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The mechanism of N_2O decomposition on Fe-ZSM-5: an isotope labeling study

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The mechanism of N_2O decomposition over an ^{18}O-labeled Fe-ZSM-5 catalyst was studied. The isotope distribution of the O_2 produced during N_2O decomposition was statistical. This shows that O_2 was formed from a pool of equilibrated surface oxygen atoms. The size of the pool was 1.0 O/Fe, i.e. most or all of the iron clusters took part in the reaction. The reactivity of the oxygen atoms in the pool was low. They did not exchange with $^{18}O_2$ to a significant extent.

KEY WORDS: N_2O decomposition; iron zeolite; $^{18}O_2$; isotope exchange; α-oxygen; Fe-ZSM-5; sublimation.

1. Introduction

Iron-containing zeolites are very promising catalysts for N_2O abatement as well as for selective oxidation reactions using N_2O as oxidant. The mechanism of N_2O decomposition on iron-containing zeolites and the properties of the oxygen species involved in the reaction are, therefore, a topic of high interest. Already in the early days of research in the field it was realized that O_2 formation could run via two mechanisms, either the reaction of N_2O with surface oxygen (equation (2)), i.e. an Eley–Rideal mechanism, or the recombination of two surface oxygen atoms to form O_2 (equation (3)), i.e. a Langmuir–Hinshelwood mechanism [1,2].

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

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

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

In these equations * stands for an active (iron) site on the catalyst surface and *-O for an active oxygen atom bound to the catalyst surface. The nature of *-O is a very important issue. Panov and his coworkers suggested that only the oxygen atoms, which were deposited from N_2O on the catalyst surface via reaction (1) (called α-oxygen atoms), take part in the reaction [3]. The argument was based on the observation that N_2O decomposition activity of their catalysts correlated with the concentration of α-sites.

In a more conventional picture one can imagine that not only the surface oxygen atoms originating from N_2O, but all reactive oxygen atoms on the catalyst surface could take part in the reaction, in particular those bound to the small iron clusters in the zeolite pores. This model implies that there is a dynamic exchange of the oxygen-atoms already present on the surface and the oxygen atoms deposited from N_2O. Both enter into a pool of reactive oxygen atoms and cannot be distinguished from each other. The size of the pool of reactive oxygen atoms determines the catalytic activity.

The group of Hall was the first to use isotope exchange experiments in order to answer these mechanistic questions. N_2O decomposition was carried out over Fe-MOR and Fe–Y, which had been exchanged with $^{18}O_2$. In the initial phase of the decomposition reaction, hardly any ^{18}O from the surface was incorporated in the O_2 formed [1,4]. This suggests that only the oxygen atoms originating from N_2O were reactive. Later a second isotope exchange experiment was carried out: Fe-MOR was first reacted with $N_2{}^{16}O$, and then a switch to $N_2{}^{18}O$ was performed [5]. A long time after the switch to $N_2{}^{18}O$, a large amount of ^{16}O was still present in the O_2 product. On the other hand, hardly any $^{18}O_2$ was detected. This suggests that a large pool of reactive surface oxygen atoms had been created by the pretreatment with $N_2{}^{16}O$, which reacted with the freshly incoming $N_2{}^{18}O$. The size of the pool was estimated to be 0.85 O/Fe. Hence, most of the iron atoms in the zeolite took part in the reaction.

This contrasts with other investigations, which indicate that only a small fraction of the iron clusters in the zeolite pores are involved in the catalysis [6,7]. Nováková *et al.* [8] showed that the concentration of reactive oxygen atoms in Fe-FER is only 0.1 O/Fe at an ion-exchange level of 0.5 Fe/Al. Their studies were carried out at low temperatures, i.e. not under reaction conditions.

Not only the size of the active oxygen pool, but also the mechanism of O_2 formation is a point of controversy. Mul *et al.* [9] convincingly showed by pulse

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experiments that O_2 is formed by recombination of surface oxygen atoms, i.e. via reaction (3). Nobukawa *et al.* studied the mechanism of O_2-formation by isotope exchange experiments [10]. Fe-ZSM-5 was first exchanged with $^{18}O_2$ and then subjected to a pulse of N_2O. The isotope distribution in the product O_2 was in agreement with an Eley–Rideal mechanism, i.e. equations (2). Two factors may explain the contradictory results. First, the experiments of Mul *et al.* were carried out in a TAP reactor, i.e. under high vacuum. These conditions might provoke the fast desorption of reactive oxygen species *-O from the catalyst and, thereby, foreclose their reaction with N_2O via equation (2). Second, the catalysts used by the two research groups were prepared by different methods. It cannot be ruled out that they contain different types of iron species and, thus, decompose N_2O according to different reaction mechanisms.

This overview shows that a clear and complete picture of the mechanism of N_2O decomposition on iron-containing zeolites does not emerge from the data published up to date. We tried to address the open questions by combined $^{18}O_2$-isotope exchange/N_2O decomposition experiments at the light-off temperature of N_2O decomposition, i.e. 673 K. The object of the experiments was to determine the size of the pool of active oxygen atoms and the mechanism of O_2-formation. Fe-ZSM-5, prepared by sublimation of $FeCl_3$ [11] or by ion-exchange in the liquid phase, was used as a catalyst.

2. Experimental

Na-ZSM-5 (Zeochem, PZ 2-40, Si/Al = 20) was ion-exchanged three times with a 1 M-NH_4NO_3 solution and subsequently calcined in O_2 at 773 K, in order to convert it into H-ZSM-5. Sublimation of $FeCl_3$, washing and calcination were carried out according to the procedure described in Ref. [12]. The iron loading of the catalyst, called Fe-ZSM-5 CVD, was 4.5 wt%. A detailed characterization of the material was described before [13,14]. It was concluded that the main iron species are binuclear clusters and/or larger oligomers.

A second Fe-ZSM-5 catalyst was prepared by aqueous ion exchange of Na-ZSM-5 with $FeCl_2 \cdot 4H_2O$, under exclusion of air, followed by filtration, washing and calcination at 773 K in air. The iron loading of this sample, called Fe-ZSM-5 IEA, was 0.8 wt% (Fe/Al = 0.23). The UV–vis spectrum indicated that it contained mainly isolated iron ions.

Fifty milligrams of pelletized Fe-ZSM-5 (250–300 μm) were 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 1 h at 673 K, in order to remove adsorbed hydrocarbons. For the incorporation of ^{18}O, the catalyst was reduced in a mixture of 20% H_2 in He at 673 K for 1 h and subsequently reoxidized with $^{18}O_2$, also at 673 K. Previous investigations had shown that treatment in H_2 at 673 K leads to a complete reduction of Fe^{III} to Fe^{II} [12]. For the reoxidation a mixture of 1% $^{18}O_2$ (93% ^{18}O, Eurisotop) in He was used. Reoxidation was performed either by a series of pulses, which were administered via a 6-port valve in an interval of 2 min, or by a step from He to 1% $^{18}O_2$ in He. After that the reactor was flushed with He for 10 min and a step to 5000 ppm N_2O in He was performed. After following the reaction with N_2O for at least 45 min, the inlet stream was switched back to He and 2 min later a second series of 15 pulses of $^{18}O_2$ was administered, in an interval of 2 min.

For measuring the isotope exchange with $^{18}O_2$ during N_2O decomposition, Fe-ZSM-5 was pretreated in 10% non-labeled O_2 in He at 673 K and flushed with He for 10 min before performing a step to 5000 ppm N_2O in He. Once steady state was reached, the mixture of 1% $^{18}O_2$ in He was repeatedly pulsed into the N_2O flow, at an interval of 2 min.

The reaction products were analyzed using a quadrupole mass spectrometer (Balzers Omnistar). The masses $m/e = 4$, 18, 20, 28, 32, 34, 36, 44 and 46 were monitored (time resolution ~3 s). He ($m/e = 4$) was used as a reference in the calibration.

The flow rate over the reactor was always kept at 25 mL_{NPT}/min, corresponding to a GHSV = 20,000/h. The pressure in the reactor was atmospheric. The dead time of the system in step-response experiments was 33 s. The graphs shown hereafter are corrected for this dead time. All experiments were performed twice to check for reproducibility.

The degree of isotope exchange was monitored via the fraction of ^{18}O in the product O_2, $^{18}f = ([^{16}O^{18}O] + 2 * [^{18}O_2])/(2 * [O_{2,tot}])$. The value of the equilibrium constant of the isotope exchange reaction $^{16}O_2 + {}^{18}O_2 \rightleftharpoons 2^{16}O^{18}O$, $K_e = [^{16}O^{18}O]^2/([^{16}O_2] * [^{18}O_2])$, 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.

3. Results

3.1. Reoxidation of Fe-ZSM-5 CVD with $^{18}O_2$

In order to incorporate a large amount of ^{18}O into Fe-ZSM-5 CVD, the iron sites were reduced to Fe^{II} by treatment with H_2 and then reoxidized with $^{18}O_2$. Calibration showed that the amount of O_2 in one pulse was 0.16 μmol. The amount of iron in the catalyst bed was 40 μmol. Stoichiometrically a consumption of 0.5 O/Fe is expected for reoxidation of Fe^{II} to Fe^{III}: $2Fe^{II} + 0.5O_2 \rightarrow 2Fe^{III} + O^{2-}$. Hence, 64 pulses of $^{18}O_2$ should be required for reoxidation of the catalyst. In practice, a complete consumption of $^{18}O_2$ was observed during the first 37 pulses. This corresponds to an incorporation of 0.3 O/Fe. In the following pulses

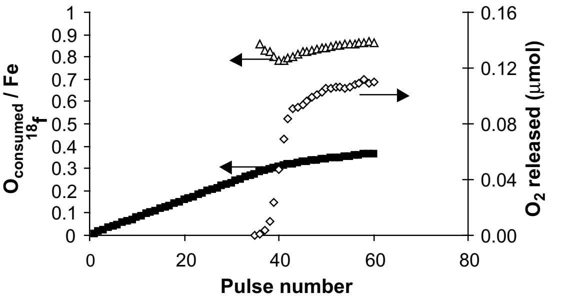

Figure 1. Reoxidation of reduced Fe-ZSM-5 CVD by a series of 60 pulses of $^{18}O_2$ at 673 K. Shown is the total amount of O consumed per Fe (full squares), the amount of O_2 in the reactor effluent (open diamonds) and the fraction of ^{18}O in the effluent O_2 (open triangles).

the amount of O_2 in the reactor effluent increased, first steeply, later gradually (figure 1). At the same time also a continuous desorption of $^{16}O_2$ from the catalyst set in, which stabilized at a value of 8 ppm. In the last pulse (nr. 60) 0.04 μmol O_2 were still consumed. In total 0.36 O/Fe were incorporated into the catalyst, i.e. reoxidation was not complete. The fraction of ^{18}O in the effluent O_2 first decreased and then gradually increased with pulse number. ^{18}f of the last pulse was 0.86, compared to 0.93 in the $^{18}O_2$ used. The total amount of ^{18}O incorporated into the catalyst was 0.34 ^{18}O/Fe. In the step to N_2O following the 60 pulses of $^{18}O_2$, an excess amount of 0.04 N_2/Fe was initially formed by the reaction $2Fe^{II} + N_2O \rightarrow 2Fe^{III} + N_2$ [12]. This confirmed that the reoxidation of the catalyst by $^{18}O_2$ had not been complete. The two numbers, i.e. 0.36 O/Fe from $^{18}O_2$ and 0.04 O/Fe from N_2O, did not add up to 0.5. We noticed, however, that the 0.2% H_2O contained in the $^{18}O_2$-mixture also contributed to reoxidation. The average oxidation state of the iron atoms after the pulses was, thus, underestimated by 10–20%.

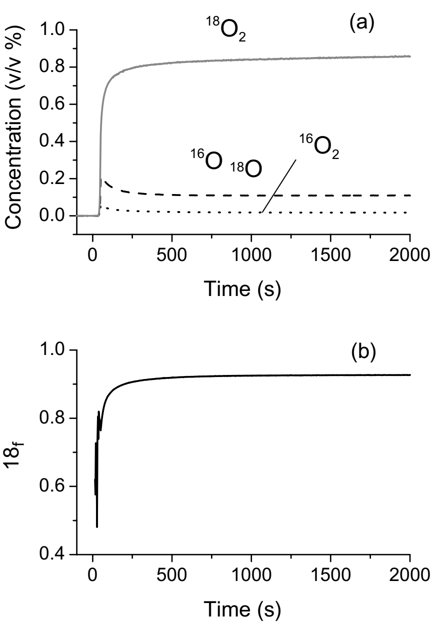

Figure 2. Step from He to 1% $^{18}O_2$ in He over Fe-ZSM-5 CVD, which was reduced in H_2 before. (a) Concentration of $^{18}O_2$ (solid), $^{16}O^{18}O$ (dashed) and $^{16}O_2$ (dotted). (b) Fraction of ^{18}O in the effluent O_2. Step and reduction performed at 673 K, GHSV = 20,000/h, 1 bar.

In order to ensure full reoxidation of the catalyst, the reduced Fe-ZSM-5 CVD was exposed to a continuous flow of $^{18}O_2$ in He for 3 h. Figure 2a shows the response to the step from He to 1% $^{18}O_2$ in He at 673 K. For approximately 35 s $^{18}O_2$ was completely consumed, corresponding to an incorporation of 0.35 O/Fe. Then the O_2-concentration increased steeply. Initial maxima were observed in the concentration of $^{16}O^{18}O$ and $^{16}O_2$. They gradually decreased, while $^{18}O_2$ gradually increased. With time on stream the isotope composition of effluent O_2 slowly approached the original composition of the $^{18}O_2$ used. Figure 2b shows that isotope exchange was extensive at the beginning, but decreased below detectability within 2000 s. By comparison with a blank experiment (step to 1% $^{18}O_2$ over an empty reactor), the amount of ^{18}O incorporated into the catalyst was calculated to be 1–1.5 ^{18}O/Fe. This value exceeds stoichiometry and must be overestimated, but we can safely state that a large amount of ^{18}O was incorporated into the catalyst. In the step to N_2O following the treatment in flowing $^{18}O_2$ only 0.003 N_2/Fe were formed by the reaction $2Fe^{II} + N_2O \rightarrow 2Fe^{III} + N_2$, i.e. the reoxidation of the catalyst by flowing $^{18}O_2$ was complete.

3.2. N_2O decomposition

Figure 3a shows the response of Fe-ZSM-5 CVD, which was reoxidized by 60 pulses of $^{18}O_2$, to a step from He to 5000 ppm N_2O in He. A large peak of N_2 was initially formed, due to the oxidation of remaining Fe^{II}-sites. Then steady-state N_2O-decomposition set in. A significant fraction of $^{16}O^{18}O$ and also a small concentration of $^{18}O_2$ (hardly visible in figure 3a) were found in the product O_2. ^{18}f had an initial value of 0.08 and slowly decreased with time (figure 3b). The isotope equilibrium constant K_e was between 3.5 and 4.0, i.e. close to the value expected for a statistical distribution of the isotopes. K_e stabilized at this value after 40 s and did not change with time on stream afterwards. The isotope fraction $^{18}f = [N_2{}^{18}O]/[N_2O_{tot}]$ in the effluent N_2O was 0.0025. Hardly any ^{18}O was incorporated into N_2O.

Similar results were obtained when the step to N_2O was performed over a catalyst, which had been reoxidized in flowing $^{18}O_2$. K_e was again between 3.5 and 4.0, but the fraction of labeled oxygen in the product O_2 was higher ($^{18}f_0 = 0.14$). The yield of N_2 and O_2 was lower than in the experiment shown in figure 3. It was reported before that the N_2O decomposition activity decreases with the initial degree of oxidation of the catalyst [12]. Table 1 shows an overview of the measured data.

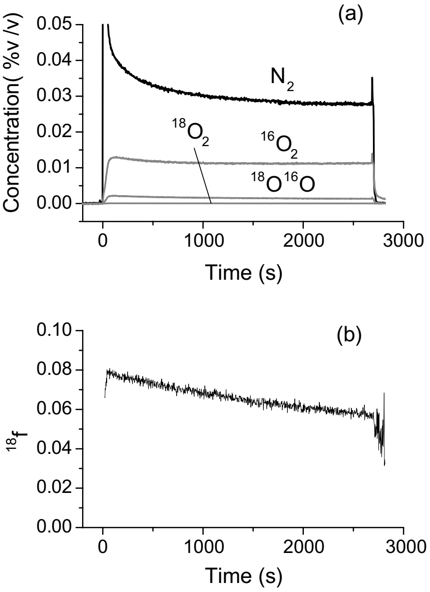

Figure 3. N_2O decomposition over Fe-ZSM-5 CVD, which was reoxidized by 60 pulses of $^{18}O_2$, at 673 K, GHSV = 20,000/h, 1 bar. The concentration of N_2O was 5000 ppm. (a) Concentration of N_2 and of the O_2-isotopes. (b) Fraction of ^{18}O in the O_2 product.

For comparison, we probed the response of a catalyst, which had been reoxidized in flowing $^{18}O_2$, to a step from He to 5000 ppm $^{16}O_2$ in He. Hardly any isotope exchange took place. An initial value of 0.006 was found for ^{18}f, which gradually decreased to $^{18}f = 0.002$, the natural abundance of ^{18}O. The total extent of isotope exchange was estimated to be no more than 0.002 O_{ex}/Fe.

The response of Fe-ZSM-5 IEA, which was reduced in H_2 and reoxidized in a flow of $^{18}O_2$, was qualitatively similar to that of Fe-ZSM-5 CVD. ^{18}f decreased from an initial value of 0.13–0.09 within 3000 s on stream. The isotope distribution in the O_2 product was, however, not statistical. K_e stabilized at a value of 2.5. The catalyst was also less active than Fe-ZSM-5 CVD. The steady-state conversion was 3.5 versus 5% for Fe-ZSM-5 CVD.

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

Several authors reported that iron-zeolites, which were treated with N_2O, readily undergo isotopic exchange with $^{18}O_2$. The oxygen atoms, which N_2O deposited on the catalyst surface, are responsible for the exchange activity. The isotope exchange with $^{18}O_2$ is therefore a good method to probe the concentration of the active surface oxygen atoms. We administered a series of $^{18}O_2$-pulses to the catalyst, 2 min after the step-down from 5000 ppm N_2O to pure He. In all pulses, ^{18}f was equal to 0.93, i.e. no measurable isotope exchange took place. In a separate experiment, pulses of $^{18}O_2$ were given during N_2O decomposition. Again, no measurable isotope exchange took place. Thus, the concentration of active surface oxygen atoms, which could catalyze isotope exchange with O_2, was practically zero at 673 K.

4. Discussion

Reduced Fe-ZSM-5 CVD reacted with 100% efficiency with $^{18}O_2$, until an incorporation of approximately 0.35 O/Fe was reached. After that the reoxidation of the remaining Fe^{II} sites became sluggish. Isotope exchange of $^{18}O_2$ with surface oxygen took place. The extent of exchange decreased with the pulse number (figure 1), i.e. with increasing average oxidation state of the iron catalyst. During the reoxidation with flowing $^{18}O_2$, isotope exchange was observed right after the step, but decreased to zero with time on stream (figure 2b). Vice versa, $^{16}O_2$ did not exchange with catalyst, which had been fully oxidized by $^{18}O_2$. Obviously O_2-isotope exchange required a certain concentration of oxygen vacancies. The fully oxidized Fe-ZSM-5 CVD could not activate O_2 at 673 K. The low exchange activity can be seen as an indication that the Fe-ZSM-5 CVD contained only a very small concentration of large Fe_2O_3 particles. Fe_2O_3 clusters are more active in the activation of O_2 at high temperatures than small iron oxide clusters or isolated iron ions [15].

Table 1
Reoxidation of reduced Fe-ZSM-5 CVD with $^{18}O_2$ and subsequent step to N_2O

No.	Reoxidation with $^{18}O_2$	O_{cons}/Fe^{a}	$^{18}O/Fe^{b}$	N_2/Fe^{c}	$^{18}f_0{}^{d}$	O_{pool}/Fe^{e}
1	45 pulses	0.32	0.30	0.04	0.09	0.86
2	60 pulses	0.36	0.34	0.03	0.08	1.07
3	Flow 3 h	1.0–1.5	1.0–1.5	0.003	0.15	1.02
4	Flow 3 h	1.0–1.5	1.0–1.5	0.004	0.14	0.98

[a] O consumed during reoxidation.
[b] ^{18}O consumed during the reoxidation.
[c] N_2 produced in the reoxidation of Fe^{II}, right after the step to N_2O.
[d] Initial ^{18}f-value during N_2O decomposition.
[e] Size of the oxygen pool, calculated between 500 and 2000 s time on stream.

During N_2O decomposition over Fe-ZSM-5 CVD, extensive exchange of the oxygen from N_2O with the catalyst surface took place. The isotope distribution in the O_2 produced during N_2O decomposition was statistical. Since O_2 was practically inert for isotope exchange, the equilibration of the isotopes during N_2O decomposition could not be caused by a fast secondary exchange of O_2 with the catalyst. The complete mixing of the isotopes in the O_2-product can therefore only be explained by assuming that the oxygen atoms on the catalyst surface readily exchanged with each other before their recombination and desorption as O_2. O_2 was, thus, formed from a pool of equilibrated oxygen atoms on the surface, similar to the model proposed by Valyon *et al.* [5]. The almost complete equilibration of the isotopes rules out an Eley–Rideal mechanism, i.e. the reaction of surface oxygen with N_2O from the gas phase (equation (2)), as claimed in Ref. [10].

The active sites in N_2O decomposition are those, which contribute to the filling of the active oxygen pool on the catalyst surface. The pool can be thought of as a stirred tank (the isotopes are completely mixed in the pool), which is emptied by O_2 desorption and replenished by deposition of oxygen atoms from N_2O. Since the incoming N_2O does not contain ^{18}O, the fraction of ^{18}O in the pool decreases with time. The size of the pool can be estimated from the rate of the decrease. The larger the pool, the slower ^{18}f will decrease. Mathematically the rate of decrease is

$$-\frac{\partial[^{18}O_{\text{surface}}]}{\partial t} = 2 \cdot {}^{18}f \cdot r_{\text{des}} \tag{4}$$

r_{des} is the rate of O_2 desorption in mol/s and can be calculated from the total O_2-concentration (sum over all isotopes) in the reactor effluent. It was nearly stable after ~100 s time on stream and is regarded as a constant here. The desorbing oxygen was equilibrated with the surface. Therefore, the isotope fraction of the product O_2 and of the surface pool are identical, i.e. $[^{18}O_{\text{surface}}] = n_{\text{pool}} * {}^{18}f$, where n_{pool} is the size of the oxygen pool in mol. The reaction rate is approximately constant in steady state; thus, equation (4) can be integrated to

$$n_{\text{pool}} = \frac{2r}{\ln\frac{^{18}f_0}{^{18}f}} \cdot t \tag{5}$$

Application of equation (5) led to pool sizes of O_{pool}/Fe ~ 1 (see table 1), i.e. close to the estimation of Valyon *et al.* [5]. The high ratio proves that all of the iron sites in the zeolite contribute to the generation of the pool and can, therefore, be regarded as active sites.

Since all iron sites are active in the reaction, every ^{18}O atom incorporated into the iron oxide clusters during reoxidation should appear in the pool. The ^{18}O atoms in the pool can be calculated from $n_{\text{pool}} * {}^{18}f_0$. These values were at least a factor of three lower than the number of ^{18}O atoms incorporated during reoxidation. This shows that a considerable exchange of lattice oxygen atoms with atoms from the iron cluster had taken place during the reoxidation, in agreement with the findings of Leglise *et al.* [4].

When O_2 was pulsed over Fe-ZSM-5 CVD during N_2O decomposition it did not undergo any isotope exchange. Although N_2O created a pool of mobile oxygen species on the catalyst, which readily exchanged with other oxygen atoms, these oxygen species were not able to activate O_2. Highly reactive α-oxygen, as discovered by the group of Panov [3,16,17] and confirmed by others [8,18], was, thus, not present under our conditions. Two factors can explain this: (i) α-oxygen is formed by depositing oxygen atoms from N_2O on the catalyst at temperatures around 523 K [19]. At these temperatures they remain adsorbed on the active sites. At 673 K the deposited oxygen atoms are not stable on the catalyst. (ii) The generation of α-sites seems to require high-temperature treatments in steam or inert gas [18,20]. Using the same catalyst as in the present investigation, Jia *et al.* [21] did not observe $^{18}O_2$-exchange activity unless Fe-ZSM-5 CVD was reduced at temperatures above 873 K.

A comparison of the behavior of Fe-ZSM-5 CVD and IEA gives information on the role that the size of iron oxide clusters plays in the reaction. On Fe-ZSM-5 CVD a complete equilibration of the oxygen isotopes was observed before their desorption as O_2, on Fe-ZSM-5 IEA the equilibration was only partial. Former material contained mainly small iron oxide clusters [14], while isolated iron sites dominated in the latter. This shows that larger iron clusters facilitate the exchange of oxygen atoms on the surface [22]. The higher mobility also leads to a faster recombination to O_2: Fe-ZSM-5 CVD was more active than Fe-ZSM-5 IEA.

5. Conclusions

The isotope labeling experiments suggest the following mechanism for N_2O decomposition on Fe-ZSM-5 prepared by sublimation of $FeCl_3$: oxygen atoms from N_2O are deposited on the catalyst surface (equation (1)). Since there was no isotope exchange within N_2O, this reaction is irreversible, i.e. N_2O adsorbs only dissociatively on the active sites. The deposited oxygen atoms exchange with the oxygen atoms of the iron oxide clusters and form a pool of mobile, active surface oxygen species, from which desorption of O_2 takes place by recombination. All the iron oxide clusters in the zeolite contribute to the generation of the oxygen pool and are, thus, active sites for N_2O decomposition. The oxygen atoms in the pool generated by N_2O are not highly active. No significant isotope exchange with $^{18}O_2$ was observed at 673 K. The high mobility of the surface oxygen atoms in Fe-ZSM-5 prepared by sublimation is a result of the formation of small iron oxide clusters in this sample. On Fe-ZSM-5 samples containing mainly isolated sites, the mobility of the surface oxygen atoms is lower and, as a result, also the rate of recombination to O_2 decreases.

Acknowledgments

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