid desorption sites is 15 times smaller than the total concentration of active sites determined by the step-up/step-down experiments [20]. Since the O_2 formation on these sites is much faster than expected from the overall turnover frequency of the reaction ($0.13\ s^{-1}$) these sites cannot be mainly responsible for the steady state activity of the catalyst. We will see later that their fraction increases after treatment of the catalyst at high temperatures.

3.3. Kinetics of N_2O decomposition

The isotope experiments described above prove that O_2 formation occurs by recombination of two surface oxygen atoms. If Reaction (2) had a significant contribution to O_2 formation the isotope distribution in O_2 would not be statistical. It has been shown that O_2 formation is the rate-limiting step of N_2O decomposition [24,29,30]. N_2 formation by Reaction (1) is assumed to be fast. Let us assume that N_2 formation is very fast with respect to O_2 formation. N_2 formation would only be limited by the concentration of oxygen vacancies created by the slow recombination and desorption of O_2 and the reaction order in N_2O should close to zero. Our pulse experiments confirm that N_2 formation strongly depends on the concentration of oxygen vacancies (cf. Fig. 5). Reported reaction orders in N_2O are, however, close to one [16,17].



Scheme 1. Possible mechanism of N_2O decomposition in steady state, including migration of the deposited oxygen atoms (here, only the migration to the next iron atom is depicted).

Based on the results of the isotope experiments we setup a modified model for N_2O decomposition, which includes the migration of the deposited oxygen atoms over the iron cluster. Three steps are considered (see Scheme 1 and the kinetic equations below): (i) the dissociation of N_2O on an active site (depicted as * in Scheme 1). We will discuss in the next section that the active sites can be identified with Fe^{2+} sites, which are isolated in the sense that they do not have Fe^{2+} neighbors (but they can have Fe^{3+} neighbors). (ii) The transfer of the deposited oxygen atom from the active site to a neighboring Fe^{3+} site, which is not active in dissociation of N_2O. Thereby, the active site becomes free to react with another molecule of N_2O. (iii) The migration of the oxygen atom over the iron cluster towards another active site (or eventually back to the same site), which has been meanwhile loaded with a second oxygen atom, followed by recombination of the two oxygen atoms and their desorption as O_2. k_3 is the overall rate constant of the migration plus recombination/desorption. Taking the stability of surface oxygen species into account it seems most likely that the migration of the deposited oxygen atoms takes place in the form of a peroxo species [34–36]. The hopping of a peroxo bond around the iron atom can also account for the complete scrambling of the oxygen atoms that was observed in our isotope experiments [33,37]:

$$N_2O + * \xrightarrow{k_1} N_2 + *{-}O$$

$$*{-}O + Fe{-}O \xrightarrow{k_2} * + Fe{-}O_2$$

$$Fe{-}O_2 + *{-}O \xrightarrow{k_3} Fe{-}O + * + O_2$$

Assuming stationary conditions for all surface species (see Appendix A), we obtain:

$$r = p_{N_2O} \cdot k_1 \cdot \frac{n}{1 + \frac{k_1}{2k_2[FeO]} p_{N_2O}}$$

where n is the number of sites taking part in the catalytic cycle (n = [*] + [*–O]). The term $n/(1 + p_{N_2O} * k_1/2k_2[FeO])$ corresponds to the fraction of vacant sites. The expression is similar to a Langmuir–Hinshelwood rate equation and it can fit our kinetic data measured in the range of 0.1–0.5 kPa N_2O at 673 and 698 K very well (Fig. 6). At 673 K, we obtain the values $n \times k_1 = 1.4 \times 10^{-6}\ s^{-1}\ kPa^{-1}\ mol\ g_{cat}^{-1}$ and $k_1/2k_2[FeO] = 1.8\ kPa^{-1}$. Fitting with the same data with an exponential rate law, $r = k \times p^a$ yielded an order in N_2O of 0.8, i.e. close to one. Our fit parameters allow us to compare the rate of N_2 and of O_2 formation. The fastest possible rate of N_2 formation is $k_1 \times n \times p_{N_2O}$ (all sites vacant). The fastest possible rate of O_2 desorption is $k_4 \times [FeO_2] \times n = k_2 \times [FeO] \times n$ (all sites occupied).

The ratio of the two rates at 673 K and 0.5 kPa N_2O is:

$$\frac{r_{max,N_2}}{r_{max,O_2}} = \frac{k_1 \cdot p_{N_2O}}{k_2[FeO]} = 1.8$$

Our analysis shows that the maximum rate of N_2 and of O_2 formation are in the same order of magnitude. Our model may still have shortcomings and does not describe the full complexity of the system. But we can take the message that O_2 formation is not orders of magnitude slower than N_2 formation. Hence, N_2 formation is not only limited by the concentration of oxygen vacancies, but also depends on the partial pressure of N_2O, which explains the nearly first order in N_2O.

We can compare our data with a recent kinetic analysis of N_2O decomposition by Wood et al. [38]. According to their results, measured on Fe-ZSM-5 prepared by hydrothermal synthesis and steaming, N_2 formation is a factor of 10 faster

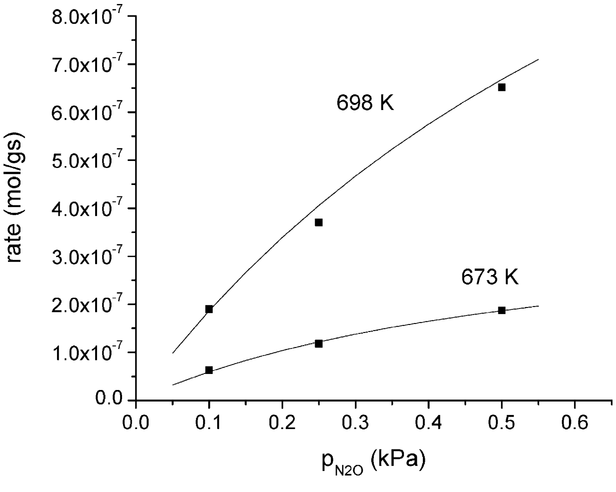


Fig. 6. Fit of N_2O decomposition rate as a function of pressure with a Langmuir–Hinshelwood expression. GHSV = 40,000 h^{-1}.

than oxygen formation at 673 K. At 773 K, the rates become equal.

3.4. The effect of high temperature treatments

In the experiments described in Section 1, Fe-ZSM-5 was calcined at 773 K and then pretreated at 673 K in the reactor (in H_2, He, O_2, etc.) before reaction with N_2O. Under these conditions, no sign of highly active surface oxygen species was found on the catalyst. When $^{18}O_2$ was pulsed over Fe-ZSM-5 CVD during N_2O decomposition at 673 K no isotope exchange with $^{18}O_2$ took place [33]. Very rapid isotope exchange with O_2 is a characteristic property of α-oxygen species [1]. The early work of Panov et al. showed that high temperature treatments of the catalyst are necessary to create a high concentration of α-oxygen species in Fe-ZSM-5 [6]. It was first believed that the high temperatures lead to the extraction of iron from an inactive position in the zeolite framework to an active extraframework position [39]. Later, it was shown, that the high temperature treatment also generates more α-sites in catalysts, where iron is located at ion-exchange (i.e. extraframework) positions [27]. Thus, the high temperature treatment does more to the iron sites than just dislocating them to extraframework positions. It somehow changes the structure of the iron sites. In the specific case of Fe-ZSM-5 CVD, it was observed that high temperature treatments increased: (i) the activity in N_2O decomposition [40]; (ii) in benzene oxidation [41]; (iii) that they also led to the formation active oxygen species, similar to α-oxygen [42].

We studied the effect of high temperature treatments on the transient response of Fe-ZSM-5 CVD in N_2O decomposition [37]. The step response dramatically changed after pretreatment at 873 K in He (Fig. 7). The initial peak of N_2 was followed by a rather long period of high N_2O decomposition activity, which slowly decayed to steady state. We will call this phenomenon transient N_2O decomposition in the following. The extent of transient N_2O decomposition strongly depended on the pretreatment of the catalyst. It was high after pretreatment in inert or reducing atmosphere, provided that water was absent, but was close to zero after pretreatment in O_2 or exposure to water vapor [37]. Pretreatment at 873 K led to a higher transient activity than pretreatment at 773 K. At 673 K, no transient activity was generated and the catalyst reached steady state immediately (see Fig. 2). This is strong indication that dehydroxylated Fe^{2+} sites catalyze the transient reaction. In order to prove that hypothesis, NO adsorption was used. NO adsorbs strongly on Fe^{2+} and is, therefore, frequently used as a probe molecule. Depending on the coordinative unsaturation of the Fe^{2+} sites NO can adsorb as trinitrosyl species $Fe(NO)_3$, with characteristic IR bands at ~1920 and ~1810 cm^{-1}, as dinitrosyl species $Fe(NO)_2$, with characteristic bands at ~1850 and ~1770 cm^{-1} or a mononitrosyl species Fe(NO), with a band around 1880 cm^{-1} [43,44]. Fig. 8 shows the spectra of NO adsorbed on Fe-ZSM-5 CVD after pretreatment in vacuum at 873 or 673 K. Spectra were recorded in the presence of 5 mbar NO and after subsequent evacuation. In both cases, one can recognize that pretreatment at 873 K led to a high concentration of di- and trinitrosyl species, whereas mononitrosyls dominate in the sample pretreated at 673 K. We can conclude that dehydroxylation at 873 K creates vacancies in the coordination sphere of iron that allow the adsorption of two or even three molecules of NO on one site. Also, in situ EXAFS measurements showed that a strong dehydroxylation of the iron sites took place in the temperature range 673–873 K [21]. Below these temperatures, water remained rather strongly adsorbed on Fe-ZSM-5 CVD. EXAFS and NO adsorption, therefore, support the idea that strongly dehydroxylated iron sites catalyze the transient reaction. The high coordinative unsaturation of these sites is responsible for their high reactivity [44].

In order to elucidate the mechanism of transient N_2O decomposition Fe-ZSM-5 CVD was labeled with ^{18}O before the step to N_2O [37]. Fig. 7 shows that the distribution of isotopes was entirely different from the analogous experiment after pretreatment at 673 K (cf. Fig. 4). As always, a peak of N_2 was observed first, due to the deposition of oxygen atoms on the surface. This reoxidation peak was followed by a small peak of N_2 and O_2, after ~100 s. The isotope distribution of O_2 in this peak was characterized by a relatively high concentration of

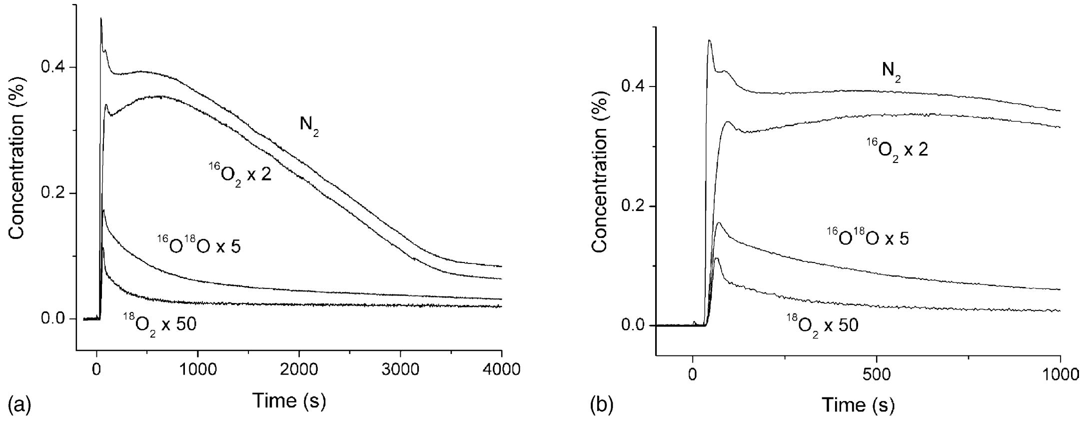


Fig. 7. Step from He to 5000 ppm N_2O over Fe-ZSM-5 CVD at 673 K: (a) catalyst was reduced in H_2 at 673 K, oxidized in 1% $^{18}O_2$ at 873 K and then treated in He at 873 K for 1 h before the reaction and (b) zoom of the first 1000 s.

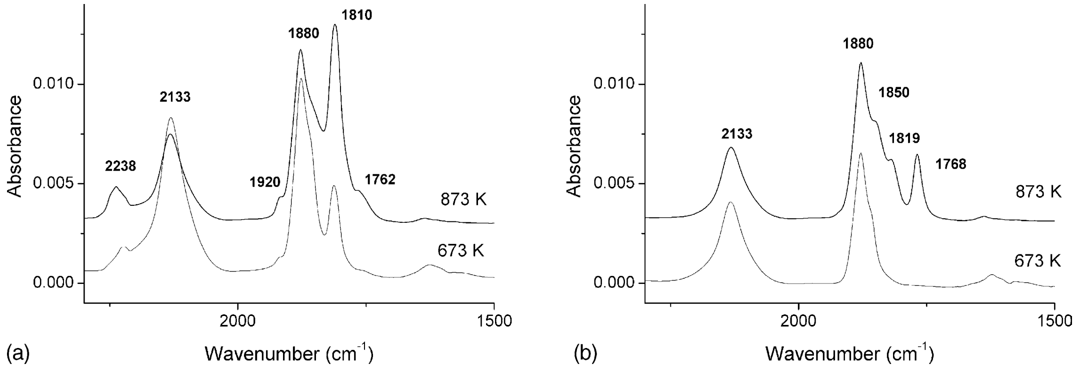
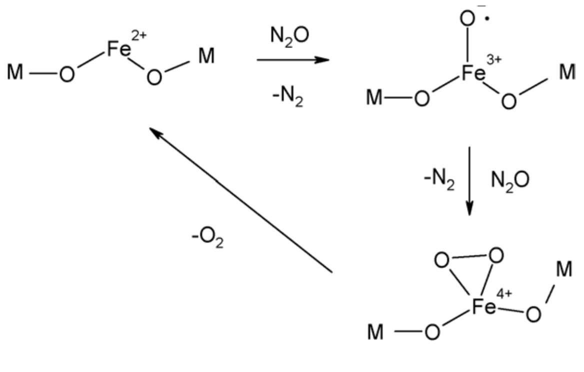


Fig. 8. IR spectra of Fe-ZSM-5 CVD after adsorption of NO for 30 min (a) and after evacuation for 5 min (b). Pretreatment at 673 or 873 K in vacuum.

$^{16}O^{18}O$ and $^{18}O_2$, i.e. extensive mixing of the deposited oxygen atoms with surface oxygen atoms took place. The process decayed quickly and the concentration of $^{16}O^{18}O$ and $^{18}O_2$ in the product O_2 rapidly decreased. During the transient reaction, i.e. between 200 and 3000 s, mainly $^{16}O_2$ was produced. Most of the oxygen atoms in O_2 originated from N_2O. After the decay of the transient reaction to steady state, the distribution of the three isotopomers was again almost statistical ($K_e = 3$). The result shows that, in contrast to the steady state reaction, transient N_2O decomposition occurs by a direct recombination of two oxygen atoms from N_2O. The high coordinative unsaturation of the dehydroxylated Fe^{2+} sites allows the deposition of two oxygen atoms from N_2O on one site, which can rapidly desorb as O_2 (see Scheme 2) [45,46]. The process decays due to a slow rehydroxylation of the iron site by traces of water. The model is supported by recent theoretical calculations of Heyden et al., which show that adsorption of water strongly inhibits N_2O decomposition on isolated iron sites [46].

In steady state the catalyst operates mainly according to the mechanism discussed in a previous section, i.e. via exchange and migration of the surface oxygen atoms before recombination and desorption as O_2 (see Scheme 1). However, in contrast to the experiment following pretreatment at 673 K, pretreatment at 873 K did not lead to a full equilibration of the isotopes in steady state. K_e only reached a value of 3.0. Moreover, the steady state activity was higher. The high temperature pretreatment generates some sites from which fast and direct O_2 desorption occurs even in steady state. Such sites had been identified in the pulse experiments described earlier (Fig. 5).



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

We can rule out the possibility that the effect of pretreatment at high temperatures is related to the dislocation of the impurities in the parent zeolite from framework to extraframework positions. The N_2O decomposition activity of the parent zeolite increased after pretreatment at high temperatures, but was still negligible compared to the activity of Fe-ZSM-5 CVD.

3.5. Titration of the active oxygen species

The highly reactive oxygen species involved in the transient reaction are reminiscent of α-oxygen species. Until now, we had not seriously attempted to detect the concentration of α-oxygen species in our catalyst. α-Oxygen species are usually generated by reaction of N_2O with the catalyst at 523 K. At this temperature, the oxygen atom from N_2O is deposited on the surface (on the α-sites) and remains adsorbed there, while N_2 is released into the gas phase.

$$* + N_2O \rightarrow N_2 + * - O_\alpha$$

The concentration of O_α can be determined from the amount of N_2 released [4,5]. We had shown above that not all deposited oxygen atoms necessarily contribute to catalytic activity (see also Ref. [47]). Some are consumed in an “irreversible” oxidation of Fe^{2+} sites. It is, therefore, important to distinguish active from inactive oxygen species. That can be done by titrating the active oxygen species with $^{18}O_2$ or CO [2]. Titration by CO is the more convenient method [47]. Moreover, it was shown that the concentration of active oxygen species determined by that method correlated very well with the activity of the samples in the hydroxylation of benzene [48]. The experimental procedure was as follows: after the desired pretreatment, Fe-ZSM-5 CVD was exposed to 5000 ppm N_2O at 523 K for 30 min and then pulses of 1% CO in He were administered. For a blank test, Fe-ZSM-5 CVD was treated in O_2 without subsequent exposure to N_2O. The catalyst had a negligibly small CO conversion (CO_2/Fe = 0.002 in 12 pulses). Pretreatment at 673 K in He, followed by reaction with N_2O at 523 K led to a similar result as in the blank, i.e. N_2O did not generate any active oxygen species. Higher pretreatment temperatures (773 and 873 K) significantly increased the CO conversion (Table 1; Fig. 9). The effect was reversed by exposure to H_2O, as reported before [47]. The highest concentration of active oxygen species was measured after reduc-

Table 1
Deposition of oxygen from N_2O at 523 K and subsequent titration by CO

Pretreatment	O_{dep}/Fe	CO_2/Fe (12 pulses)	Transient activity at 673 K	Steady state yield at 673 K (%)
Blank		0.002	–	–
O_2 at 773 K	0.0001	0.0025	None	6
He at 673 K	0.0003	0.001	None	8
He at 773 K	0.006	0.006	Moderate	9
He at 873 K	0.057	0.026	High	10
He at 873 K, H_2O at 523 K	0.029	0.005	None	10
H_2 at 673 K	0.33	0.016	None	12
H_2 at 873 K	0.35	0.044	High	19
CO at 873 K	0.40	0.036	High	14

For comparison: transient activity and steady state activity at 673 K after the same pretreatment.

tion in H_2 or in CO at 873 K. Surprisingly, even reduction at 673 K (followed by flushing in He for 1 h) was effective in generating active sites.

Except for the prereduced samples, the ratio between the concentration of active oxygen species and the concentration of deposited oxygen atoms was between 0.5 and 1.0 (Table 1). H_2O treatment led to a significant reduction of the ratio active oxygen/deposited oxygen. In the prereduced samples, only a small fraction of the deposited oxygen atoms was active for CO oxidation because most of the deposited oxygen atoms were consumed in the stoichiometric reoxidation of Fe^{2+} (Reaction (4)) and did not lead to active surface species. In general, the concentration of active oxygen species was extremely small in relation to the total iron loading. The CO_2/Fe ratios are in the same order of magnitude as the N_2/Fe ratios in the step-down/step-up experiments, which were used to determine the concentration of active sites in steady state N_2O decomposition (cf. Section 1). We will show, however, that there is no simple correlation between the numbers obtained from the CO pulses and from the N_2O decomposition experiments at higher temperatures. The concentration of active oxygen species determined by the CO pulses is comparable to those reported in Ref. [23] for similar CVD catalysts. Samples with lower iron loadings, after pretreatment at even higher temperatures (up to 1323 K) reach much higher ratios of active oxygen per iron [47,48].

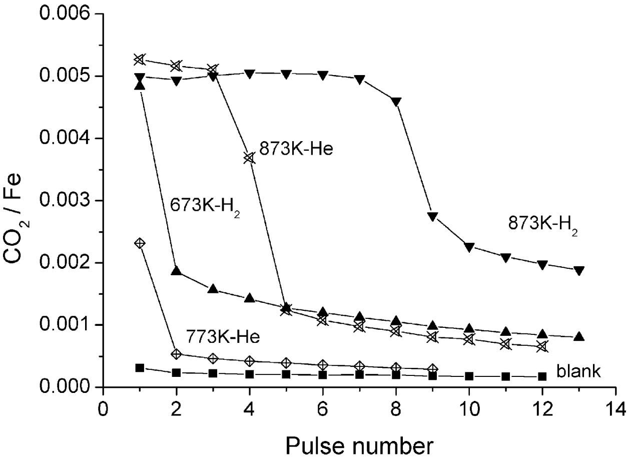


Fig. 9. Yield of CO_2 in pulses of CO at 523 K, after different pretreatments of Fe-ZSM-5 CVD and exposure to N_2O at 523 K.

The data in Table 1 show that two types of pretreatment lead to the generation of active oxygen species: (i) dehydroxylation in inert gas at high temperatures and (ii) reduction of the iron sites by H_2 or CO. The effect of dehydroxylation on the concentration of active oxygen species is similar to its effect on the transient activity. We can conclude that the two phenomena are related. An oxygen atom is deposited on a coordinatively unsaturated iron site and this surface oxygen atom has a high reactivity towards CO. The situation is different for the reduced samples. Here, the appearance of active oxygen species is decoupled from transient activity. What is the origin of the active oxygen species in the prereduced samples? Basically, prereduced Fe-ZSM-5 CVD reacts with N_2O according to Reaction (4). One molecule of N_2O oxidizes two (neighbored) Fe^{2+} ions to Fe^{3+} and the oxygen is incorporated into the oxide cluster as O^{2-}. An O^{2-} species is not different from the other oxygen atoms of the iron oxide cluster and should not have a high reactivity. Remember that calcined Fe-ZSM-5, without exposure to N_2O, hardly reacted with CO at 523 K. Yet, a small fraction of the deposited oxygen atoms is not incorporated into the oxide cluster as O^{2-}, but bound in a reactive form. As a tentative explanation, we propose that the structure of some iron clusters does not allow the deposition of N_2O according to Reaction (4). If there is, for example, an uneven number of iron atoms in the cluster or if sites are isolated N_2O reacts with a single iron atom according to:

$$Fe^{2+} + N_2O \rightarrow Fe^{3+}{-}O^{-} + N_2 \qquad (5)$$

and thereby, creates an active O^- species (see also Section 4).

3.6. Relation between active oxygen species and N_2O decomposition activity

We attempted to find a correlation between the concentration of active oxygen species measured in the CO titration experiments and the activity of the samples in N_2O decomposition, but had to come to the conclusion that a quantitative correlation between the two does not exist (see Table 1). The presence of active oxygen species is not a prerequisite for N_2O decomposition activity (see entries 2 and 3). If active oxygen species are found, their concentration does not directly translate into steady state activity. The reasons are manifold. N_2O decomposition is limited by the recombination rate of the surface oxygen atoms and we had seen that the mobility of the surface oxygen atoms plays a large role in the reaction. The mobility of the oxygen atoms may lead to a rearrangement of the structure of the iron oxide clusters at high temperatures. In the titration experiments at 523 K, however, the oxygen atoms are presumably static on the surface. Their reaction with CO has different criteria than their recombination to O_2 at higher temperatures [49].

The temperature effect can be (partly) eliminated by probing the concentration of active oxygen species after N_2O decomposition at 673 K. At 673 K, the deposited oxygen atoms are not stable on the catalyst surface and desorb as O_2. During the cooling of the catalyst in N_2O to 523 K, the desorbed oxygen species are restored by redeposition of oxygen atoms from N_2O. Pulsing CO then probes the active oxygen species on a surface that was equilibrated with N_2O at 673 K. Fig. 10 shows that such a surface contains less active oxygen species. This confirms our hypothesis that the structure of the catalytically active surface changes due to the high mobility of the oxygen species at high temperatures. We note in passing that even at 523 K, the catalyst surface is not entirely static. Active surface oxygen species, once titrated by CO, cannot be fully regenerated by a second treatment with N_2O.

3.7. The effect of steaming

It was confirmed by several authors that steaming is more efficient in generating a high concentration of active oxygen species than a simple high temperature treatment in air/inert gas/vacuum/H_2 [15,23,27]. There is convincing evidence that steaming generates extraframework iron–aluminum oxide clusters, which are the active sites in the hydroxylation of benzene (i.e. α-sites) [50]. Our results on steamed Fe-ZSM-5 CVD samples point into a similar direction. The step response in N_2O decomposition at 673 K of a steamed Fe-ZSM-5 catalyst is distinctly different from a non-steamed sample. The steamed catalyst shows transient activity even without pretreatment at high temperatures (see also Ref. [41]), i.e. there are highly reactive sites that do not need to be activated by dehydroxylation. Also, the pattern of the isotope distribution during the transient reaction is entirely different. NO adsorption on the catalyst shows an additional band at 1890 cm^{-1} that is not present in non-steamed materials. A more detailed description of the results is beyond the scope of this contribution, but we would like to leave you with the message that steaming creates an iron site that is qualitatively different from the active sites created by simple dehydroxylation at high temperatures.

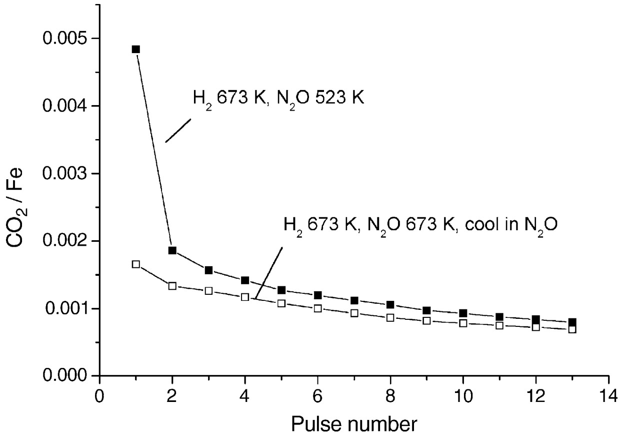


Fig. 10. Yield of CO_2 in pulses of CO at 523 K, after pretreatment of Fe-ZSM-5 CVD in H_2 at 673 K and reaction with N_2O at either 673 or 523 K.

3.8. The nature of the active oxygen species

The nature of the active oxygen species in the Fe-ZSM-5/N_2O system was first discussed in a review of Panov et al. [4]. By comparison with the reactivity of known surface oxygen species (O^-, $O_2{}^-$, etc.) the authors concluded that the reactivity of α-oxygen was most similar to that of the O^- radical anion. The question on which sites these active oxygen species are created is more difficult to answer. Especially on catalysts with very high iron loadings, only a small fraction of the iron sites is capable of generating active oxygen species. What distinguishes them from the other, inactive iron sites? As mentioned in the introduction, the first proposal was that α-oxygen species are generated on binuclear iron sites and it was believed that the stoichiometry O_α/Fe_α is 0.5. Later experiments showed, however, that one oxygen atom from N_2O is deposited per active Fe atom, i.e. $O_\alpha/Fe_\alpha = 1$ [27,47].

$$\begin{aligned}&Fe^{2+}-\mu-(OH)-Fe^{2+}+2N_2O\\&\quad\rightarrow O^- -Fe^{3+}-\mu-(OH)-Fe^{3+}-O^-\end{aligned}$$

That stoichiometry is unexpected for a binuclear iron cluster. Intuitively, one would expect that a binuclear iron cluster reacts with N_2O according to Reaction (4), i.e. upon formation of O^{2-}, which is a lot more stable than O^-. Our results described above show that on a reduced iron oxide cluster most of the N_2O molecules indeed react according to Reaction (4). If the deposited oxygen atom is bound as O^- instead of O^{2-}, there must be some special reason for that. Dehydroxylation, for example, may play a role. A strongly dehydroxylated binuclear iron cluster wants to fill its open coordination sites and may prefer to bind two oxygen atoms from N_2O as O^- than just one as O^{2-}. It is, however, difficult to understand why such a cluster would not react with O_2, as, for example, the enzyme methane monooxygenase, which is often compared with Fe-ZSM-5, does. The inertness towards O_2 is one of the typical features of α-sites. For our CVD catalysts, we observed that transient activity disappeared when the samples (after pretreatments at high temperature) were exposed to O_2 at 673 K before the step to N_2O. This indicates that binuclear (or larger) iron sites may be involved in the transient reaction, but they are different from α-sites because they are not inert towards O_2.

On an isolated Fe^{2+} site, the formation of O^- occurs naturally. Fe^{2+} can take up only one electron from N_2O and a Fe^{3+}–O^- species is formed (Reaction (5)). The species may also be written as $Fe^{IV} = O$. We, therefore, favor the notion that active oxygen species are formed on isolated Fe^{2+} sites. Also other authors recently considered the possibility that isolated iron sites contribute to the activity of Fe-ZSM-5 catalysts in benzene oxidation [48,51]. The model also naturally explains why their concentration of active sites is so small in Fe-ZSM-5 samples with high iron loadings. They contain very few isolated sites.

One should, however, consider the possibility that more than one type of iron sites leads to the creation of active oxygen species. The experiments described in the last sections show that the behavior of the samples after dehydroxylation, reduction or steaming (all of which generate active sites) is qualitatively different, i.e. different species may be involved. Last, but not least the role of the zeolite matrix should not be forgotten. To the best of our knowledge, it has not been possible to generate α-sites in a non-zeolitic matrix up to date. That proves that the zeolite pores must play a role in stabilizing the active sites [52].

4. Conclusions

Fe-ZSM-5 samples prepared by chemical vapor deposition were proposed to be model catalysts containing binuclear iron sites, with a structure similar to the active site in MMO. That picture is certainly oversimplified. Fe-ZSM-5 CVD contains a mixture of small iron oxide clusters whose size may be larger than two iron atoms. Only a very small fraction of the iron sites in the catalyst participates in N_2O decomposition. Highly active oxygen species, which resemble α-oxygen, are not found. Active oxygen species can, however, be created when the catalyst is pretreated at high temperatures (873 K) in inert gas. Under these conditions, Fe^{2+} sites are generates by autoreduction of the catalyst and these sites are strongly dehydroxylated. The coordinative unsaturation of these sites is responsible for their high reactivity. Reduction or steaming of the catalyst also increase the N_2O decomposition activity of the catalyst and generate active oxygen species when N_2O reacts with the catalyst at low temperatures. In both cases, the high activity is not related to dehydroxylation.

Due to the complexity of the system the question why some iron sites are highly active, while others are not is still not easy to answer. We favor the notion that the active iron sites are isolated Fe^{2+} ions, which react with N_2O upon formation of a Fe^{3+}–O^- species, whereas Fe^{2+} dimers incorporate the oxygen atom as an inactive O^{2-}. A firm proof for that hypothesis still has to come.

Appendix A. Kinetic model for N_2O decomposition

$$N_2O + * \xrightarrow{k_1} N_2 + *{-}O$$

$$*{-}O + Fe{-}O \xrightarrow{k_2} * + Fe{-}O_2$$

$$Fe{-}O_2 + *{-}O \xrightarrow{k_3} Fe{-}O + * + O_2$$

Steady state condition for the concentration of vacancies:

$$\frac{d[*{-}O]}{dt} = 0 \Rightarrow$$

$$k_1 \cdot p_{N_2O} \cdot [*] = k_2 \cdot [*{-}O] \cdot [Fe{-}O] + k_3 \cdot [*{-}O] \cdot [Fe{-}O_2]$$

$$\frac{d[Fe{-}O_2]}{dt} = 0 \Rightarrow$$

$$k_2 \cdot [*{-}O] \cdot [Fe{-}O] = k_3 \cdot [*{-}O] \cdot [Fe{-}O_2] \Rightarrow$$

$$[Fe{-}O_2] = \frac{k_2}{k_3} * [Fe{-}O] \Rightarrow$$

$$k_1 \cdot p_{N_2O} \cdot [*] = 2 \cdot k_2 \cdot [*{-}O] \cdot [Fe{-}O]$$

Balance over the number of sites:

$$n = [*] + [*{-}O] = [*] \cdot \left(1 + \frac{k_1 \cdot p_{N_2O}}{2k_2 \cdot [Fe{-}O]}\right)$$

Reaction rate:

$$r = k_3[*{-}O][Fe{-}O] = \frac{k_1}{2} p_{N_2O}[*] = \frac{k_1}{2} p_{N_2O} \frac{n}{1 + \frac{k_1 p_{N_2O}}{2k_2[Fe{-}O]}}$$

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