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Experimental techniques for investigating the surface oxygen formation in the N_2O decomposition on Fe-MFI zeolites

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Abstract

Several experimental techniques were used to investigate the formation of surface oxygen in the N_2O decomposition on an Fe-MFI zeolite. These techniques consisted of multipulse and step experiments as transient methods at ambient pressure and experiments in a closed set-up of Panov and co-workers at strongly reduced pressure. The total amount of surface oxygen determined through multipulse experiments was in the range of the amount obtained in the vacuum set-up at 523 K (40–50 μmol O $g_{catalyst}^{-1}$). In contrast, the step technique revealed considerably higher values, up to 110 μmol O $g_{catalyst}^{-1}$, indicating an accumulation of oxygen in the zeolite. This phenomenon might also be responsible for the observation that higher reaction temperatures increase the total amount of surface oxygen, which can be deposited in the zeolite. In contrast to experiments in the vacuum set-up, the temperature-programmed desorption after multipulse and step experiments shows the presence of various oxygen species differing in thermal stability. The influence of temperature on the rate of surface oxygen formation was determined from step and vacuum experiments. The results of the step experiments lead to a lower activation energy, 14 kJ mol^{-1}, than the experiments in the vacuum set-up (49 kJ mol^{-1}), probably due to sorption and mass transfer effects. Comparing the rate of surface oxygen formation and of total N_2O decomposition reveals that the former is very fast and not rate determining for the latter. Furthermore, the rate of total N_2O decomposition seems to be inhibited by adsorbed N_2O, detected in the transient experiments. This observation is considered in an adequate kinetic model.

Keywords: Nitrous oxide; Partial oxidation; α-Oxygen; Zeolite; Fe-ZSM5; Kinetics; Transient experiment; Multipulse; Step technique

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1. Introduction

Classical steady state experiments give information on global kinetics of reactions, but they do not provide information on the elementary steps of a reaction and the surface species involved. Transient kinetic methods are believed to be a distinctive step forwards for modelling of catalytic reaction pathways and a powerful tool to study changes in the surface distribution and their effect on chemical rates [1].

Redox reactions with nitrous oxide are important examples where transient techniques can give a further insight into the proceeding of a reaction. Important elementary steps of the mechanism can be detected using different catalysts. Iron containing zeolites of MFI type are particularly interesting catalysts for these reactions because they have been successfully applied in the abatement of N_2O in waste gases as well as in partial oxidations of hydrocarbons with N_2O [2–8].

In the N_2O decomposition the following steps are generally accepted:

$$Z + N_2O \rightarrow N_2 + Z\text{–}O \tag{1}$$

$$2Z\text{–}O \rightarrow O_2 + 2Z \tag{2}$$

$$Z\text{–}O + N_2O \rightarrow N_2 + O_2 + Z \tag{3}$$

Many investigations in the literature particularly focus on the first reaction (Eq. (1)), where an atomic, surface bound oxygen species is formed during the interaction of N_2O with active iron sites in the zeolite Z [9–25]. This step initiates not only the stoichiometric N_2O decomposition to nitrogen and oxygen, but also provides a selective oxygen species called “α-oxygen” by Panov and co-workers [3,4,9–12]. This oxygen species was found to be very reactive in the oxidation of H_2, CO, methane and benzene, even at room temperature, and very selective in the hydroxylation of aromatics [3–6] and the oxidative dehydrogenation of propane [7,8]. This is schematically shown in Eq. (4), where HC

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stands for hydrocarbons and HCO for the product of oxidation:

$$Z\text{–}O + HC \rightarrow HCO + Z \qquad (4)$$

The equal nature of surface oxygen species for partial oxidation and decomposition reactions is still intensively debated.

The most prominent method to study the formation and reactivity of surface oxygen was developed by Panov and coworkers [3,9–12]. They quantify the amount of surface oxygen in a closed, static vacuum set-up through N_2O decomposition in a temperature-programmed or an isothermal experiment at low temperatures ($\leq$523 K). Subsequently, the exchange rate of surface oxygen with $^{18}O_2$ isotopes is determined. Results obtained with MFI zeolites containing different iron amounts indicate that the surface oxygen is stable up to 573 K, but that it can be completely exchanged with $^{18}O_2$ already at room temperature. Kinetic studies revealed that the activation energy is about 42 kJ mol^{-1} for the surface oxygen formation [3,9]. Another sort of experiments was performed in the temporal analysis of products (TAP) reactor as an open flow system under strongly reduced pressure, in steady state and transient, pulse mode [8,14,15,26]. Interestingly, Perez-Ramirez et al. found that increasing reaction temperature from 523 to 573 K resulted in an increase of the surface oxygen amount and that a major part of iron in the zeolite was not capable for activating N_2O molecules under conditions in the TAP reactor [8,26]. TAP investigations have also shown at temperatures higher than 573 K that the O_2 formation is time-delayed as compared to the N_2 formation [8,14,15]. It supports the idea that the formation of molecular oxygen is rate determining for the N_2O decomposition. However, it is still under debate which elementary step determines the rate of O_2 formation. The recombination of surface oxygen via Eq. (2) has been favoured for a long time [8,14,15,19] in agreement with findings in a fixed bed reactor under steady state conditions [15]. However, recent studies have shown that also the O_2 desorption can determine the rate of total N_2O decomposition [26,27], in concordance with DFT-model calculations [28]. Finally, the reaction of N_2O with surface oxygen (Eq. (3)) is also still a candidate, according to results in Refs. [24,25,29–32].

The methods described adopted operating conditions such as strongly reduced pressure with very low N_2O concentrations. It is generally questionable if these results can be used for kinetic and mechanistic interpretations of results obtained under technically relevant conditions slightly above ambient pressure. Therefore, several transient response techniques have also been applied under atmospheric pressure [16–25], sometimes combined with subsequent temperature-programmed desorption of the surface bound species as well as with isotopic labelling experiments [21,22]. Step experiments with N_2O were carried out at temperatures lower than 573 K to exclusively study the surface oxygen formation on ZSM5 zeolites with low iron contents ($\leq$1000 ppm Fe, w/w [16–18] and 0.38% Fe, w/w [19]). The same experiments were also performed at 673 K, above the light-off temperature of the total N_2O decomposition, with zeolites containing high iron amounts (3.5–4.5% Fe, w/w) [20–23]. In addition, Wood et al. [19] have shown that step experiments are suitable to determine the kinetics of the surface oxygen formation. Recently, we proposed a multipulse method under ambient pressure combined with temperature-programmed desorption, suitable for a quantitative tracking of the surface oxygen formation [24,25]. We have shown that this technique gives reliable data about the amount of surface oxygen formed in zeolites with high and low iron contents. As a result we concluded that the pre-treatment of the zeolite affects the surface oxygen formation. Moreover, we found further evidence that different surface oxygen species exist which differ in thermal stability and reactivity, in agreement to results of other groups [8,13,16,20–23,32].

Summarising all these investigations, several different, sometimes contradicting results can be found. This may be due to either the use of differently prepared iron containing ZSM5 zeolites or the application of different investigation methods. Frequently, both of these aspects should be considered. Therefore, the present work will focus on the comparison of different transient techniques for studying the activation of N_2O and the formation of surface oxygen under different operational conditions, multipulse and step experiments. Results using these methods are compared to results obtained through batch experiments in a closed vacuum set-up. Such a comparison has not been done so far, but it allows for showing the influence of the methodology on the surface oxygen formation. It will be demonstrated which quantitative information can be derived with each method and how the findings are related to each other. Finally, the kinetics of the surface oxygen formation are compared to the kinetics of the total nitrous oxide decomposition measured in a fixed bed reactor under steady state conditions.

2. Experimental

2.1. Preparation of the catalyst

The iron containing ZSM5 zeolite (Fe-MFI) was prepared through solid-state ion exchange of the NH_4-form (SM27, Si/Al = 11.5, Süd-Chemie AG, Germany) with $FeCl_2\cdot4H_2O$. The procedure is detailed described in Refs. [33,34]. The final catalyst powder, containing 4.98% Fe (w/w) determined by ICP, was pressed into tablets and crushed to a particle size fraction of 250–500 μm which was used in all experiments. The characteristics of the catalyst were described in Refs. [24,25].

2.2. Catalytic investigations

2.2.1. Static vacuum experiments

The experiments were carried out in a closed, static vacuum system located in the Boreskov Institute of Catalysis (group of G.I. Panov). The set-up, the experimental procedure and the way of analysing were described in detail in Refs. [9–11]. In the following, a short summary of the procedure will be given.

The surface oxygen amount was determined by measuring both low temperature N_2O decomposition and isotope exchange with $^{18}O_2$. The sample (1.0 g) was pre-treated in vacuum at 823 K for 1.5 h followed by purging with either O_2 or He (160 Pa) at 823 K for 1.5 h in order to remove adsorbed species. Afterwards, the sample was cooled to 493 K and the reactor (25 cm^3) containing the catalyst was closed. A pre-chamber (715 cm^3)

was filled with N_2O to achieve a pressure of 267 Pa. To start the reaction, reactor and pre-chamber were connected. The N_2O consumption and N_2 formation were measured versus time by mass spectrometry until the reaction was completed. After loading the catalyst with surface oxygen, the reaction temperature was decreased to 373 K and $^{18}O_2$ was fed into the reactor (133 Pa). After the complete isotopic exchange, the temperature was increased to 823 K with a ramp of 50 K min^{-1} to quantify the amount of species desorbed.

In the kinetic measurements, only 0.15 g of the zeolite was used in a small reactor (6.5 cm^3). The N_2O decomposition experiments were started at a pressure of 40 Pa, pure N_2O, in the temperature range of 423–513 K.

2.2.2. *Transient experiments*

Transient studies of N_2O decomposition were performed in a set-up for catalyst characterisation (Autochem 2910, Micromeritics) containing a quartz glass reactor (i.d. 9 mm). The reaction products were monitored in an on-line mode using a quadrupole mass spectrometer (QMS 422; Pfeiffer Vacuum). The intensity of the following signals was measured simultaneously: 4, 18, 28, 32, 40 and 44 m/e. The detailed description of the analysis is given in Ref. [24].

Prior to all transient investigations, the catalyst was treated with He for 2 h at 773 K in order to remove adsorbed hydrocarbons and physisorbed water. Thereafter, the catalyst was cooled to reaction temperature in a helium flow of 50 $ml_{NTP}\, min^{-1}$. After the experiment, the temperature was increased from reaction temperature to either 773 or 1173 K with a ramp of 10 K min^{-1} to follow the desorption of deposited chemical species.

The *step experiments* were carried out according to the procedure of Kiwi-Minsker et al. [16] and Wood et al. [19]. Firstly, helium flowed through the reactor containing 0.2 g of catalyst with a flow rate of 25 $ml_{NTP}\, min^{-1}$ at the reaction temperature (423–623 K). At a certain time, the reactor feed was switched to 1% (v/v) N_2O/1% (v/v) Ar/98% (v/v) He (25 $ml_{NTP}\, min^{-1}$). Argon was used as an inert tracer to check the reactor behaviour. N_2O decomposition was monitored for 30 min before the inlet stream was switched back to He.

In the *multipulse experiments*, 0.1 g of catalyst was placed in a quartz reactor. At the reaction temperature (423–623 K), a certain number of pulses (50 or 100) of the mixture 1% (v/v) N_2O/1% (v/v) Ar/98% (v/v) He was injected into a helium flow of 10 $ml_{NTP}\, min^{-1}$ via a sample loop (vol. = 1 ml). Each pulse contained 0.31 μmol N_2O. The area of each response peak in the multipulse sequence was integrated with the software MatLab. The experimental procedure and analysis are described in detail in Refs. [24,25].

2.2.3. *Steady state experiments in the fixed bed reactor*

Steady state N_2O decomposition was carried out in the temperature range from 573 to 773 K using a quartz fixed bed reactor of 11.5 mm inner diameter and 250 mm length. The catalyst (0.4–1.0 g) was diluted with silicon carbide particles in the same size fraction. The total flow over the reactor was varied from 100 to 300 $ml_{NTP}\, min^{-1}$ to obtain a range of modified space velocities ($GHSV_{mod}$) of 2.16–12.5 $ml_{NTP}\, g_{catalyst}^{-1}\, s^{-1}$. The modified space velocity is defined as ratio of the total flow rate under normal conditions and of the catalyst mass. Two different molar fractions of N_2O in helium, 0.001 and 0.01, were used as reactor feed. The N_2O concentrations were determined with non-dispersive infrared spectroscopy (Binos, Leybold Heraeus) at the reactor entrance, through bypassing the reactor, and at the reactor exit. Experiments were performed by decreasing the temperature in steps of 25 K starting at 773 K. At each temperature, care was taken to wait until steady state conditions were reached.

3. Results and discussion

3.1. *Determination and characterisation of surface oxygen*

3.1.1. *Static vacuum technique*

According to Panov and co-workers, it is possible to quantify the amount of a surface oxygen species, called α-oxygen [9], formed in the N_2O decomposition at temperatures below 573 K in a static vacuum set-up. Table 1 shows the results of experiments obtained with our zeolite in this apparatus. In the N_2O decomposition at 493 K, an amount of 48 ± 4 μmol surface oxygen per gram catalyst was determined from formed N_2 amount. The subsequent isotopic exchange experiment with $^{18}O_2$ showed that all oxygen formed in the N_2O decomposition can be exchanged. In the temperature-programmed desorption after the isotopic exchange, all surface oxygen was desorbed at 823 K (Table 1), and N_2O was detected only in traces in this period. In the following, so determined surface oxygen amount will be used as a reference for the results obtained with other methods.

It has to be emphasised that whether the sample is pre-treated in helium or O_2 has no influence on the surface oxygen amount. This result dissents the findings of Jia et al. [13] and Pirngruber and co-workers [20–23] who did not observe an isotopic exchange of surface oxygen without a special pre-treatment of the ZSM5 zeolites containing similar iron amounts. The reason for this discrepancy might be the different method of iron introduction through chemical vapour deposition with $FeCl_3$, which provides different iron species.

3.1.2. *Multipulse technique*

Fig. 1 shows the results of the multipulse studies at different temperatures. During the multipulse sequence, the molar

Table 1
Determination of the surface oxygen content in the static vacuum set-up

Method	Temperature (K)	O/Cat (N_2) (μmol g^{-1})
N_2O decomposition	493	48 ± 4[a]
Isotope exchange with $^{18}O_2$	373	46 ± 3[b]
Temperature programmed desorption up to 823 K	–	45 ± 3

[a] Surface oxygen amount calculated from N_2 formation during N_2O decomposition.

[b] $^{18}O_2$ consumptions after surface oxygen loading from N_2O at 493 K.

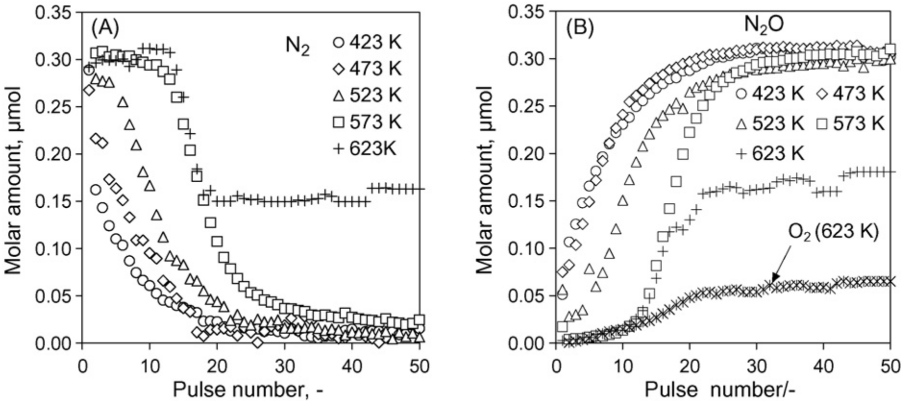

Fig. 1. Multipulse experiments: influence of reaction temperature: (A) N_2 formation, (B) N_2O and O_2 formation.

amounts of N_2 decreased and those of N_2O increased with increasing pulse number. No molecular oxygen was detected during the whole sequence up to a reaction temperature of 573 K. The amount of surface oxygen, calculated by summarising the formed N_2, increased from 16 μmol $g_{catalyst}^{-1}$ at 423 K to 63 μmol $g_{catalyst}^{-1}$ at 573 K (Table 2, O/Cat (N_2)). In our previous investigation, the surface oxygen content was determined with different amounts of catalyst and under different total flow rates at 523 K [24]. Thereby, it was observed that the shape of the curves was determined by the residence time of the pulses in the catalyst bed, but the amount of surface oxygen was not affected. Thus, the corresponding quantitative values, also given in Table 2, show the accuracy of this method and support that the measured influence of temperature on the total surface oxygen content is significant. This effect, also found by other research groups [8,19,26], will be discussed in more detail after the presentation of the step experiments.

At 623 K, molecular oxygen was formed after 10 pulses, and after 20 pulses a steady state N_2O consumption (Fig. 1(A)) was observed accompanied by a steady state formation of N_2 and O_2 (Fig. 1(B)). These findings confirm the assumption that the surface oxygen formed in MFI zeolites is stable up to 573 K. Higher temperatures seem to accelerate the migration and the recombination of the oxygen species, the desorption of O_2, or the reaction of N_2O with surface oxygen. After correcting the N_2 formation at 623 K by subtracting twice the amount of formed O_2, a surface oxygen content of 64 μmol O $g_{catalyst}^{-1}$ can be determined (Table 2). This value is similar to that obtained at 573 K, where no molecular oxygen is formed, and therefore seems to be the capacity limit of the zeolite for surface oxygen. The calculated amount for this limit is slightly higher, but it is still in the range of the amount determined in the static vacuum set-up (Table 1). This suggests that a surface oxygen species similar to "α-oxygen" can also be quantified with the multipulse technique [3,9–12].

The subsequent temperature-programmed desorption up to 773 and 1173 K show that higher temperatures in the multipulse sequence lead to higher amounts of oxygen desorbed (Table 2). Up to 773 K, this is only a small part of oxygen that is formed during the N_2O decomposition, as also shown in Ref. [24]. The rest of oxygen remains bound more strongly in the zeolite and is consumed for the oxidation of iron species in the zeolite. This would be in agreement to results of other research groups obtained with zeolites containing similar iron amounts [20,23,35]. The strongly bound oxygen desorbs up to 1173 K, but, as shown in Table 2, the amount of oxygen desorbed was higher than the amount of oxygen formed multipulse sequence. The excess of oxygen originates from iron oxide clusters in the zeolite, which can be shown in a blank test by heating up the zeolite in helium without previous N_2O decomposition [24].

Table 2
Quantitative results obtained with the multipulse technique at different conditions

Mass (g)	Total flow (ml min^{-1}) (NTP)	Temperature (K)	O/Cat (N_2)[a] (μmol g^{-1})	O/Cat (O_2)[b] (μmol g^{-1})		N_2O/Cat[c] (μmol g^{-1})	Ref.
				773 K	1173 K		
0.10	10	423	16	Traces	38	10	Fig. 1
0.10	10	473	21	Traces	–	11	Fig. 1
0.10	10	523	40	14	56	8	Fig. 1
0.10	10	573	63	18	–	13	Fig. 1
0.10	10	623	64[d]	–	93	16	Fig. 1
0.20	10	523	41	14	–	7	[24]
0.20	50	523	41	13	–	8	[24]

[a] Formed N_2 during pulse sequence = surface oxygen.
[b] Oxygen desorbed after temperature-programmed desorption up to 773 and 1173 K.
[c] Desorbed N_2O up to 1173 K.
[d] Corrected by subtracting twice the amount of formed O_2.

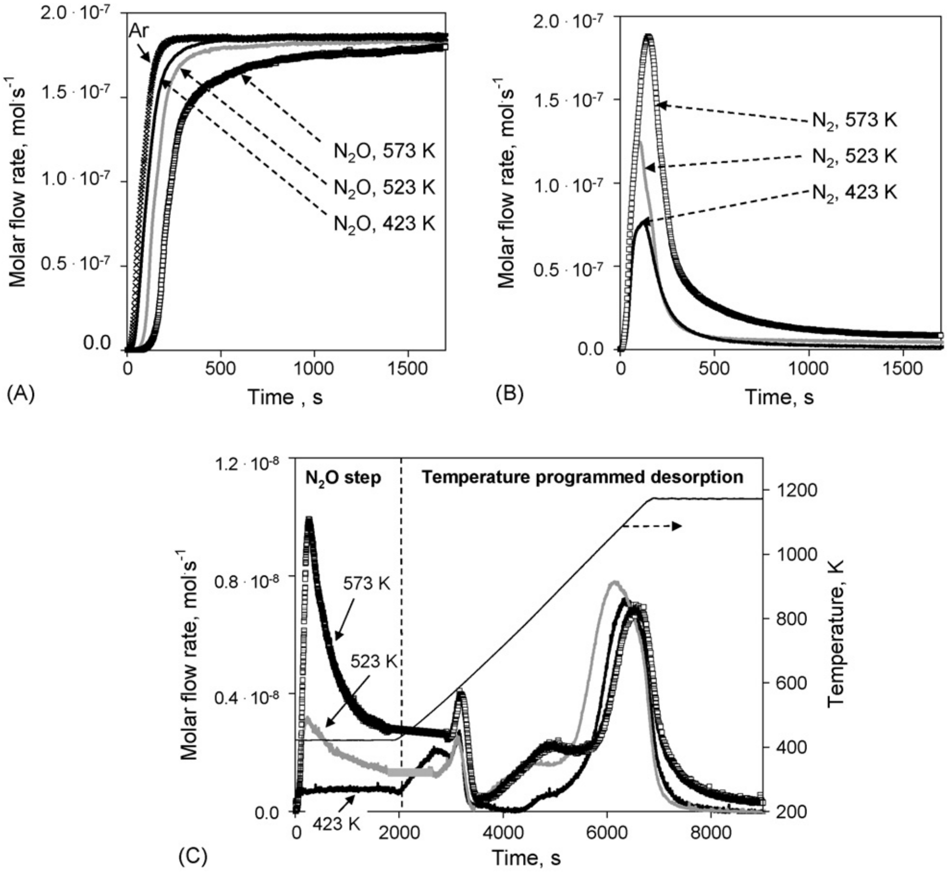

Fig. 2. Step experiments: (A) N_2O formation and (B) N_2 formation during the N_2O step at different temperatures; (C) O_2 formation during the step and in the subsequent temperature-programmed desorption up to 1173 K.

Remarkably, the results in Table 2 show that the amount of oxygen desorbed up to 1173 K depends on the temperature at which the multipulse experiment was carried out. This observation will be further discussed in the next section.

The amount of N_2O detected during the temperature-programmed desorption does not significantly depend on the reaction temperature (Table 2). As already shown in Refs. [24,25], this amount explains well the difference between N_2O consumption and N_2 formation during the pulses. Bulky iron oxide species, present in the over-exchanged Fe-MFI, were identified as sites for this remarkable sorption. The results of Wood et al. support the relevance of strongly adsorbed N_2O due to its high sorption enthalpy ($\Delta H_S \approx -67\,\mathrm{kJ\,mol^{-1}}$) [29]. Its possible role for the kinetics will be shown in Section 3.3.

3.1.3. Step technique

The results of the step experiments reflect qualitatively the same trends as those of the multipulse experiments (Fig. 2). The increase of the temperature from 423 to 573 K in the experiment leads to an enhanced N_2O consumption (Fig. 2(A)) and N_2 formation (Fig. 2(B)). Thus, the surface oxygen amount, calculated by the N_2 formed, increases with higher reaction temperatures (Table 3). Wood et al. [19] and Perez-Ramirez et al. [8,26] also found this effect on ZSM5 zeolites containing 0.38% Fe (w/w) and 0.68% Fe (w/w), respectively, in the range of 500–573 K. In contrast, Kiwi-Minsker et al. [16] observed no influence of the reaction temperature for zeolites containing ≤1000 ppm Fe (w/w) in the range of 523–603 K. A possible explanation could be that the temperature increases the number of active iron species in the Fe-MFI, particularly in zeolites

Table 3
Quantitative results of N_2O step experiments at different temperatures

Temperature (K)	Converted N_2O (μmol g^{-1})	O/Cat (N_2, I)[a] (μmol g^{-1})	O/Cat (N_2, II)[b] (μmol g^{-1})	O/Cat (O_2)[c] (μmol g^{-1})
423	78	75	67	109
473	119	96	79	127
523	127	117	87	123
573	255	223	112	130

[a] N_2 formed during the N_2O step.

[b] N_2 formed during the N_2O step and corrected by subtraction twice the formed O_2.

[c] O_2 formed in the subsequent temperature-programmed desorption up to 1173 K, given as atomic oxygen per mass of catalyst.

with higher iron contents, during the interaction with N_2O. Further explanations can be the accumulation of oxygen on single Fe sites in the zeolites resulting in adsorbed O_2^- and O_3^- species, as recently reported by Heyden et al. [27,28] and by Kondratenko and Perez-Ramirez [26], or the formation of oxygen species bound to different sites. DFT calculations in Refs. [27,28] revealed that the activation energy increases if additional oxygen species are deposited through N_2O decomposition at sites which are already occupied by surface oxygen. In this case, higher temperatures would favour this accumulation. However, the promoting effect of temperature on the surface oxygen content can also be explained if the surface oxygen deposition on different sites needs to overcome different activation barriers.

In the temperature-programmed desorption after the step experiments, two main oxygen desorption peaks can be observed, in the range of 770–800 and 1070–1130 K (Fig. 2(C)), as found in the desorption after the multipulse experiments. The amount of O_2 desorbed in the lower range is only a small part of that totally desorbed up to 1173 K. This gives further evidence for the formation and the presence of different oxygen species. As in the multipulse experiments, N_2O desorbed up to 773 K after the step experiments. This explains why the N_2O consumption during the step is always higher than the N_2 formation (Table 3), as also found by Kiwi-Minsker et al. [16]. The absence of N_2O desorption in the temperature-programmed desorption after experiments in the closed vacuum set-up (Section 3.1.1) should be due to the fact that the vacuum conditions provoke the fast desorption of any surface species. This was suggested by Pirngruber and Roy [21] and also observed in the TAP reactor [14,15].

Some significant differences between step and multipulse technique have to be outlined. In the step experiments, more N_2 is formed and more N_2O is consumed than in the multipulse experiments (Table 3). Molecular oxygen is significantly formed already at 473 K during the step experiments (Fig. 2(C)). This might be due to the higher average N_2O gas phase concentration in the step experiment which enhances the reaction of N_2O with surface bound oxygen (Eq. (3)) in contrast to the mulitpulse and static vacuum technique. This explanation is supported by results of Nobukawa et al. using a ZSM5 zeolite containing 2.9% Fe (w/w). They determined that the reaction of N_2O with surface oxygen is the rate determining step for the O_2 formation [30], which was already suggested in early studies of Kapteijn et al. [31]. After correcting the amount of the formed N_2 by subtracting twice the formed O_2 amount (Table 3, 4th column), the calculated surface oxygen contents are still higher than those obtained from the multipulse experiments. A reasonable explanation could be the formation of NO adsorbed in the zeolite which is formed at high N_2O gas phase concentrations during the step, as shown by other authors [17,36,37]. Due to the reaction equation of the NO formation, $N_2O + Z \rightarrow NO\text{–}Z + 0.5N_2$, this process would falsify the determination of surface oxygen from the formed N_2 or the converted N_2O amount using the step technique. On the other hand, the formation of NO and the resulting effects would contradict the observation that the total amount of oxygen, desorbed up to temperatures of 1173 K after the step experiment, is also higher than after the multipulse sequence. In addition, the total oxygen amount is nearly independent of the reaction temperature (Table 3, 5th column). The most reasonable explanation for the higher values is the above-mentioned accumulation of oxygen on single Fe sites in the zeolites. This phenomenon should be enhanced with higher N_2O concentrations as present during a step, but not in a single pulse of the sequence.

In the temperature-programmed desorption, a third oxygen peak in the range of 570–580 K can be observed. This is in agreement with Pirngruber's findings applying the step technique. He attributed the part of surface oxygen desorbing at low temperatures to a fast desorption process of less stable bound oxygen [20]. However, this effect must also be due to the high iron content and the therefore resulting high surface oxygen density in the zeolite because investigations with the same technique did not report about this behaviour when zeolites with low iron amounts were used [16–19].

The results of the multipulse and step experiments, together with subsequent temperature-programmed desorption, show the existence of several oxygen species in the zeolite. As shown by other research groups, these species differ in stability and reactivity, particularly, in zeolites with high iron contents [13,20–23,32], but also with low iron contents [8,16–18,32]. For example, recent pulse studies in the TAP reactor published in Ref. [8] revealed a short living oxygen species referred to as 'nascent or hot oxygen transients' and long-lived oxygen species referred to as 'thermally accommodated oxygen' according to Kameoka et al. [39]. The former species is highly reactive, but converts rapidly to highly stabilised species, which is inactive for propane conversion [8]. The results of multipulse and step experiments indicate that the atmospheric conditions and higher N_2O concentrations probably accelerate these undesirable transformations. This would also explain earlier results investigating the CO oxidation in a transient mode at atmospheric conditions [16,25]. In contrast, only one oxygen species can be detected in the closed vacuum set-up. It is completely exchangeable with $^{18}O_2$ and it completely desorbs up to 823 K. Moreover, Panov and co-workers have shown that this surface oxygen species is completely consumed in CO, H_2, CH_4, and benzene oxidation [3,4,10,12]. These obviously contradictory results cannot be fully explained at the moment. One likely reason might be the "clean" atmosphere, particularly the absence of moisture, in the closed vacuum set-up. Since water was found to have a deactivating effect on the total N_2O decomposition, even in trace amounts of several ppms [27], all measurements in open systems can suffer from it. This was also remarked for investigations of the N_2O decomposition in the TAP reactor [26].

3.2. *Kinetics of surface oxygen formation*

In order to get information on the kinetics of the N_2O activation forming surface oxygen, results obtained in the static vacuum set-up and from the step experiments have been analysed. Principally, kinetic parameters can also be determined from the multipulse experiments, but an appropriate model for the pulse reactor has to be developed. This has not been done so far.

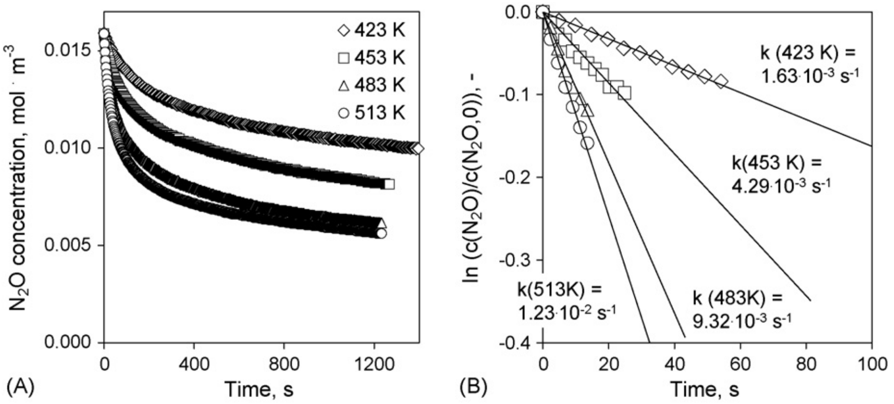

Fig. 3. N_2O decomposition in the static vacuum set-up in the temperature range 423–513 K: (A) N_2O concentration vs. time; (B) determination of the rate constants.

In the static vacuum set-up, kinetic measurements were performed at different temperatures. Firstly, the same conditions were chosen as in the determination of the total surface oxygen concentration: catalyst mass of 1 g and a N_2O pressure of 267 Pa. It was observed that the temperature does not affect the reaction rate under these conditions. The reason is that the mass transfer from the pre-chamber to the reactor limits the rate. Therefore, less catalyst (0.15 g) and lower N_2O pressures (20 Pa) were used. The N_2O consumption versus time, shown in Fig. 3(A), was fitted assuming a batch reactor model and a first order rate law. The constants of the initial rate were determined from the linear plot of logarithmic relative concentrations versus time (Fig. 3(B)). The slope of the curve in the Arrhenius plot (Fig. 4) reveals an activation energy of $49\,\mathrm{kJ\,mol^{-1}}$ in the temperature range 423–483 K. The pre-exponential factor is $2993\,\mathrm{s^{-1}}$. At higher temperatures, the plot indicates that the mass transfer from the pre-chamber to the reactor starts to limit the reaction kinetics as found at higher pressures and higher catalyst amounts. The value for the activation energy corresponds well to results of Panov et al. who determined $42\,\mathrm{kJ\,mol^{-1}}$ for zeolites with 0.06–0.35% Fe (w/w) [9].

Step results were analysed with the kinetic model suggested by Wood et al. [19] to determine the temperature dependency of the N_2 formation rate:

$$r_{N_2} = k\theta(t)c_{N_2O} \quad \text{with} \quad \theta(t) = \theta_0\,\mathrm{e}^{(-kc_{N_2O}t)} \tag{4}$$

Therein, $\theta(t)$ represents the number of sites where oxygen is deposited, and θ_0 is the initial number of these sites. The N_2 formation rate (r_{N_2}) was corrected by subtracting twice the amount of the formed O_2, assuming that the resulting rate only reflects the surface oxygen formation. Plotting the so determined rate constants k for each temperature in an Arrhenius plot, gives an activation energy of $\approx 14\,\mathrm{kJ\,mol^{-1}}$ and a pre-exponential factor of $2.4\times10^6\,\mathrm{ml\,g_{catalyst}^{-1}\,s^{-1}}$ (Fig. 4).

In order to compare these parameters with those determined from measurements in the vacuum set-up, the pre-exponential factor determined from the latter measurements has to be converted with respect to the volume of the apparatus (reactor + pre-chamber) and the catalyst mass. This conversion results in a modified pre-exponential factor of $1.02\times10^7\,\mathrm{ml\,g^{-1}\,s^{-1}}$. Thus, activation energies and pre-exponential factors measured in the vacuum set-up are higher than measured with the step technique. At first sight, this might be due to weaknesses in the applied reactor model, but this would not explain these big differences. Another reason might be the O_2 desorption during the step, even if considered in the N_2 formation rate. However, in this case a higher activation energy should be expected, because it is generally accepted that O_2 formation and desorption have to overcome a higher activation barrier (see the following section). Therefore, it is more likely that the diffusion of N_2O in the zeolite can limit the formation rate of surface oxygen in the step experiments. This is also indicated by the measurements of Wood et al. [19] though they excluded this effect. To clarify this, further experiments have to be done using smaller catalyst particles. A second reasonable explanation might be possible if the N_2O sorption is considered [29]. The enthalpy of N_2O sorption would decrease the observed activation energy for the surface oxygen formation ("apparent" activation energy) as compared to the true activation energy. This effect is generally explained in Ref. [38] and should be particularly valid for higher gas phase concentrations of N_2O, such as in the conditions of step and steady state experiments.

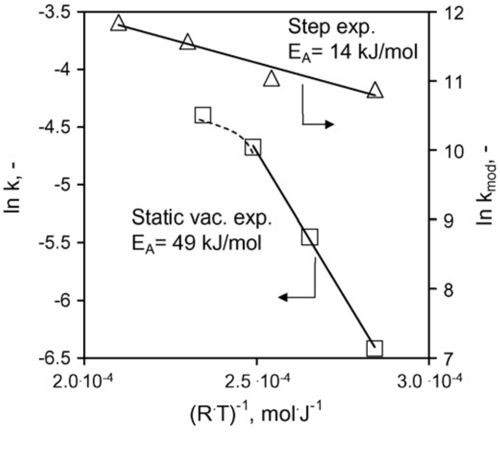

Fig. 4. Temperature dependency of the rate constant for surface oxygen formation (Arrhenius plot) obtained through step experiments and in the static vacuum set-up.

Both of the determined activation energies are lower than $70\,\mathrm{kJ\,mol^{-1}}$ for Fe-ZSM5 with 0.38% Fe (w/w) reported by

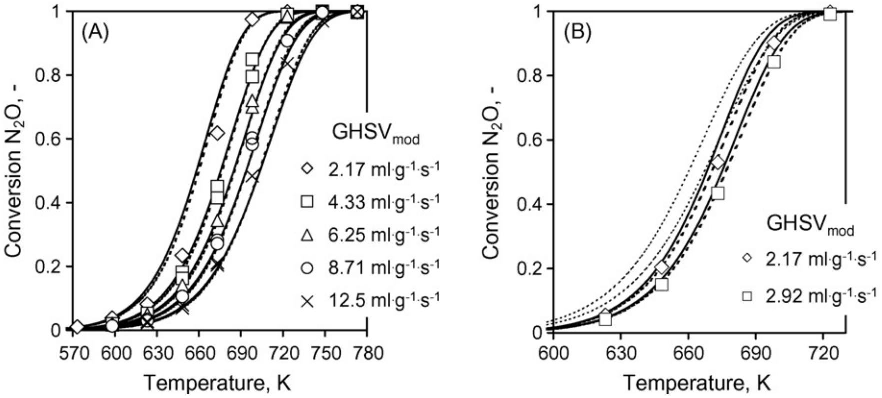

Fig. 5. Steady state N_2O decomposition in the temperature range 573–773 K: inlet molar fraction (A) $x(N_2O, 0) = 0.001$, (B) $x(N_2O, 0) = 0.01$; solid lines: first order models (Table 4), thin dotted lines: first order model for $x(N_2O, 0) = 0.01$ with parameters obtained by fitting the experimental data with $x(N_2O, 0) = 0.001$, thick dotted lines: inhibition model (Table 4).

Wood et al. [19]. Modelling of the kinetics of the total N_2O decomposition on the basis of single pulse experiments in the TAP reactor by Kondratenko and Perez-Ramirez reveals an activation energy of 120 kJ mol^{-1} for the surface oxygen formation when using an Fe-silicalite (Si/Al = ∞, 0.68% Fe, w/w), and of 69 kJ mol^{-1} when using an Fe-ZSM5 (Si/Al = 31, 0.67% Fe, w/w) [26]. Notice that the surface oxygen formation was not measured independently in this study. DFT calculations by Heyden et al. [28] show that the surface oxygen formation at empty sites is not activated at all ($E_A = 0$ kJ mol^{-1}), but at sites already occupied by an atomic oxygen species an activation energy of 115–130 kJ mol^{-1} was determined. Thus, it is possible to get higher and lower values for the activation energy than the ones presented in the present study depending on the oxidation state of the zeolite and the iron species therein. Moreover, the differences can also be explained with the high iron content in our sample, which leads to different iron species with different activation barriers for the surface oxygen formation. In order to prove this theory, the rate of surface oxygen formation has to be investigated using zeolites with lower iron contents.

3.3. Kinetics of the total N_2O decomposition

Steady state measurements of the stoichiometric N_2O decomposition should demonstrate how N_2O activation and surface oxygen formation are linked to the rate of total N_2O decomposition. The results of the steady state measurements are shown for a N_2O molar fraction of 0.001 in Fig. 5(A) and of 0.01 in Fig. 5(B) in the reactor feed at different residence times in the temperature range of 573–773 K. An integral reactor model was used for the kinetic analysis of the experimental data. The data for each inlet molar fraction of N_2O can be fitted with a first order rate law. The range of kinetic parameters are consistent with literature data, where activation energies vary between 140 and 185 kJ mol^{-1} depending on the iron amount in zeolites and on the partial pressure of water in the feed [2,9,12,19,22,26,27,29,31].

The results in Table 4 show that the estimation of activation energy and of pre-exponential factor are significantly different for different inlet concentrations (Table 4). In Fig. 5(B) the parameters obtained from the measurement with a molar N_2O fraction of 0.001 at the inlet were used to simulate the data set obtained with a molar fraction of 0.01 (Fig. 5(B): thin dotted lines). This illustrates that it is not possible to describe the measurements at both molar fractions of N_2O in the reactor feed with one set of parameters. The effective reaction order is obviously lower than 1. This was also found by Kondratenko and Perez-Ramirez when increasing the N_2O concentration in TAP experiments. Their kinetic model takes this effect into account regarding a saturation of the surface by oxygen [26]. Earlier, Kapteijn et al. [31] found the same under steady state conditions with a N_2O inlet concentration of 1500 ppm. As far as we know, no more data can be found in the literature where the N_2O inlet concentration was varied. In order to describe all measurements, we developed a model containing a term representing an inhibition by N_2O itself (Table 4, Fig. 5: thick dotted lines). Although this model has no detailed mechanistic background, the temperature dependency of the inhibition parameter *B* indicates its nature of a sorption equilibrium constant. This would support the importance of molecularly adsorbed N_2O found in the transient experiments (Section 3.1). If the temperature dependency of *B*

Table 4
Total N_2O decomposition in the temperature range 573–773 K: models and estimated parameters for different inlet concentrations

Model	Inlet molar fraction $x(N_2O,0)$, -	Parameters
First order: $r = kc(N_2O)$, $k = k_0\,e^{-E_A/RT}$	0.001	$k_0 = 2.41 \times 10^{13}$ ml g^{-1} s^{-1}, $E_A = 162$ kJ mol^{-1}
	0.01	$k_0 = 9.23 \times 10^{13}$ ml g^{-1} s^{-1}, $E_A = 185$ kJ mol^{-1}
Inhibition: $r = kc(N_2O)/[1 + Bc(N_2O)]$, $k = k_0\,e^{-E_A/RT}$, $B = B_0\,e^{-E'_A/RT}$	0.001–0.01	$k_0 = 4.49 \times 10^{12}$ ml g^{-1} s^{-1}, $E_A = 152$ kJ mol^{-1}, $B_0 = 1.10 \times 10^{12}$ mol m^{-3}, $E'_A = -46.5$ kJ mol^{-1}

is interpreted as enthalpy for the sorption of N_2O, this value is close to that determined by Wood et al. ($\Delta H_S \approx -67\,kJ\,mol^{-1}$) [29]. Remarkably, the temperature dependency of the inhibition parameter B results in a decrease of the activation energy for the total N_2O decomposition, as also assumed after the kinetic analysis of surface oxygen formation rate measured through the step technique.

Comparing the kinetic parameters determined for the total N_2O decomposition with those for the rate of surface oxygen formation support the assumption that the latter is not determining for the total process due to its high rate and its low activation barrier. Although investigations suggest that the recombination of atomic surface bound oxygen (Eq. (2)) [15,19–23,28] or the O_2 desorption [26–28] are rate determining for the total N_2O decomposition at high iron loaded zeolites, the reaction of surface oxygen with N_2O (Eq. (3)) should not be excluded in these considerations, as shown by results in Refs. [2,29,31,32]. Pulse experiments may suppress this reaction due to much lower N_2O concentrations in the gas phase than under steady state conditions.

4. Conclusions

Several methods were used to study the N_2O decomposition and the surface oxygen formation on an Fe-MFI zeolite. Transient methods in multipulse and step mode were applied under different operational conditions at atmospheric pressure. The results were compared to those obtained in a static vacuum set-up of Panov and co-workers. The comparison of the results obtained with each method leads to the following conclusions:

- In the multipulse method under atmospheric conditions, each pulse contains a low N_2O amount, which suppresses side reactions, like O_2 formation. The calculated amount of surface oxygen deposited in the zeolite is similar to that determined in the closed vacuum set-up for measurements in the same temperature range (40–50 $\mu mol\, g_{catalyst}^{-1}$). This suggests that the measured surface oxygen species is similar to the α-oxygen species defined by Panov and co-workers. However, in the temperature-programmed desorption after the multipulse sequence, the existence of adsorbed N_2O and of several oxygen species with different thermal stability can be observed.
- Qualitatively, the step technique under atmospheric conditions leads to similar results as the multipulse technique concerning the existence of different oxygen species. However, due to higher gas phase concentrations of N_2O during the steps, the formation of molecular oxygen is already observed at lower temperatures than in the multipulse experiments. High gas phase concentrations of N_2O should also be responsible for the determination of higher surface oxygen contents because side reactions are enhanced under these conditions, like the NO formation, the oxygen accumulation of in the zeolite forming O_2^- and O_3^- species, and the transformation of active to inactive oxygen.
- The amount of surface oxygen determined through multipulse and step experiments depends on the temperature. This might be due to the facts that either the mentioned accumulation of oxygen is an activated process or the formation of oxygen species bound to different sites needs to overcome different activation barriers. The influence of temperature on the amount of deposited surface oxygen has to be regarded in the discussion of any active surface oxygen species in iron containing zeolites.
- In contrast to the transient methods at ambient pressure, the measurements in the closed vacuum set-up of Panov and co-workers reveal a single surface oxygen species. Under these conditions, the desorption of surface species is provoked. Therefore, loosely bound oxygen species and adsorbed N_2O cannot be detected. Furthermore, a possible transformation of active surface oxygen to strongly bound oxygen seems to be suppressed since in the temperature-programmed desorption in the vacuum set-up the formed surface oxygen completely desorbs. The most important advantage of the vacuum method is the “clean atmosphere” in a closed system. It prevents all influences of impurities as compared to open systems.
- The kinetic analysis of experiments both in transient mode and in the closed vacuum system revealed that the formation of surface oxygen species is faster than the total N_2O decomposition. An activation energy of $49\,kJ\,mol^{-1}$ was determined from the measurements in the vacuum set-up. At high temperatures and high N_2O concentrations, the surface oxygen formation can even be limited by mass transfer processes. This effect should be taken into account if kinetic models based on the mechanism are developed for partial oxidations with N_2O and for N_2O abatement processes.
- Steady state measurements of the total N_2O decomposition kinetics with different inlet concentrations can be described with a formal model containing an inhibition by N_2O ($E_A = 152\,kJ\,mol^{-1}$). The inhibition parameter in the model can be interpreted as a sorption equilibrium constant of N_2O with a sorption enthalpy of $-47\,kJ\,mol^{-1}$. This observation considers the results of the transient methods showing the presence of adsorbed N_2O.

In general, studies about the formation of surface oxygen through the activation of N_2O should be combined more often with investigations of partial hydrocarbon oxidation with N_2O, such as the hydroxylation of aromatics, the oxidative dehydrogenation of propene and the propene epoxidation. Information about the amount of surface oxygen, its formation kinetics and the role of different oxygen species might give a deeper insight into the mechanism and the proceeding of these challenging and forthcoming applications.

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