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The interaction of N_2O with ZSM-5-type zeolites: A transient, multipulse investigation

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Abstract

The interaction of N_2O with MFI zeolites was investigated by a multipulse transient response method at 250 °C with subsequent temperature-programmed desorption. It was shown that the active sites for the formation of a surface oxygen species can be determined quantitatively using this method under the conditions of catalytic applications. Iron content and several pretreatment procedures influenced the formation of surface oxygen and molecular N_2O sorption. For example, fresh zeolites with high and low iron content formed significantly more surface oxygen than zeolites that had been pretreated in N_2O. The calcination at higher temperatures had an effect only on the activity of the zeolites with high iron content, which was not as pronounced as has been reported in the literature. The adsorption of molecular N_2O as an elementary step of N_2O activation in iron-containing zeolites cannot be neglected, because it was found to be thermally quite stable. All results indicate that in these zeolites not only one, but several oxygen species were formed that differ in thermal stability and thus in reactivity.

Keywords: Iron-containing MFI zeolites; Surface oxygen; Transient response method; Nitrous oxide decomposition; N_2O sorption

1. Introduction

Iron-containing zeolites of the ZSM-5 type play an important role as catalysts for the abatement of nitrous oxide in waste gases and partial oxidation with nitrous oxide as the oxidant. One important reason for the suitability of iron-containing zeolites for these applications is the formation of a monoatomic surface oxygen species [1–3] that has an extremely high reactivity for the oxidation of CO [1,4], H_2 [5], and different hydrocarbons including benzene and methane [3,6–8], even at room temperature. The catalytic properties of zeolites in these reactions relate to the amount and stability of this active surface oxygen species, called α-oxygen, which is formed at moderate temperatures (200–300 °C) [3]. Different iron species are considered corresponding active sites, and this question remains a matter of intense debate [9–16], but correlation between certain sites and the surface oxygen formation has not yet been found. In the abatement of N_2O, the formation of a monoatomic surface oxygen species is also the initial step of the catalytic cycle, and the corresponding sites in the zeolites are assumed to be similar to those for partial oxidation [2,10–12,17–20]. One method of preparing active zeolites for both applications is to incorporate iron into the framework of ZSM-5 during the synthesis (H–Fe-ZSM-5), followed by extraction of iron from the framework by high-temperature calcination and/or steaming [1–3,12,18]. As a second method, iron can be introduced into the zeolite by several ion exchange and impregnation procedures [5,9,10,17,19–21]. The amount of surface oxygen and its reactivity depend on the preparation and pretreatment of the zeolite.

Until now, the concentration of active surface oxygen has mostly been measured in a static vacuum setup, directly determined via the formation of nitrogen, by Panov

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and coworkers [1,9,22]. Indirectly, the reactive surface oxygen content was determined via isotope exchange with $^{18}O_2$. This method should also allow a distinction between reactive and nonreactive oxygen species formed after the activation of N_2O [1–3,22,23]. Recently, step experiments with N_2O and pulse experiments with $^{18}O_2$ as dynamic methods have been performed [18,24,25]. The step technique seems promising, because very low concentrations of surface oxygen can be determined quantitatively under atmospheric pressure conditions, which are valid for catalytic applications [18,24,26]. However, despite the application of sensitive, dynamic methods, formation and special characteristics of a surface oxygen species, like thermal stability and activity peculiarities, are not yet fully understood and are intensely debated. For example, results of Pirngruber [20], Jia et al. [23], Kiwi-Minsker et al. [24], and our preliminary results [27] indicated that various oxygen species with different properties ("surface oxygen pool") likely are formed during the interaction of N_2O with ZSM-5-type zeolites. Moreover, it has been recently found that iron-containing zeolites that have been prepared differently contain different iron species but show similar activity in stoichiometric N_2O decomposition. This indicates that the rates of each elementary step in the N_2O decomposition mechanism must be reconsidered [28].

In the present investigation, a transient multipulse technique combined with temperature-programmed desorption (TPD) studies was applied to determine the formation and the characteristics of the surface oxygen species on ZSM-5 zeolites. The first goal was to demonstrate the applicability and accuracy of the method as well as what kind of quantitative information can be derived with it. As a reference, ZSM-5 zeolite with a high iron content ("overexchanged"), which has been shown to be very active in N_2O decomposition and reduction [29,30], was chosen. The method has also been applied to the same zeolite without the extra addition of iron species, which is generally suitable for the partial oxidation of benzene [31]. Both zeolites were pretreated with different procedures; thus it was possible to determine the influence of some zeolite properties on the nature of the surface oxygen species that are valid for partial oxidation and N_2O abatement.

2. Experimental

2.1. Multipulse and desorption experiments

All transient-response studies were performed in an apparatus containing a quartz glass reactor (AutoChem 2910, Micromeritics). A quadruple mass spectrometer (QMS 422; Pfeiffer Vacuum) was used in an on-line mode to determine the composition of the gas phase. The intensity of the following signals was measured simultaneously: 4, 28, 32, and 44 m/e. Molar flows of N_2, O_2, and N_2O were determined from these signals. After zero gas measurements with pure helium, calibration was done using several gas mixtures of known compositions for N_2, O_2, and N_2O in helium before and after each experiment. To determine the correct molar flow of N_2 (F_{N_2}), the signal at 28 m/e was corrected by substracting the contribution of the N_2O fragment of the signal at 28 m/e in the calibration with the following equation:

$$F_{N_2} = \frac{I_{28} - \frac{f_{28,N_2O}}{f_{44,N_2O}} \cdot I_{44}}{f_{28,N_2}}, \tag{1}$$

where I_{28} and I_{44} is the intensity of the signal at 28 and 44 m/e, respectively, and f_{28,N_2O}, f_{28,N_2}, f_{44,N_2O} are the factors derived from the calibration with the gas mixtures.

Before all catalytic investigations, the zeolite samples were calcined in a flow of pure He at 500 °C to remove adsorbed components. After this pretreatment, the zeolites (mass = 0.05–0.5 g) were cooled to 250 °C in a helium flow of 50 ml/min (NTP). At this temperature, a certain number of pulses (50 or 100) were injected to a helium flow of 10 or 50 ml/min at normal conditions via a sample loop with a volume of 1 ml. The loop gas contains 1% (vol/vol) N_2O in helium. At a loop temperature of 110 °C, one pulse contains 0.31 µmol N_2O. After the pulse sequence, temperature was increased from 250 to 500 °C with a ramp of 10 °C/min to follow the desorption of the surface-bound species formed during the pulses.

Peak areas in the multipulse sequence were integrated using MatLab software. This program uses a trapezoidal numerical integration method that computes an approximation of the integral. The amount of deposited oxygen was calculated by summarizing all peak areas of nitrogen.

2.2. Zeolites

The initial ZSM-5-type zeolite was an NH_4 form (SM27, synthesized without an organic template; AlsiPenta GmbH) with a molar Si:Al ratio of 11.8, which contains iron in traces (Fe content = 0.035% (wt/wt); molar Fe:Al ratio = 0.007). Additional iron species were introduced via a solid-state ion exchange with $FeCl_2 \cdot 4H_2O$ (sample: Fe-MFI) to obtain a Fe:Al ratio of 0.75 (Fe content = 5.66% (wt/wt)). The detailed preparation procedure was described elsewhere [29,30]. The protonated zeolite form (sample: H-MFI) was obtained after calcination of the NH_4 form in an air flow for 2 h at 550 °C.

To investigate the influence of pretreatment conditions on the transient response behavior, zeolite samples were calcined in a flow of helium for 2 h at 900 °C (sample: Fe-MFI-HT and H-MFI-HT) or in a flow of 1% N_2O in a helium flow of 50 ml/min (NTP) for 2 h at 500 °C (sample: Fe-MFI-N_2O and H-MFI-N_2O).

2.3. Additional characterization

The chemical composition of the zeolite samples was determined by X-ray fluorescence (XRF) (Shimadzu 1700).

Table 1
Characterisation of the zeolite samples

Catalyst	Element composition[a]		Micropore volume[b]	Crystalline phases	Crystallinity Q_{Al}[c]	Si/Al framework[d]	N_2O sorption capacity[e]
	Si/Al (–)	Fe (wt%)	(cm^3/g)	(–)	(–)	(–)	(μmol/g)
Fe-MFI	11.8	5.66	120	ZSM-5 + hematite	0.80	n.d.	19.5
Fe-MFI-HT	11.8	5.66	111	ZSM-5 + hematite	0.69	n.d.	7.8
H-MFI	11.8	0.035	133	ZSM-5	0.81	13.0	4.1
H-MFI-HT	11.8	0.035	127	ZSM-5	0.70	39.5	2.0
Fe_2O_3/Na-MFI	11.8	5.66	–	–	–	13.0	31.0

[a] Determined with XRF.
[b] Calculated from the sorption isotherm of argon at 77 K with t-plot method, equivalent to the sorbed argon amount at $p/p_0 = 0.02$.
[c] Related to α-Al_2O_3 taken as 100% crystalline ($Q_{\mathrm{Al}} = 1$).
[d] Determined with ^{27}Al-NMR.
[e] Amount of adsorbed N_2O calculated from the step experiment at 50 °C.

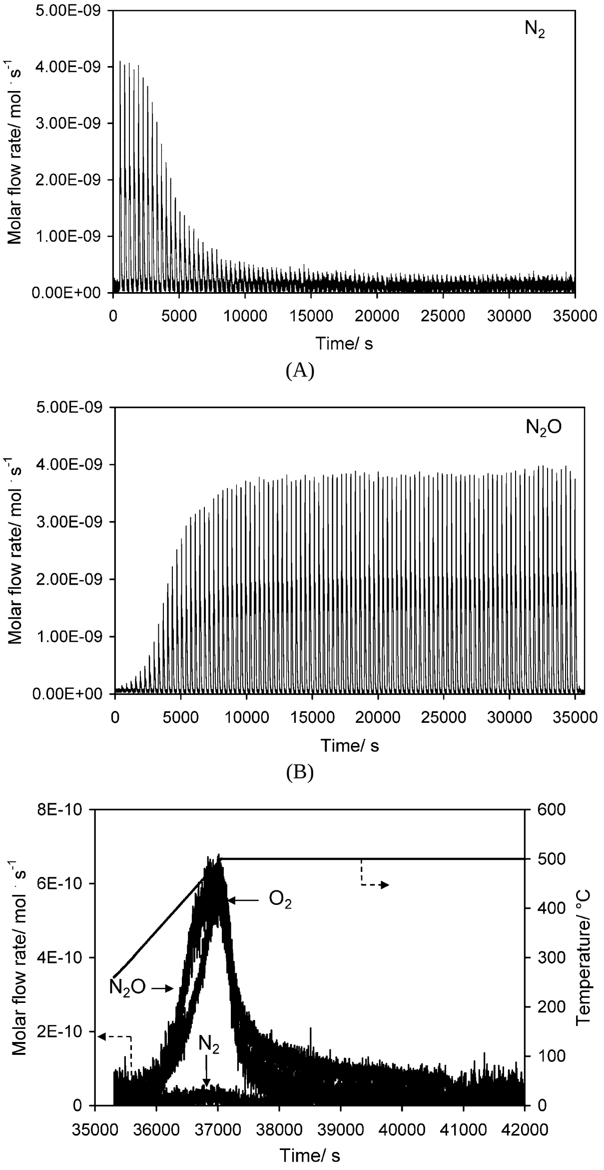
The influence of the calcination procedure on the zeolite's characteristics was studied by X-ray diffraction (XRD) (Cu-K_α radiation; Regaku F-DMAX IIIC), ^{27}Al MAS NMR spectroscopy (Bruker NMR type MSL-400; resonance frequency = 104.3 MHz, rotation speed = 10 kHz), sorption of argon at 77 K (ASAP 2000, Micromeritics), as well as temperature-programmed reduction (TPR) with hydrogen and TPD of ammonia (TPR-H_2, TPD-NH_3; AutoChem 2910, Micromeritics). In TPR-H_2, zeolites were heated from 50 to 900 °C in 5% (vol/vol) H_2 in helium at a ramp rate of 10 °C/min. The profiles were deconvoluted and fitted by Gaussian functions. In TPD-NH_3, zeolites were saturated with a flow of 10% (vol/vol) NH_3 in helium at 50 °C. Subsequently, NH_3 was desorbed in a helium flow of 25 ml/min up to a temperature of 600 °C (ramp rate 10 °C/min). The sorption capacity of N_2O at 50 °C was determined using a step technique. Therein, the flow of helium was switched to a helium flow containing 1% (vol/vol) N_2O and 1% (vol/vol) Ar as an inert standard at a certain time. The area between the N_2O and the Ar signal was integrated to determine the molar amount of adsorbed N_2O. The analysis of the gas stream in the temperature-programmed and step experiments was performed with mass spectroscopy (QMS 422; Pfeiffer Vacuum). Quantitative results are given in Table 1.

3. Results

3.1. Multipulse method: Explanation and validation

In the multipulse experiments, a sequence of definite molar N_2O amount (0.31 μmol N_2O) was injected to a continuous flow of inert gas at 250 °C. This temperature was chosen because it is commonly used as a standard condition in the literature to suppress the formation of molecular oxygen [3, 10,24].

Figs. 1A–1B displays the response behaviors during a sequence of 100 pulses over the Fe-MFI (mass = 0.1 g). It can be observed that in the beginning of the pulse sequence, N_2O is totally consumed and converted to N_2. With increasing pulse number, the consumption of N_2O and the formation of N_2 decreased. No molecular oxygen was formed, and thus



(C)

Fig. 1. Results of multi-pulse response experiments and temperature programmed desorption: (A) N_2 responses, (B) N_2O responses at 250 °C and (C) desorption of N_2O, N_2 and O_2 up to 500 °C (Fe-MFI, zeolite mass = 0.1 g, total flow 10 ml/min (NTP)).

Table 2
Quantitative results of the multi pulse respond method for Fe-MFI

Sample	Mass (g)	Flow (ml/min (NTP))	O/Cat (N_2)[a] (µmol/g)	O/Cat (O_2)[b] (µmol/g)	N_2O/Cat[c] (µmol/g)
Fresh (Fig. 1)	0.10	10	40.0	14.0	7.0
Fresh (Fig. 2)	0.05	50	42.0	12.0	10.0
Fresh (Fig. 2)	0.10	50	40.0	11.0	7.5
Fresh (Fig. 2)	0.20	50	41.0	13.0	7.5
Fresh (Fig. 3)	0.20	10	41.0	14.0	7.0
1. Repeat (Fig. 3)	0.20	10	17.1	17.2	1.0
2. Repeat (Fig. 3)	0.20	10	17.0	17.2	n.d.

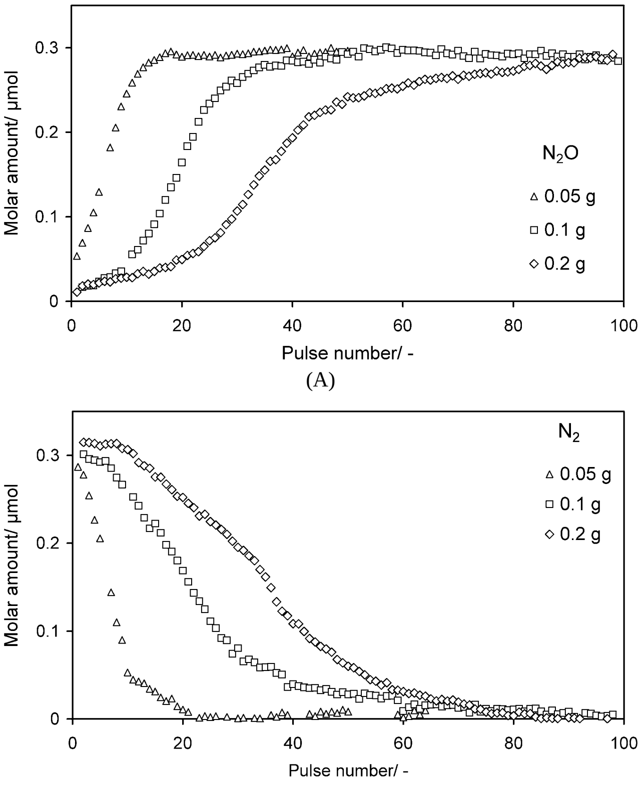
[a] Molar amount O/zeolite mass calculated via formed N_2 during pulse sequence.
[b] Molar amount O/zeolite mass calculated via desorbed O_2 after pulse sequence up to 500 °C.
[c] Molar amount adsorbed N_2O/zeolite mass calculated via desorbed N_2O after pulse sequence up to 500 °C.

the zeolite was stepwise-loaded with surface oxygen. The responses on each pulse in the multipulse sequence reflected increased oxygen loading of the zeolite reduced the rate of further surface oxygen formation. At the end of the pulse sequence, no more N_2 was formed, and the area of N_2O pulses reached a stable value.

After the pulse sequence, the temperature was increased to 500 °C (Fig. 1C). During this period, molecular oxygen desorbed from the catalyst sample because of the recombination of surface-bound oxygen species formed on the zeolite during the pulse sequence to molecular oxygen. In addition, molecular N_2O desorbed from the zeolite in the same temperature range as molecular oxygen.

Besides qualitative results, certain characteristic values can be quantitatively determined (Table 2). The amount of surface oxygen per zeolite mass, O/Cat, was calculated from the amount of formed nitrogen and revealed the oxygen storage capacity of the zeolite. The amount of desorbed oxygen and the temperature of the O_2 desorption maximum (∼495 °C) (Fig. 1C) indicates the stability and reactivity of the oxygen species. The quantitative results show that 40 µmol atomic oxygen per gram of catalyst (O/Cat) was formed, but only about 35% of the surface-bound oxygen was desorbed as O_2 up to temperature of 500 °C (first line of Table 2, $m_{\text{cat}} = 0.1$ g). The molar amount of desorbed N_2O, formed during the pulse sequence, N_2O/Cat, was 7 µmol N_2O/g.

To prove these findings and validate the method, different amounts of Fe-MFI were placed in the reactor. Fig. 2 plots the results as molar amounts of N_2O and N_2 as functions of pulse number. The molar amounts were determined by numerical integration of each pulse area using a MatLab trapezoidal numerical integration routine. It was observed that with increasing zeolite mass, the formed amount of nitrogen and the plateau of stable N_2O amount were reached with higher pulse numbers. Molecular oxygen was not found during any of the multipulse sequences. Table 2 shows that during each experiment, the same amounts of surface oxygen related to the zeolite mass were formed and the same amounts of O_2 and N_2O related to the zeolite mass were desorbed. The rate of the flow in which the pulses were injected has an influence on the trend of the multipulse sequence, but not on the quantitative values, O/Cat and N_2O/Cat (Table 2). Thus the multipulse technique is generally suitable for investigating the intrinsic formation of the surface-bound oxygen species. However, in each case only approximately 35% of the surface oxygen was recombined to molecular oxygen up to 500 °C, and a significant amount of N_2O was molecularly adsorbed in the zeolite, which is stable up to 500 °C.



(A)
(B)

Fig. 2. Influence of catalyst mass on the multi-pulse response behaviour: (A) N_2O, (B) N_2 (Fe-MFI, total flow 50 ml/min (NTP)).

The multipulse sequence was repeated several times to study the role of the surface oxygen, which seems to be stable up to 500 °C. Between each pulse sequence, the sample was heated to 500 °C in helium. Fig. 3 shows that more nitrogen was formed and more nitrous oxide consumed in the

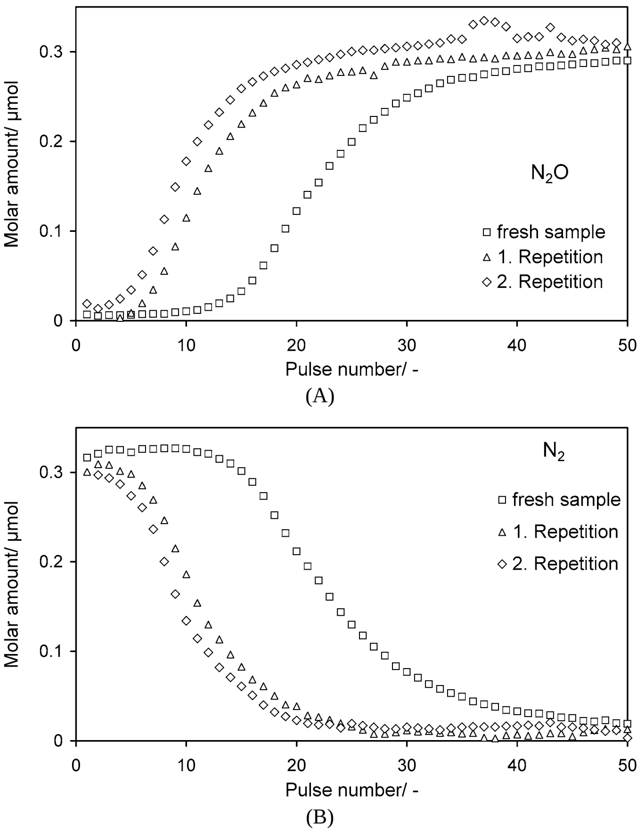


Fig. 3. Results of repeated multi-pulse experiments with intermediate treatment in Helium at 500 °C (Fe-MFI, $m = 0.2$ g, total flow 10 ml/min (NTP)): (A) N_2O, (B) N_2.

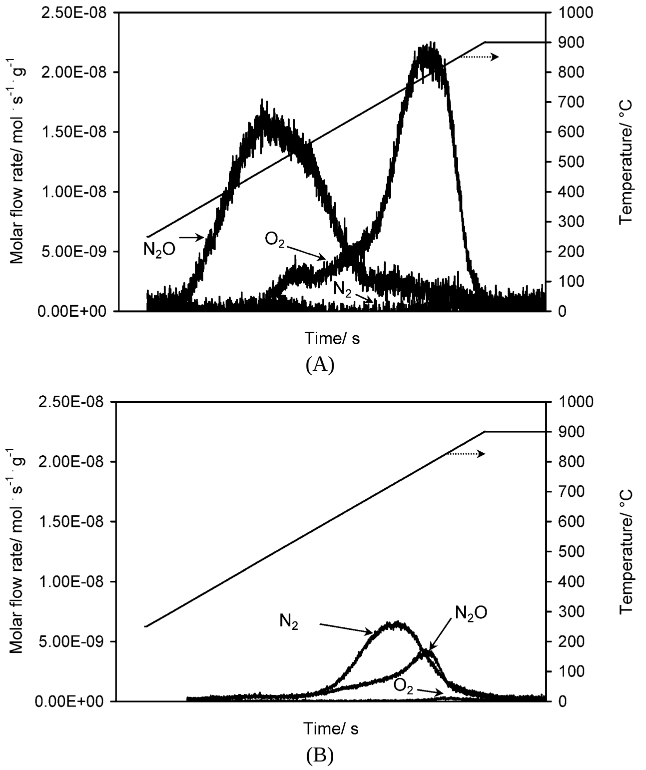


Fig. 4. Desorption of N_2O, O_2 and N_2 after the multi-pulse sequence up to 900 °C: (A) Fe-MFI, $m = 0.1$ g, (B) H-MFI, $m = 0.5$ g.

first pulse sequence than in the subsequent two sequences. After the second pulse sequence, the results did not change. The quantitative values in Table 2 confirm that the helium-pretreated zeolite was able to form and stabilize almost 2.5 times more surface oxygen than a zeolite that had already interacted with N_2O and was loaded with oxygen at 250 °C. This supports the finding that indeed the main part of the surface oxygen is stable at temperatures >500 °C. Because no molecular oxygen is formed during the repeated pulse sequences, oxygen was also not removed with additional gas phase N_2O at 250 °C. Nevertheless, the "oxidized zeolite" is still able to form surface oxygen that can be completely removed by heating in helium at 500 °C. This indicates that the surface-bound oxygen in the zeolite formed during interaction with N_2O comprised several species that differ in stability and reactivity. It was also remarkable that the desorption of N_2O during the temperature increase after the pulse sequence became smaller after the first repeated experiment and that no N_2O was desorbed after the second repetition up to 500 °C (Table 2).

The temperature limit of the desorption experiment after the pulse sequence was increased up to 900 °C to determine the stability of the formed surface oxygen. Fig. 4A clearly shows two temperature regions for the oxygen desorption, one at about 495 °C and the other at about 800 °C. Most of the oxygen was desorbed in the high-temperature region. A total amount of 56 µmol O/Cat can be calculated, which is more than that formed during the pulse sequence. Thus it must be assumed that a part of the desorbed oxygen originated from the zeolite and iron–oxo species. In addition, molecular N_2O also desorbed at higher temperatures, indicating a strong sorption of molecular N_2O. Blank experiments in which the samples were heated in helium and air showed that no carbon oxides were adsorbed or formed from total oxidation of any carbonaceous impurities in the zeolite.

3.2. Comparison of Fe-MFI and H-MFI

It is widely accepted that any kind of iron species in the zeolite is essential for the formation of the surface oxygen. For determining the role of the iron, the multipulse method was also applied to the protonated form of the zeolite (H-MFI), which contains iron only in traces (Table 1). Although measurable formation of N_2 during the pulse sequence was observed only at a higher zeolite mass for H-MFI, qualitative trends for N_2O and N_2 pulse area with increasing pulse number were similar to those of Fe-MFI. The quantitative values in Table 3 show that the amount of surface-bound oxygen per catalyst mass (O/Cat) of H-MFI is 15 times lower than that of Fe-MFI. In addition, at H-MFI, molecular N_2O, but not molecular oxygen, was desorbed up to a temperature of 500 °C. Increasing the temperature after the multipulse sequence up to 900 °C resulted in desorption of O_2, N_2, and N_2O (Fig. 4B). In contrast to Fe-MFI, the N_2

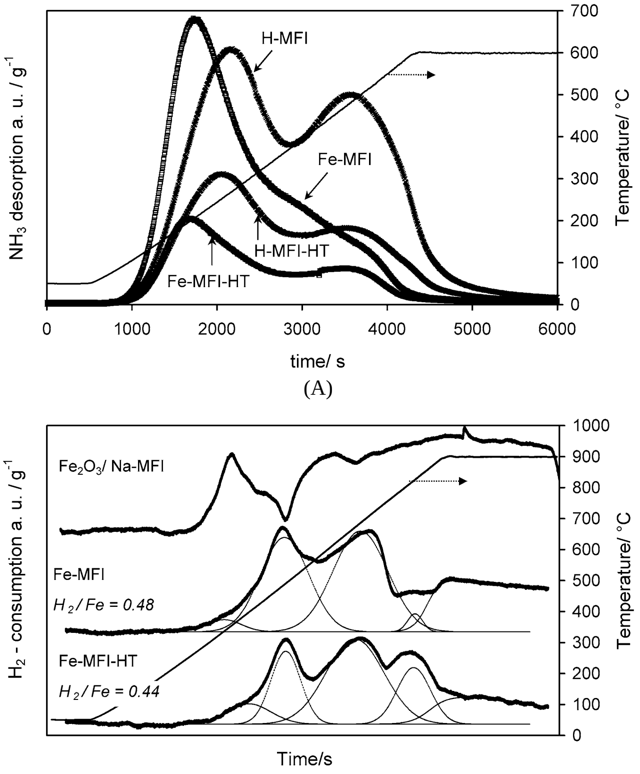
Table 3
Comparison of quantitative results of the multi pulse respond method for Fe-MFI and H-MFI

Catalyst	Calcination temperature (°C)	Calcination atmosphere (–)	Mass (g)	O/Cat (N_2)[a] (μmol/g)	O/Cat (O_2)[b] (μmol/g)	N_2O/Cat[c] (μmol/g)
Fe-MFI	500	Helium	0.1	40.0	14.0	7.0
H-MFI	500	Helium	0.5	2.8	n.d.	0.4
Fe-MFI-HT	900	Helium	0.1	46.0	10.0	n.d.
H-MFI-HT	900	Helium	0.5	2.6	n.d.	n.d.
Fe-MFI-N_2O	500	1% (vol/vol) N_2O/He	0.1	28.7	18.6	n.d.
H-MFI-N_2O	500	1% (vol/vol) N_2O/He	0.5	1	n.d.	n.d.

[a] Molar amount O/zeolite mass calculated via formed N_2 during pulse sequence.

[b] Molar amount O/zeolite mass calculated via desorbed O_2 after pulse sequence up to 500 °C.

[c] Molar amount adsorbed N_2O/zeolite mass calculated via desorbed N_2O after pulse sequence up to 500 °C.



(A)

(B)

Fig. 5. Characterisation of acid–base properties and redox-properties of the different zeolites: (A) temperature-programmed desorption of NH_3 (TPD-NH_3), (B) temperature-programmed reduction with H_2 (TPR-H_2).

formation indicated that a part of the adsorbed N_2O decomposed at H-MFI. Because this decomposition leads to only a small oxygen signal (0.7 O/Cat), it must be assumed that additional surface oxygen is formed. The other part of N_2O is more strongly bound to the zeolite than at Fe-MFI. However, a comparison of Figs. 4A and 4B clearly shows that the amounts of desorbed O_2 and N_2O are much lower than those on Fe-MFI.

The addition of iron species into the zeolite via solid-state exchange decreased the sorption capacity of NH_3, particularly in the high-temperature region between 330 °C and 600 °C (Fig. 5A), and the micropore volume (Table 1). These results show the presence of iron–oxo species inside the zeolite pores, which compensate charges of the zeolites as cations and are present as iron oxide clusters, partly detectable with XRD (Table 1). The results of the sorption experiments at 50 °C, in which no surface oxygen formation was observed, demonstrate that H-MFI adsorbed almost five times less N_2O than Fe-MFI (Table 1, last column). The redox properties of the iron species in Fe-MFI are characterized by the TPR profile in Fig. 5B. Two distinct peaks were detected with their maximums at approximately 490 and 685 °C. In addition, a shoulder in the H_2 consumption was visible at temperatures of 340 and 825 °C. Consequently, the profile was fitted with four Gaussian functions up to 900 °C (Fig. 5B). The total area of these functions led to a molar H_2 consumption per mol of iron of 0.48, which is close to the theoretical value of 0.5 necessary to reduce all iron(III) to iron(II). At the end of the temperature ramp at 900 °C, the baseline was not reached; thus further reduction of the iron–oxo species must be assumed. Comparing the TPR profile of Fe-MFI with that of a mechanical mixture of Fe_2O_3 and Na-MFI containing the same iron amount clearly shows that the shoulder at 340 °C and the corresponding peak must be attributed to the reduction of iron(III) to iron(II) in iron(III) oxides. The other peaks in Fe-MFI must be attributed to iron–oxo species, oxide clusters, or cations, which can be present only in the zeolite.

Surface oxygen formation clearly depends on the iron content in the zeolite. However, because the iron content of Fe-MFI is 100 times higher than of H-MFI (Table 1), not all iron species seem to be able to form surface oxygen. This fact is generally in concordance with results reported by other researchers. The presence of iron oxide in the zeolite mainly determined the sorption capacity of N_2O, because the mixture Fe_2O_3/Na-MFI adsorbed 1.5 times more N_2O than the Fe-MFI (Table 1). The relationship between the zeolite characteristics and surface oxygen formation, as well as the sorption of molecular N_2O is discussed later in this paper.

3.3. *Influence of zeolite pretreatment conditions on surface oxygen formation*

Several investigations have shown that the pretreatment of zeolite is important for its catalytic activity in waste gas applications and partial oxidations. For example, calcination of the zeolite at 700–1100 °C enhances its catalytic activity in several applications, but the reasons for this effect remain unclear. One possibility is that this pretreatment leads to the formation of additional sites for the surface oxygen formation [9–11,21,26,32]. Another is that the number of Brønsted acid sites is strongly decreased with this pretreatment [6,31,33]. Thus the goal was to determine whether such pretreatment has an influence on the amount and stability of surface-bound oxygen. Table 3 shows that calcination for 2 h in helium at 900 °C had a significant influence on surface oxygen formation for Fe-MFI, but not for H-MFI. Significantly more surface-bound oxygen was formed on Fe-MFI-HT, but the amount of oxygen desorbed up to 500 °C did not change after high-temperature calcination. For both Fe-MFI-HT and H-MFI-HT, no molecular N_2O desorbed up to 500 °C (Table 3) and 900 °C (not shown). In addition, the sorption capacity for N_2O at 50 °C was significantly reduced for both zeolites after helium pretreatment at 900 °C.

High-temperature calcination influenced the zeolite characteristics (Table 1). Although XRD patterns showed almost no change in crystallinity, the sorption capacity for argon and NH_3 (Fig. 5A) was significantly decreased, due to a loss of micropore volume (Table 1) and acidity for both zeolites. It was reported previously that a change in these characteristics indicates dealumination of the zeolites [31], which was quantified with ^{27}Al-NMR for H-MFI and is represented by the framework Si:Al ratio in Table 1. Because the amount of the surface-bound oxygen did not change for the H-MFI-HT compared with the H-MFI, acidity, micropore volume, and the presence of extra-framework aluminium had no affect on surface oxygen formation. The increased amount of surface-bound oxygen at Fe-MFI-HT compared with Fe-MFI results from a reorganization of the extra-framework iron species in the zeolite as shown in the TPR profiles (Fig. 5B). At Fe-MFI-HT, the total molar H_2 consumption per mol of iron was slightly reduced ($H_2/Fe \sim 0.44$) compared with Fe-MFI, and the area of the peaks at 490 and 685 °C was decreased. The maximum of the corresponding peak to fit the shoulder at low temperatures shifted from 340 to 400 °C, and the area increased. In addition, the peak at 825 °C increased. The relationship between the change in zeolite characteristics and surface oxygen formation, as well as N_2O sorption behavior, is discussed in the next section.

Both of the zeolites were also calcined in 1% (vol/vol) N_2O/helium at 500 °C before the pulse sequence. Fig. 6 shows that this pretreatment led to similar results as in the repeated multipulse experiment at 250 °C (Fig. 4, Table 3). On both zeolites, Fe-MFI-N_2O and H-MFI-N_2O, nitrogen formation and the N_2O consumption were lower than they would have been had the zeolites been pretreated in helium. Quantitative results reveal that the amount of surface-bound oxygen was reduced by almost 30% for Fe-MFI-N_2O and 65% for H-MFI-N_2O (Table 3). Similar to the findings of the repeated multipulse experiment of Fe-MFI (Section 3.1), helium-pretreated zeolites formed more surface oxygen than those previously exposed to N_2O. Thus, independent of the iron content, MFI zeolites were oxidized by N_2O and surface oxygen. At both of the N_2O-pretreated zeolites, desorption of N_2O during the temperature increase was suppressed, indicating that the “oxidized” zeolites lose the ability to adsorb molecular N_2O.

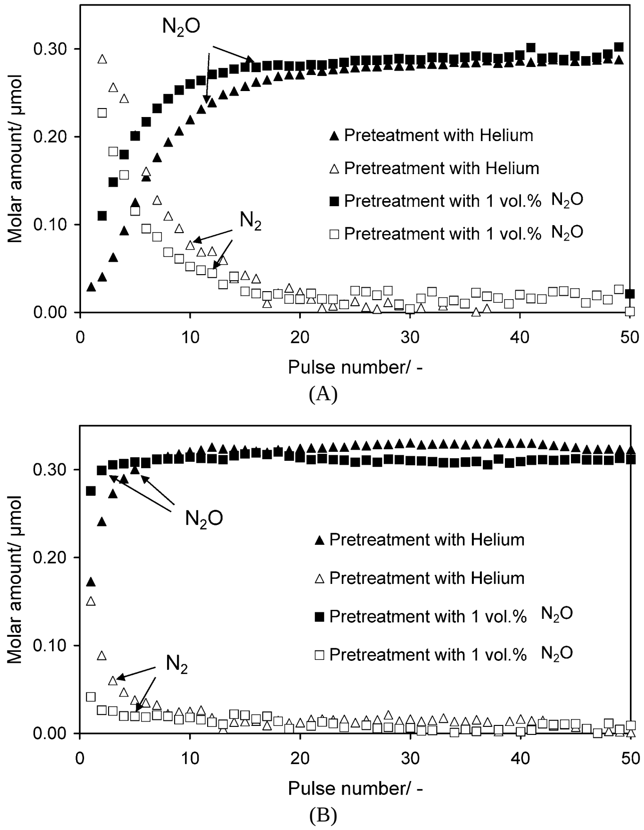


Fig. 6. Influence of N_2O pretreatment on the multi-pulse response behaviour (total flow 10 ml/min (NTP)): (A) Fe-MFI, $m = 0.1$ g; (B) H-MFI, $m = 0.5$ g.

4. Discussion

The multipulse technique is a sensitive tool for determining the activation of nitrous oxide. The method enables one to follow quantitatively the formation of a surface oxygen species for zeolites under conditions of catalytic applications, like partial oxidation and waste gas treatment, which is an advantage over the common static vacuum technique. The molar amount of the surface oxygen related to the zeolite mass (O/Cat) can be determined by summarizing the amount of nitrogen in each pulse response over the entire pulse sequence, because no molecular oxygen was formed. The accuracy for the determination of the molar amounts is ±5%. The nitrogen amount was not equal to the amount of consumed N_2O, particularly for the parent zeolites, Fe-MFI and H-MFI, contradicting the findings of Panov et al. using the static vacuum setup at the same temperature [4,5]. The present results confirmed the more recent findings of Kiwi-Minsker et al., who also found a discrepancy between consumed N_2O and formed N_2 using a transient step technique [24]. One reason for this must be the sorption of molecular nitrous oxide in the zeolite (Fig. 3, Table 2). This initial step of N_2O activation can be preferentially studied with the multipulse technique under atmospheric pressure, because N_2O should immediately desorb under vacuum conditions.

In contrast to the transient step techniques, the multipulse technique is more suitable for studying the formation of surface oxygen, because the gas phase concentration of N_2O is always very low. This property allows maximum suppression of the reaction of surface oxygen with gas phase N_2O, which is kinetically favored over the recombination of atomic oxygen to molecular oxygen [17,20].

The multipulse method has been validated by changing the zeolite mass and the flow rate. Because all quantitative results for the reference sample, Fe-MFI, were in the same range (Table 2), the influence of external mass transfer on the rate of surface oxygen formation can be excluded.

Concerning comparisons with results in the literature, one has to keep in mind that other zeolites are usually prepared in a different way, which has a significant impact on the active sites for N_2O activation and the behavior of surface oxygen [9,12,21,28]. The effect of preparation method can only be studied using many differently prepared zeolites, which has not yet been done. Table 4 presents important literature results for MFI zeolites with similar chemical compositions obtained with different methods. In part, the values for the surface oxygen amount related to the molar amount of iron have been calculated with data given in the corresponding references. These results are used as basis for the following discussion of the role of zeolite characteristics in surface oxygen formation from N_2O.

Table 4 shows that the quantitative results on surface oxygen loadings related to the iron amount are in the same range as those for other iron-containing zeolites. Regarding these results, first one must distinguish between two groups of iron-containing zeolites, one in which iron is introduced into the zeolites by postsynthetic methods using various ion-exchange or impregnation procedures, and the other in which iron is introduced in the synthesis mixture of the zeolite itself. Zeolites of the first group usually contain more iron than those of the second group. Second, literature results show that higher iron concentrations in the zeolite lead to higher surface oxygen loadings related to the catalyst mass, but the amount of surface oxygen related to the iron concentration generally increases with decreasing iron content. This effect must result from the fact that with increasing iron content, the relative part of nonactive iron increases. In the first group, nonactive iron is attributed to the formation of large iron oxide clusters; in the second group, nonactive iron may also be located in the zeolite framework. This was the case for the zeolites Fe MFI and H-MFI in the present study. In the Fe-MFI zeolite, a value of 0.039 mol oxygen per mol iron was determined (Table 3). This low value results from the large hematite clusters as iron oxide species, which were identified with XRD and are inactive for surface oxygen formation (Table 1). Nevertheless, the profiles of NH_3 TPD (Fig. 5A) show also a 40% reduction of Brønsted acid sites in the Fe-MFI compared with H-MFI [27]. This must be due to the presence of cationic iron species, which are assumed to be isolated cations [13,19] or binuclear cationic species [9,14,15,24]. The TPR profile of Fe-MFI in Fig. 5B displays typical behavior of an iron-containing zeolite [34–37]. Literature results for zeolites with similar iron content and Si:Al ratio [35–37] show that due to the high iron content, numerous different iron–oxo species are present in the zeolite, and discriminating between the reduction of iron oxides and iron cations is undoubtedly difficult. The comparison of TPR profiles (Fig. 5B) of Fe_2O_3/Na-MFI and Fe-MFI clearly indicates that the large iron oxide clusters in Fe-MFI, also visible on XRD, are reduced at 340 °C. Cationic species are reduced at temperatures >400 °C [19,36,37]. Thus peaks at 490 and 685 °C probably represent the reduction of cations and small iron oxide clusters, which are favored in surface oxygen formation. The small oxide clusters may be similar to the nanoclusters with the Fe_4O_4 structure proposed by Joyner and Stockenhuber. They can undergo autoreduction in helium and cannot be reduced with H_2 to metallic iron up to 1000 °C [16]. In the H-MFI, the value of 0.447 mol surface oxygen per mol iron is near the maximum values reported by other research groups (Table 4) and supports the general opinion that binuclear iron clusters play important roles in surface oxygen formation [9,14,15,24].

According to the literature, the pretreatment of the ZSM-5 zeolites at 700–1100 °C mostly leads to a distinct increase in surface oxygen formation during N_2O activation. It is assumed that this treatment forms special, active iron–oxo species [9,10,12,22,23]. After pretreatment of the zeolites, surface oxygen amount increased only at the iron-containing samples, Fe-MFI and Fe-MFI-HT, by approximately 10% (Tables 3 and 4). Any significant activation of the H-MFI due to extraction of iron from the zeolite framework, as was reported previously [9,10,22–24], cannot be confirmed. A possible explanation for this is that the iron species are already in an adequate extra-framework position for surface oxygen formation. A contribution of the Brønsted acid sites to the surface oxygen formation can also be excluded, because these sites were significantly reduced after the high-temperature treatment. The higher amount of formed surface oxygen at Fe-MFI-HT compared with Fe-MFI can be attributed to a partial reorganization of the iron species. Although the reflex for hematite in the XRD pattern remained unchanged, the relative reduction of Brønsted acid sites density, derived from the NH_3-TPD profiles, was stronger for Fe-MFI-HT than for H-MFI-HT. Thus it can be assumed that a part of the iron(III) oxide was transformed to charge compensating iron cations or extra-framework Fe–O–Al clusters, an assumption also recently proposed by Hensen et al. [10]. The change in TPR profiles shown in Fig. 5B, showing the formation of iron cations or extra-framework Fe–O–Al clusters from iron(III) oxides, displayed by a peak shift from 340 to 400 °C and an increased peak area, supports this

Table 4
Comparison of quantitative results obtained with different methods and zeolites from the literature with results of the present study

Initial iron position[a]	Si/Al	Fe (wt%)	Site/Fe (mol/mol)	Pretreatment: Temperature/atmosphere	Method for surface oxygen determination	Reference
PI	19.4	3.68	0.022	550 °C/air	Static vacuum	[10]
PI	19.4	3.68	0.040	700 °C/air	Static vacuum	
PI	19.4	3.68	0.015	550 °C/air	$^{18}O_2$ exchange	[10]
PI	19.4	3.68	0.038	700 °C/air	$^{18}O_2$ exchange	
PI	20	4.5	1	400 °C/O_2–He	$^{18}O_2$ exchange	[25]
PI	23	4	0	500 °C/H_2	Static vacuum	[23]
PI	23	4	0.278	700 °C/H_2	Static vacuum	
PI	23	4	0	500 °C/H_2	$^{18}O_2$ exchange	[23]
PI	23	4	0.070	700 °C/H_2	$^{18}O_2$ exchange	
PI	45	0.14	0.013	550 °C/air	Static vacuum	[9]
PI	45	0.14	0.080	900 °C/air	Static vacuum	
PI	80	0.38	0.110	500 °C/air–He	Transient step	[18]
PI	11.8	5.66	0.039	500 °C/He	Multipulse	This work
PI	11.8	5.66	0.045	900 °C/He	Multipulse	This work
PI	11.8	5.66	0.028	500 °C/N_2O	Multipulse	This work
FW	21	0.31	0.111	550 °C/air	Static vacuum	[9]
FW	21	0.31	0.111	900 °C/air	Static vacuum	
FW	25	0.1	0.045	550 °C/He	Transient step	[24]
FW	25	0.10	0.195	1050 °C/He	Transient step	
FW	50	0.004	0	600 °C/air	Static vacuum	[1]
FW	50	0.080	0.047	600 °C/air	Static vacuum	
FW	50	0.50	0.061	600 °C/air	Static vacuum	
FW	52.2	0.38	0.127	550 °C/air	Static vacuum	[22]
FW	52.2	0.38	0.439	900 °C/air	Static vacuum	
FW	11.8	0.035	0.447	550 °C/air–He	Multipulse	This work
FW	11.8	0.035	0.415	900 °C/He	Multipulse	This work
FW	11.8	0.035	0.160	550 °C/N_2O	Multipulse	This work

[a] PI: postsynthetic iron introduction (ion exchange, impregnation); FW: initially, iron in framework position (addition to synthesis mixture of the zeolite).

concept. According to previous reports [35–37], binuclear iron(III)–oxo cations are reduced by H_2 at approximately 400 °C. Our previous XPS measurements with similar zeolites [32] support and extend this theory. Therein, it was found that iron oxide species formed at the outer zeolite surface migrated into the zeolite channels and transformed to cationic iron species, which are active in benzene hydroxylation with N_2O. Consequently, on the one hand, the greater surface oxygen formation for Fe-MFI-HT must be due to the formation of iron–oxo cations after pretreatment in helium at 900 °C. On the other hand, these species and the small iron oxide clusters are probably autoreduced, as indicated by the decreased hydrogen consumption per mol of iron (Fig. 5B). Based on previous results [16,19,24,25], this phenomenon also enhances surface oxygen formation.

Nonetheless, surface oxygen formation on the studied zeolites did generally not show this sensitivity on the activation procedure as is reported in literature (Table 4). Therefore, the effect of the activation procedure on surface oxygen formation depends strongly on the parent zeolites [21].

In the temperature ramp after the pulse sequence, molecular oxygen was formed and nitrous oxide was desorbed at the zeolites, which were pretreated at 500 °C in helium. Only a small part of the molecular oxygen desorbed at temperatures <500 °C. Thus the high activity of the Fe-MFI in the stationary decomposition of N_2O [29,30] must be due to the high rate of the reaction of gas phase N_2O with surface oxygen. In other words, this means that the rate of recombination of surface oxygen to O_2 plays a minor role in stationary N_2O abatement on the zeolite, as has been suggested previously [17,19].

The high thermal stability of the surface oxygen at the studied zeolite contradicts several results reported in the literature. Commonly, O_2 desorbed in a temperature range of 300–400 °C [10,18,24]. Indirectly, the quantitative values of Kiwi-Minsker et al. also support the present result, because only ~60% of the oxygen desorbed up to 500 °C, which was formed after the activation of N_2O [24]. In the present case, it was only 30–35%. For the Fe-MFI, high-temperature desorption of the main part of oxygen up to 900 °C clearly indicates the presence of another, very stable oxygen species, which confirms the TPD-O_2 results of Yoshida et al. These authors also assumed a low- and high-temperature-stable oxygen species [38]. Repetition of the N_2O multipulse sequence with intermediate treatment in helium flow at 500 °C and pretreatment of the zeolites with N_2O supports the formation of this thermally stable surface oxygen. This oxygen is likely used for the oxidation of cationic iron(II) species or small iron oxide clusters with a mixed oxidation state, like Fe_3O_4, formed during helium pretreatment, as has been suggested previously [24]. “Oxidation” of the zeolites did not totally prevent N_2O activation; it only significantly reduced the activity of surface oxygen formation. The “oxidized” zeolites can form almost the same amount of oxygen from the N_2O activation as is desorbed up to 500 °C (Table 2).

The fact that at Fe-MFI, slightly more surface oxygen desorbed up to 900 °C than was formed during N_2O activation in the multipulse sequence can be explained similarly. Before the multipulse sequence, the zeolites were treated in helium only at 500 °C. During the subsequent TPD up to 900 °C, additional iron–oxo species were autoreduced in helium at temperatures >500 °C [16,19,25]. This led to a release of thermally stable oxygen, which was initially present in the zeolite. Such a phenomenon could explain the discrepancy between formed surface oxygen and desorbed O_2 reported by Hensen et al. [10].

At H-MFI, the formation of molecular oxygen at higher temperatures must be attributed to the decomposition of adsorbed N_2O. Moreover, the lack of oxygen balance indicated a thermally activated deposition of oxygen in the zeolite, which has not yet been reported and requires further validation.

The role of the N_2O sorption in the catalytic activity of ZSM-5 zeolites cannot be neglected. This has been investigated in detail by Wood et al. [19] and Waclaw et al. [21], who found different sorption complexes of N_2O with iron cations and Brønsted acid sites in ZSM-5 zeolites, similar to those of the present study, by means of Fourier transform infrared (FTIR) spectroscopy. Nonetheless, such strong sorption of N_2O has not been reported to date. A falsification of the signal at 44 m/e with CO_2, resulting from oxidation of any hydrocarbons [19], can be excluded. It has been proven that the interaction of CO_2 with the zeolites is very weak as a result of TPD up to 500 °C after multipulse experiments with 1% (vol/vol) of both CO and CO_2 in He at 250 °C [27]. The location of the N_2O sorption of the zeolites cannot be specified in detail, as previously in [21]. A comparison of Fe-MFI and H-MFI (Fig. 4) indicates that Brønsted acid sites and iron–oxo species provide sites for the sorption of molecular N_2O. But because the amount of desorbed N_2O was significantly greater in Fe-MFI than in H-MFI, iron oxide species are mainly responsible for the N_2O sorption. The measurements of sorption capacity at 50 °C (Table 1) for all zeolites and the mixture of $Fe_2O_3/\text{Na-MFI}$ gave a clear proof of the validity of this concept. This conclusion is also in concordance with results of Duma and Hönicke [39], who found that molecular N_2O was adsorbed on highly dispersed silica-supported iron oxide and desorbed in a temperature range similar to that in the present study.

After pretreatment of the zeolites at 900 °C in helium, no molecular N_2O desorbed from Fe-MFI-HT or H-MFI-HT (Table 3), and the sorption capacity of N_2O at 50 °C was significantly reduced at both of the zeolites (Table 1). Therefore, dehydroxylation and dealumination of the zeolites, and the aforementioned transformation of iron oxide to cationic iron species under these conditions, must be the reason for the decreased sorption capacity. Moreover, if the zeolites were pretreated with N_2O, either by repeating the multipulse sequence (Fig. 3) or at 500 °C (Fig. 6), then the sorption capacity of molecular N_2O decreased (Table 3). Wood et al. [19] found a similar behavior using FTIR spectroscopy. They assumed that the oxidation of Fe(II) to Fe(III) species with N_2O was responsible for the reduced sorption capacity. This phenomenon remains unclear and awaits further validation.

All results support the idea of a surface oxygen pool containing several species located at various sites with different stabilities [23–25,27]. Jia et al. [23] and Hensen et al. [10] reported a discrepancy between the amount of surface oxygen that is formed from N_2O and can be exchanged with ^{18}O (Table 4). Our own preliminary studies [27] and those of Kiwi-Minsker et al. [24] demonstrate this discrepancy in CO oxidation. Thus, in contrast to the findings of Panov’s group [1,3–5,9,22], the formation of surface oxygen after N_2O activation must be distinguished from an active oxygen species important for partial oxidation and N_2O abatement.

5. Conclusions

1. The multipulse method offers a detailed, quantitative method for studying the interaction of N_2O, sorption, and surface oxygen formation with MFI zeolites as a function of the oxygen-loading status.
2. For H-MFI zeolites, where iron is introduced in the zeolite synthesis mixture, a special activation procedure does not necessarily influence surface oxygen formation. In Fe-MFI zeolites, where iron is introduced by postsynthetic methods like ion exchange and impregnation, several iron species influence surface oxygen formation and can be affected by the pretreatment procedure. In the present example of solid-state “overexchanged” zeolites, iron oxide species can be transformed to cationic iron species by high-temperature calcination, which enhances surface oxygen formation.
3. Helium-pretreated zeolites can form significantly more surface oxygen and adsorb significant more N_2O than zeolites pretreated in N_2O, at both high and low temperatures. Thus proposed correlations of surface oxygen content with the zeolites’ catalytic activity in any application must be verified according to the determination method.

4. Sorption of molecular N_2O proceeds on iron oxide species and Brønsted acid protons. In particular, the presence of the oxides increases the sorption capacity. Several adsorbed N_2O species exist that can be very thermally stable. The sorption capacity of N_2O and the stability of adsorbed N_2O depend on pretreatment conditions and may have a significant impact on zeolite-catalyzed oxidation reactions with N_2O.
5. The desorption results of surface oxygen showed that only a minor part of the surface oxygen can be desorbed with increasing temperature up to 500 °C. Most of the oxygen adsorbs strongly to the zeolite surface. These results imply the existence of different oxygen species formed by N_2O activation that vary in stability and reactivity. Supported by other investigations, the assumption of one active surface oxygen as the key species in catalytic application must be reconsidered.

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