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Nitrous oxide decomposition and surface oxygen formation on Fe-ZSM-5

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Abstract

An investigation was conducted of the decomposition of N_2O over Fe-ZSM-5. The zeolite used in this study was prepared with Fe and Al in the framework and is designated as Fe/Al-MFI (Si/Al = 84 and Fe/Al = 0.38). The as-prepared material was then calcined to remove the templating agent and pretreated at temperatures up to 1123 K. EXAFS characterization of the pretreated catalyst indicates that Fe is present as isolated Fe cations at cation-exhchange sites associated with framework Al. Above 548 K, N_2O decomposes stoichiometrically to N_2 and O_2, but below 548 K, N_2O decomposes to adsorbed oxygen and gas-phase N_2. Surface oxygen loadings are in the range of $O/Fe_{total} = 0.10$–0.14. For the stoichiometric decomposition of N_2O to N_2 and O_2, the calculated values of the apparent activation energy and the preexponential factor are 44.2 kcal/mol and 9.9×10^8 mol $N_2O/(\text{s mol } Fe_{total} \text{ Pa } N_2O)$, respectively. The first step in the overall decomposition sequence is the dissociative adsorption of N_2O to produce N_2 and an adsorbed O atom. The activation energy for this step is 16.8 kcal/mol and the preexponential factor is 1.4×10^1 mol $N_2O/(\text{s mol } Fe_{total} \text{ Pa } N_2O)$. The desorption of O_2 from iron sites occurs with an apparent activation energy of 45.7 kcal/mol and a preexponential factor of 8.9×10^{12} mol $O_2/(\text{s mol } Fe_{total})$.

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Keywords: N_2O; Fe-ZSM-5

1. Introduction

Fe-ZSM-5 is an active catalyst for a number of reactions. This material has been shown to promote the stoichiometric decomposition of N_2O to N_2 and O_2 [1–11]. Kinetic studies confirm that the decomposition of nitrous oxide is first order in N_2O concentration, and zero order with respect to O_2 concentration [2]. Work by Panov and co-workers has also shown that above 523 K, N_2O will decompose on Fe-ZSM-5 to N_2 and an active form of oxygen referred to as α-oxygen [1,3,12]. This latter species reacts with benzene to form a precursor to phenol [3,13–15] and with methane to form methoxy species [3,13,16,17]. While phenol can be desorbed as a stable product at temperatures > 523 K, methoxy species decompose without the formation of methanol. Methanol can be formed, however, at lower temperatures by reaction with water.

The state of iron in Fe-ZSM-5 is strongly dependent on the method of iron exchange and the pretreatment of the as-exchanged material. EXAFS studies conducted by Joyner and Stockenhuber show the presence of isolated iron cations, large clusters of Fe_3O_4, as well as Fe_4O_4 nanoclusters [18]. On the other hand, the analysis of EXAFS data by Battiston et al. [19,20], Marturano et al. [21,22], and Jia et al. [23] of fully exchanged H-ZSM-5 (Fe/Al = 1) shows evidence for diferric oxo/hydoxyl-bridged clusters. Marturano et al. have also shown that the distribution of iron in Fe-ZSM-5 is strongly dependent on the source of the parent ZSM-5, and have noted that with some ZSM-5 samples particles of Fe_2O_3 can form after calcinations of the as-exchanged material [21]. Mössbauer spectroscopy has also been used to provide evidence for di-iron sites in studies reported by Dubkov et al. [24]. Evidence for isolated Fe sites in partially exchanged samples of ZSM-5 have been reported in several recent studies. Lobree et al. have reported that for Fe/Al ratios below ~ 0.6, Fe^{3+} cations exchange on a one to one basis with Brønsted acid protons in H-ZSM-5 [25]. EXAFS analyses conducted by our group have confirmed that for $Fe/Al < 1.0$ isolated Fe^{3+} cations associated with single charge-exchange sites are present in Fe-ZSM-5 prepared by solid-state exchange of H-ZSM-5 with $FeCl_3$ and by high-temperature pretreatment of Fe/Al-MFI [26,27].

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The present work was undertaken to elucidate the elementary processes involved in the decomposition of N_2O on Fe-ZSM-5. These studies were conducted on Fe-ZSM-5 prepared by thermal pretreatment of Fe/Al-MFI ($Si/Al = 84$ and $Fe/Al = 0.38$). Both temperature-programmed and isothermal transient-response experiments were used for this purpose. Based on these experiments it was possible to determine the extent of surface oxygen loading on Fe-ZSM-5 and to calculate the kinetic parameters for several of the elementary steps occurring during N_2O decomposition.

2. Experimental

Fe-ZSM-5 was prepared by the fluoride synthesis route in the following manner [28]. Ammonium fluoride, tetrapropalammonium bromide, aluminum nitrate, iron chloride, and water were placed in a Teflon-lined bomb reactor and stirred until all solids dissolved. Ludox LS-30 was then added to the mixture and the reactor was placed in an oven at 433 K for 7 days. The resulting material was heated in air over an 8-h period to a temperature of 823 K and then maintained at this temperature for 6 h. The Fe-ZSM-5 product was then ion-exchanged with 1 M ammonium nitrate, washed with deionized water, and dried overnight at 373 K. The resulting material, referred to as Fe/Al-MFI, was activated by calcining in air at 623 K and then heating in He at 1123 K for 6 h. Elemental analysis of the sample (Galbraith Laboratories) used in this work is shown in Table 1. EXAFS measurements performed on this sample indicate that before activation at 1123 K in He, iron is located in tetrahedral positions in the MFI framework, but that after activation, the iron migrates to the charge-exchange positions associated with framework Al and is present as isolated Fe^{3+} cations [27].

Nitrous oxide decomposition was carried out in a quartz microreactor containing 100 mg of catalyst. The effluent from the reactor was monitored using an MKS Spectra Mini-Lab mass spectrometer. Prior to each experiment, the sample (100 mg) was heated in flowing He (60 cm^3/min) from 298 to 773 K over a period of 1 h. Upon reaching 773 K, the sample was pretreated for 2 h in 3.0% N_2O in He, purged in He for 1 h, and then cooled to the temperature of the experiment.

For the transient N_2O decomposition experiments, a flow system was used which had two different possible flow configurations. In the first configuration, referred to as the bypass mode, 15,000 ppm N_2O in He (60 cm^3/min) bypassed the reactor and flowed directly to the mass spectrometer, while He (60 cm^3/min) flowed through the reactor and then to the exhaust. In the second configuration, referred to as the flow mode, 15,000 ppm N_2O in He (60 cm^3/min) flowed through the reactor and then to the mass spectrometer, while pure He (60 cm^3/min) bypassed the reactor and flowed directly to the exhaust. For these experiments, 100 mg of catalyst was used.

Table 1
Sample elemental analysis

Sample	Si (wt%)	Al (wt%)	Fe (wt%)	Si/Al	Fe/Al
Fe-ZSM-5	42.79	0.49	0.38	84	0.38

3. Results and discussion

The decomposition of N_2O was measured by temperature-programmed reaction, following sample pretreatment at 773 K in 3.0% N_2O. The sample was cooled to 298 K in He and exposed to 15,000 ppm N_2O in He (total flow rate = 60 cm^3/min) for 8 min at 298 K, after which the temperature was increased at 5 K/min from 298 to 773 K. Fig. 1a shows that decomposition of N_2O to N_2 and O_2 begins above 623 K. No evidence of NO formation was observed over the entire temperature range studied. Additionally, no evidence of surface oxygen accumulation was detected during this experiment since the ratio of N_2/O_2 remains equal to two. Fig. 1b shows a plot of $\ln(k)$ versus $1/T$, calculated over the temperature range of 608–708 K. For this analysis, the reactor was treated as a plug-flow reactor. The slope of this plot gives an activation energy of 44.2 kcal/mol for the steady-state rate of N_2O decomposition. The associated preexponential factor is 9.9×10^8 mol $N_2O/(s\,mol\ Fe\ Pa\ N_2O)$ based on the total amount of iron in the sample.

The apparent activation energies and preexponential factors for the stoichiometric decomposition of N_2O found in this study and those reported previously are summarized in Table 2 [1,8]. The activation energy and preexponential factor determined in the present work are consistent with those we have reported earlier for Fe-ZSM-5 made by solid-state exchange of H-ZSM-5 [8]. It is notable, though, that our measured activation energies are consistently higher than those reported by Panov et al. [1]. These differences could be due to differences in the manner of sample pretreatment in different laboratories. Zhu et al. have reported that the apparent activation energy can increase by 41% as a consequence of raising the calcinations temperature from 823 to 973 K, and that the preexponential factor for N_2O decomposition can increase by five orders of magnitude [9]. The apparent activation energy determined in the present study is also consistent with that determined theoretically by Ryder et al., 39.4 kcal/mol [29].

Transient-response experiments were performed to investigate the initial stages of N_2O decomposition. Following the pretreatment at 773 K in 3.0% N_2O, the sample was purged in He and then cooled to the temperature of the experiment. Once at the temperature of the experiment, the flow system was placed in the bypass mode. After 5 min in bypass mode, the system was switched to the flow mode; i.e., 15,000 ppm N_2O in He flowed through the reactor and then to the mass spectrometer while He bypassed the reactor and flowed to the exhaust. After 10 min of sample exposure to the N_2O/He mixture, the system was switched back to bypass mode for

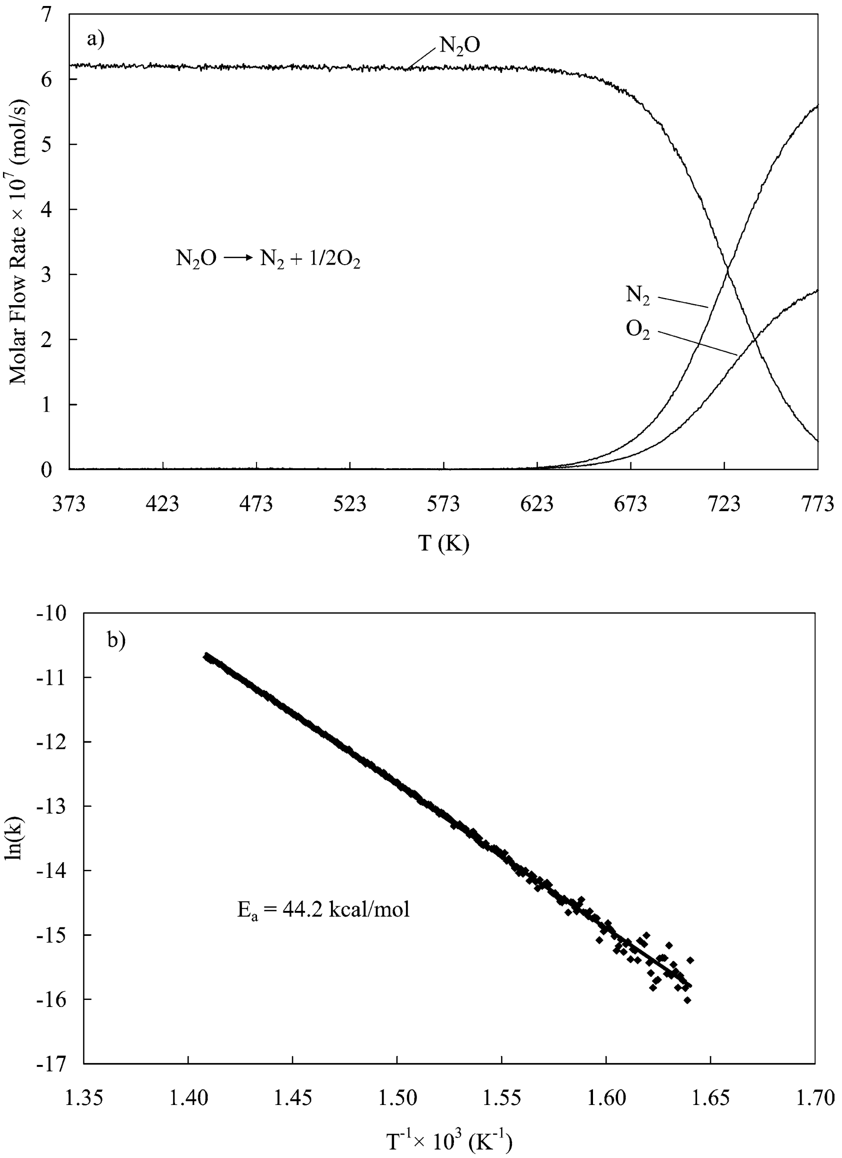

Fig. 1. (a) Temperature-programmed decomposition profile observed during the passage of 15,000 ppm N_2O in He over Fe-ZSM-5. (b) Arrhenius plot for N_2O decomposition. The weight of catalyst used was 100 mg and the gas flow rate was 60 cm^3/min.

Table 2
Activation energies and preexponential factors calculated for stoichiometric decomposition of N_2O to N_2 and O_2

Sample[a]	Fe (wt%)	Activation energy (kcal/mol)	Preexponential factor (mol N_2O/s mol Fe Pa N_2O)	Ref.
Fe-ZSM-5(0.38)	0.38	44.2	9.9×10^8	This work
Fe-ZSM-5(0.17)	0.57	42.1	1.8×10^8	[8]
Fe-ZSM-5(0.33)	1.11	42.3	3.0×10^9	[8]
Fe-ZSM-5(0.033)	0.056	35 ± 4	3.1×10^7	[1]
Fe-ZSM-5(0.21)	0.35	37 ± 1.5	1.0×10^8	[1]

[a] Samples are designated as Fe-ZSM-5(x), where x indicates the Fe/Al ratio. The Si/Al ratio is 84 in this work, 25 in [8], and 50 in [1].

10 min to purge the sample. The system was then placed back in flow mode for an additional 10 min.

Fig. 2 shows the results of a transient experiment carried out at 530 K. Upon switching from the bypass mode to the flow mode, the concentration of N_2O was observed to decrease and a corresponding burst of N_2 appeared in the products from the reactor. However, no detectable amount of O_2 was observed. The formation of N_2 without the corresponding formation of O_2 indicates that oxygen had accumulated in the Fe-ZSM-5. It should be noted that the decrease in the

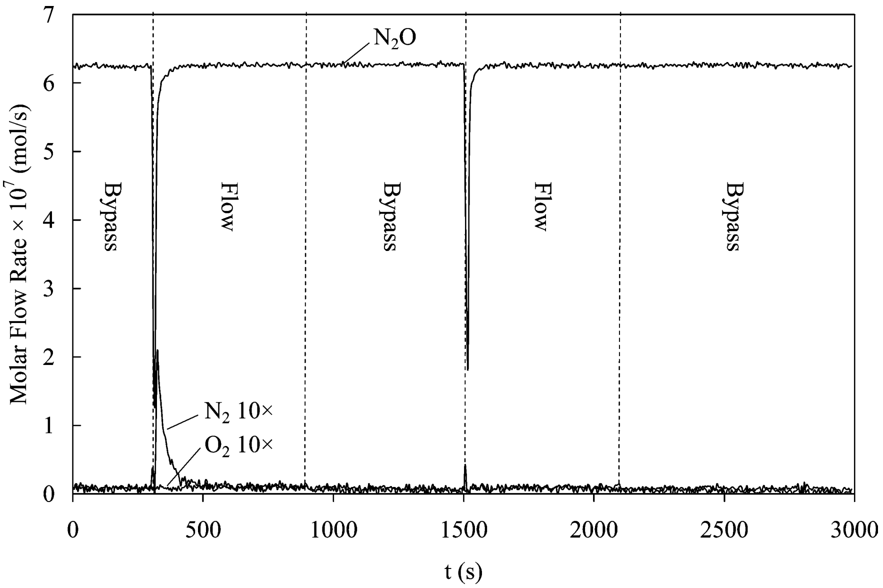

Fig. 2. Transient-response decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5 at 530 K. The N_2 and O_2 signals have been multiplied by 10 for clarity of presentation. The weight of catalyst used was 100 mg and the gas flow rate was 60 cm^3/min.

concentration of N_2O is much greater than that associated with the formation of N_2. This discrepancy is attributable to the presence of He in the reactor when the system is switched from the bypass to the flow mode. Switching to the flow mode momentarily dilutes the N_2O stream entering the reactor with He retained in the reactor, resulting in a decrease in the N_2O concentration. However, the concentration of N_2O reaches 90% of its maximum steady-state value at the point that the N_2 signal has attained its maximum value. After 10 min in the flow mode, the system was placed back in the bypass mode and the catalyst was purged in He while the mass spectrometer measured the concentration of N_2O in the stream bypassing the reactor. After 10 min in the bypass mode, the system was again switched back to the flow mode. Upon reexposure of the catalyst to N_2O at 530 K, neither N_2 nor O_2 formation was detected. Identical behavior was observed for temperatures of up to ~540 K. These results suggest that for temperature up to 540 K, the accumulation of adsorbed oxygen on the Fe sites active for N_2O decomposition results in the progressive loss of these sites. Similar experiments have been reported recently by Kiwi-Minsker et al. in studies conducted with H-ZSM-5 (Si/Al = 25–42) with a low content of Fe (70–1000 ppm) [11]. For the materials investigated, the accumulation of oxygen on Fe sites continues up to 603 K.

Fig. 3 shows the results of a transient-response experiment performed at 588 K in a manner identical to that shown in Fig. 2. Upon initial switching from the bypass to the flow mode, a burst of N_2 was observed, as in the experiment at 530 K. However, this peak was then followed by the formation of stoichiometric amounts of N_2 and O_2. After the system was placed back in the bypass mode and then switched back to the flow mode a second burst of N_2 was observed followed by the stoichiometric formation of N_2 and O_2. Steady-state levels of N_2 and O_2 were observed if the reaction was allowed to continue.

Table 3
Surface oxygen loading on active iron sites

Temperature (K)	O/Fe_{total}[a]	Fe_{active}/Fe_{total}[b]
509	0.10	0.10
520	0.11	0.10
530	0.13	0.10
540	0.14	0.10

[a] Values were calculated by measuring the total amount of N_2 produced.
[b] Values were calculated from the y-intercept of a plot of $\ln(r_{N_2})$ versus t.

Fig. 4 shows the rate of N_2 formation for transient-response experiments conducted at 509, 520, 530, and 540 K. As noted earlier, no O_2 formation was detected below 548 K. Therefore, the total amount of surface oxygen loaded at each temperature equals the total amount of N_2 formed at each temperature (see Table 3). The surface loading by oxygen increases with increasing temperature, from O/Fe = 0.10 to 0.14. These results indicate that at temperatures below 548 K, less than 15% of the total Fe in the catalyst is involved in N_2O decomposition, assuming that the stoichiometry of adsorbed oxygen and iron is 1:1.

The rate coefficient for the N_2O decomposition to form N_2 and adsorbed O atoms can be determined from an analysis of the data in Fig. 4. The rate of N_2 formation can be related to the rate of disappearance of unoccupied active iron sites as shown in

$$r_{N_2} = -d[*]/dt = k_1[*]P_{N_2O}, \tag{1}$$

where r_{N_2} is the rate of N_2 formation, [*] is the concentration of unoccupied active iron sites, t is time, and k_1 is the rate coefficient for the dissociative adsorption of N_2O. Solution

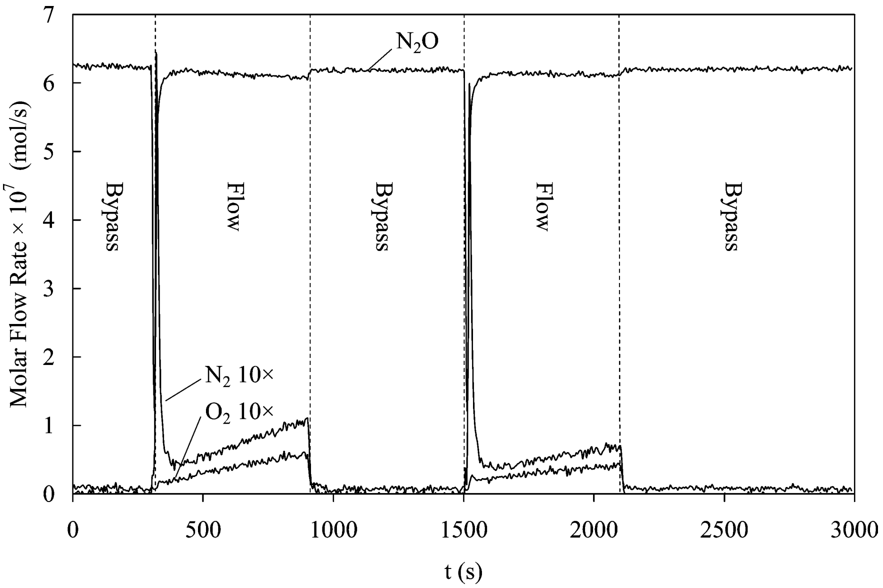

Fig. 3. Transient-response decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5 at 588 K. The N_2 and O_2 signals have been multiplied by 10 for clarity of presentation. The weight of catalyst used was 100 mg and the gas flow rate was 60 cm^3/min.

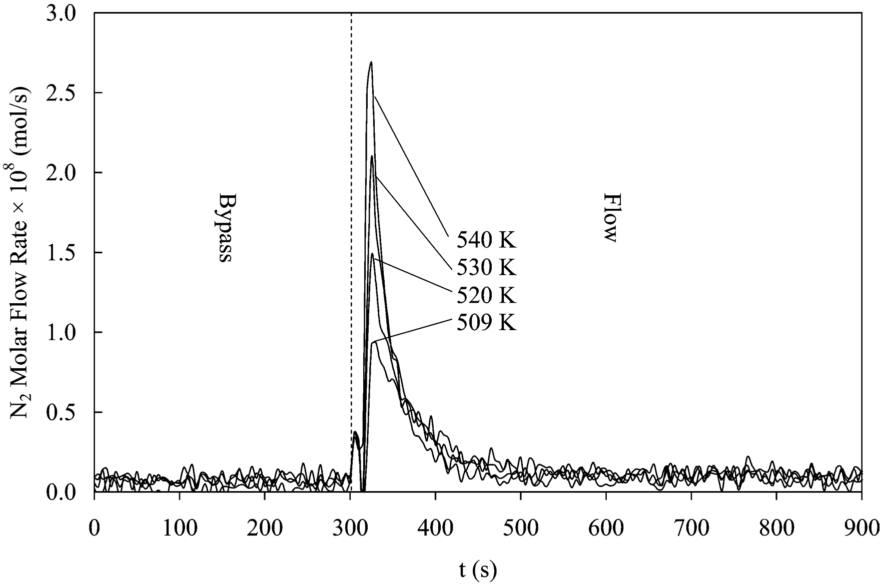

Fig. 4. N_2 formation during transient decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5. The weight of catalyst used was 100 mg and the gas flow rate was 60 cm^3/min.

of Eq. (1) gives

$$[^*] = [^*]_0 \exp(-k_1 P_{N_2O} t), \qquad (2)$$

where $[^*]_0$ is the initial concentration of unoccupied active iron sites. Substituting Eq. (2) into Eq. (1), and taking the natural logarithm of r_{N_2}, one obtains

$$\ln(r_{N_2}) = \ln\bigl(k_1[^*]_0 P_{N_2O}\bigr) - k_1 P_{N_2O} t. \qquad (3)$$

At each temperature, a plot of $\ln(r_{N_2})$ versus t gives a straight line, the slope of which corresponds to $k_1 P_{N_2O}$. To determine k_1, the value of $k_1 P_{N_2O}$ is divided by the steady-state value of P_{N_2O} measured during the transient-response experiments shown in Figs. 2 and 3. Fig. 5 shows a plot of $\ln(k_1)$ versus $1/T$. A Wiesz–Prater analysis indicates that the slight curvature in the data is not symptomatic of a transition from a kinetically limited regime to a mass-transfer-limited regime. The slope of the line fitted through the data gives an activation energy for N_2O decomposition to form N_2 and adsorbed O [see Reaction (1)] of 16.8 kcal/mol. The preexponential factor for the process is 1.4×10^1 mol N_2O/(s mol Fe Pa N_2O), calculated based on the total amount of iron in the sample and 1.3×10^2 mol N_2O/(s mol Fe Pa N_2O) based on the amount of active Fe (see below). For comparison, Panov et al. have reported an apparent activation energy of 10 kcal/mol [1]. The value of

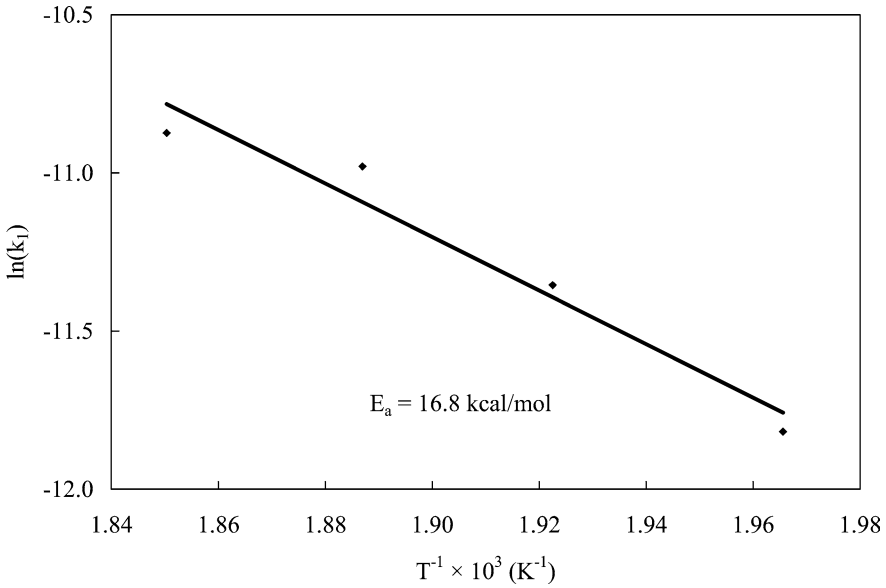

Fig. 5. Plot of $\ln(k_1)$ vs $1/T$.

$[^*]_0$ can be determined from intercept of the plot of $\ln(r_{N_2})$ versus t. By this means, the ratio of Fe sites active for N_2O decomposition to the total number of active sites is determined to be 0.1. This figure taken together with the measured values of O/Fe of 0.10–0.14 supports the assumption (see above) that the ratio of O atoms to active Fe sites is essentially 1:1. The values of O/Fe reported here are a factor of two lower than those reported by Panov and co-workers [1], 0.20–0.25, and by Jia et al., 0.25 [23]. The differences in the values of O/Fe reported here and those reported earlier are likely to be a consequence of the manner of catalyst preparation and pretreatment. Dubkov et al. have shown that Fe-ZSM-5 made by cation exchange of H-ZSM-5 with $FeCl_3$ and by hydrothermal synthesis, in a manner similar to that used in the current study, exhibit different values of O/Fe [24]. They measured values of O/Fe = 0.06 for Fe-ZSM-5 prepared by impregnation of H-ZSM-5 with a solution of $FeCl_3$ and then activated in air at 973 K, and O/Fe = 0.12 for Fe-MFI synthesized hydrothermally and then activated in air at 973 K. Following activation at 1173 K in vacuum, the value of O/Fe for Fe-ZSM-5 prepared by cation exchange increased to 0.43. More recently, Kiwi-Minsker et al. have reported that the O/Fe ratio for samples of H-ZSM-5 containing 70–1000 ppm of Fe is ∼0.06 if pretreatment in He is carried out at temperatures between 823 and 1023 K for 1 h but increases to ∼1.0 if He pretreatment is conducted at 1323 K for 8 h [11].

The strong effect of pretreatment temperature and time observed experimentally is not fully understood. One interpretation is that $Z[Fe(OH)_2]$ species in the as-prepared zeolite must be dehydrated to produce Z[FeO] structures. Ryder et al. have shown through DFT calculations that the latter species could serve as the active center for N_2O decomposition [29]. The requirement of high pretreatment temperatures would be consistent with recent DFT calculations for the process $Z[Fe(OH)_2] \leftrightarrow Z[FeO] + H_2O$, which show that this reaction is endothermic by 56.2 kcal/mol [30]. Therefore, the partial pressure of water vapor in the gas phase would need to be less than 10^{-4} Pa at 1323 K for the reaction to proceed fully to the right. This study shows, as well, that the heat of adsorption of molecular H_2O by Z[FeO] is 40.8 kcal/mol, and that the activation barrier to form $Z[Fe(OH)_2]$ is 22.1 kcal/mol. Thus, one would expect that in the presence of water vapor, Z[FeO] should readily convert back to $Z[Fe(OH)_2]$. In agreement with this projection, Kiwi-Minsker et al. have demonstrated that the exposure of low-Fe content H-ZSM-5 to water vapor at 523 K following the pretreatment for 8 h at 1323 K reduces the value of O/Fe from ∼1.0 to ∼0.5.

An experiment was performed in which surface oxygen was loaded on the sample at 528 K by N_2O decomposition, after which the sample was purged in He and heated from 528 to 773 K in He at 30 K/min while monitoring the effluent from the reactor using mass spectrometry. As shown in Fig. 6, O_2 is observed to desorb from the sample with a peak in the O_2 signal centered at 610 K. The total amount of O_2 desorbed corresponds to 0.013 O_2/Fe or 0.13 O_2/Fe_{active}. In a similar experiment Kiwi-Minsker et al. observed an O_2 desorption at a temperature of 666 K [11].

Several authors have proposed that N_2O decomposition proceeds via Reactions (1)–(3) [29,31,32]. In Reaction (1), N_2O adsorbs dissociatively on a vacant iron site, *, releasing a N_2 molecule and leaving an O atom on the site. In Reaction (2), a second N_2O molecule decomposes on the same site, so that now two O atoms are attached to the same site. These atoms recombine in Reaction (3) to form an O_2 molecule, which then desorbs from the iron site.

1. $N_2O + {}^* \rightarrow N_2 + O^*$
2. $N_2O + O^* \rightarrow N_2 + O^*O$

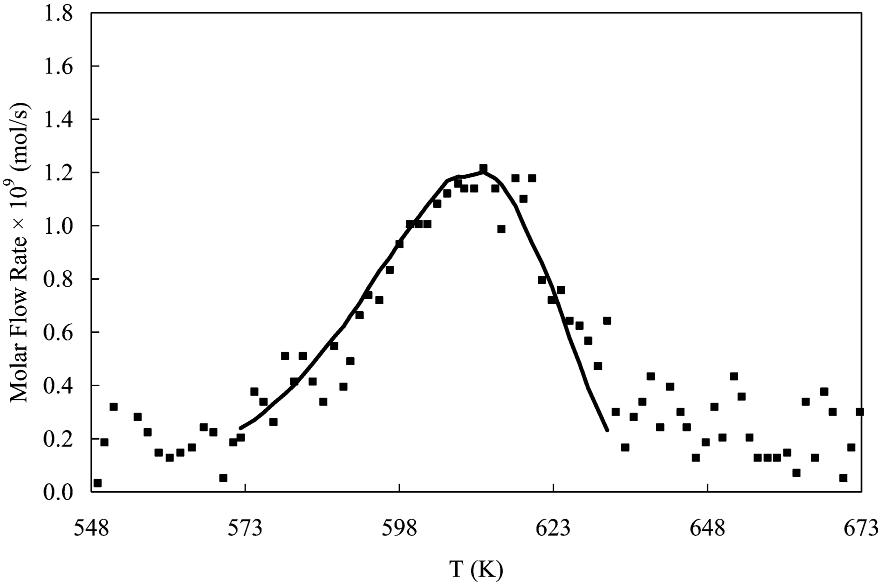

Fig. 6. TPD of O_2 in He following decomposition of 15,000 ppm N_2O in He over Fe-ZSM-5 at 528 K. The weight of catalyst used was 100 mg and the gas flow rate was 60 cm^3/min. The dots correspond to the experimental data and the solid line corresponds to a simulation of O_2 desorption based upon the rate parameters obtained from an analysis of the experimental data. The simulation was performed over the same temperature range used for the integration to determine the total amount of O_2 desorbed.

3. $O^*O \rightarrow {}^* + O_2$

In light of the above mechanism, we conclude that while most of the active Fe was loaded with only one O atom through Step 1, a small fraction (~13%) of the Fe in the sample is loaded with two O atoms, proceeding through Steps 1 and 2. This is consistent with theoretical calculations which show that the rate of Step 2 is much lower than that of Step 1 [32]. From Step 3 the rate of O_2 formation can be expressed as

$$r_{O_2} = k_3[O^*O], \tag{4}$$

where k_3 represents the rate constant for Step 3 and $[O^*O]$ represents the concentration of sites loaded with two O atoms. The value of k_3 can then be calculated from the data shown in Fig. 6 using Eq. (4). Fig. 7 shows a plot of $\ln(k_3)$ versus $1/T$. The slope of this line corresponds to the activation energy for O_2 desorption, 45.7 kcal/mol. The preexponential factor based on the total Fe in the sample is 8.9×10^{12} mol N_2O/(s mol Fe). The solid curve in Fig. 6 is based on a simulation of the data using the rate parameters obtained from an analysis of the data. The close agreement between experiment and theory demonstrates that the proposed model for O_2 desorption is reasonable.

It is noted that the activation energy for the recombinative desorption of O_2 is almost identical to the apparent activation energy for N_2O decomposition, 44.2 kcal/mol. This means that O_2 desorption is the most energetically demanding step in the mechanism N_2O decomposition and suggests that the fractional coverage of active Fe sites by O^*O should be substantial. Eq. (4) and the experimentally determined value of k_3 were used to calculate the fractional coverage of active Fe sites by two oxygen atoms at different temperatures during the temperature-programmed N_2O decomposition experiment shown in Fig. 1a. These calculations show that at 675 K, for example, $[O^*O]/Fe_{active} = 0.24$.

4. Conclusions

The decomposition of N_2O on Fe-ZSM-5 was investigated with the aim of identifying the fraction of Fe sites involved in the decomposition process and the rate parameters for some of the elementary steps. From transient-response experiments it was established that ~0.1 of all Fe sites in Fe-ZSM-5 are involved in N_2O decomposition. N_2 is formed by the dissociative adsorption of N_2O on either a vacant Fe site or one containing a single atom of oxygen. The rate coefficient for the first of these processes ($N_2O + {}^* \rightarrow N_2 + O^*$) has an activation energy of 16.8 kcal/mol and a preexponential factor of 1.4×10^1 mol N_2O/(s mol Fe_{total} Pa N_2O). O_2 desorption does not occur until two O atoms are associated with the same adsorption site. The activation energy for the associative desorption of O_2 is 45.7 kcal/mol and the preexponential factor is 8.9×10^{12} mol O_2/(s mol Fe_{total}). The apparent activation energy for steady-state decomposition of N_2O is 44.2 kcal/mol and the associated preexponential factor is 9.9×10^8 mol N_2O/(s mol Fe_{total} Pa N_2O) assuming that all Fe sites are active, and is a factor of 10 higher if it is based on the fraction of active Fe sites, 0.1.

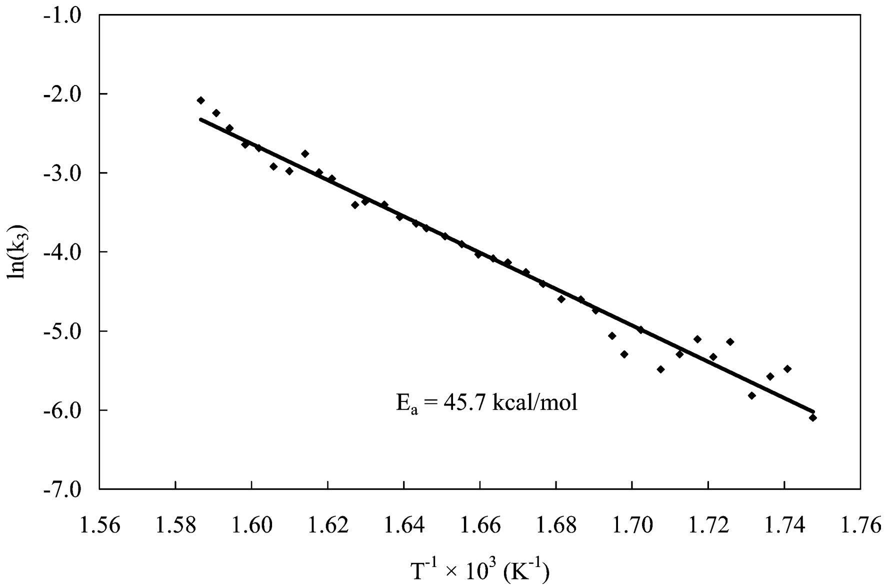

Fig. 7. Plot of $\ln(k_3)$ vs $1/T$.

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References

[1] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, J. Mol. Catal. 61 (1990) 85.
[2] F. Kapteijn, G. Marbán, J. Rodriguez-Mirasol, J.A. Moulijn, J. Catal. 167 (1997) 256.
[3] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.
[4] C. Sang, C.R.F. Lund, Catal. Lett. 70 (2000) 165.
[5] E.M. El-Malki, R.A. van Santen, W.M.H. Sachtler, Micropor. Mater. 35-36 (2000) 235.
[6] E.M. El-Malki, R.A. van Santen, W.M.H. Sachtler, J. Catal. 196 (2000) 212.
[7] C. Sang, C.R.F. Lund, Catal. Lett. 73 (2001) 73.
[8] B.R. Wood, J.A. Reimer, A.T. Bell, J. Catal. 209 (2002) 151.
[9] Q. Zhu, B.L. Mojet, R.A.J. Janssen, E.J.M. Hensen, J. van Grondelle, P.C.M.M. Magusin, R.A. van Santen, Catal. Lett. 81 (2002) 205.
[10] J. Pérez-Ramírez, F. Kapteijn, J.C. Groen, A. Doménech, G. Mul, J.A. Moulijn, J. Catal. 214 (2003) 33.
[11] L. Kiwi-Minsker, D.A. Bulushev, A. Renken, J. Catal. 219 (2003) 273.
[12] K.A. Dubkov, V.I. Sobolev, G.I. Panov, Kinet. Catal. 39 (1998) 72.
[13] K.A. Dubkov, V.I. Sobolev, E.P. Talsi, M.A. Rodkin, N.H. Watkins, A.A. Shteinman, G.I. Panov, J. Mol. Catal. A: Chem. 123 (1997) 155.
[14] L.V. Pirutko, V.S. Chernyavsky, A.K. Uriarte, G.I. Panov, Appl. Catal. A 227 (2002) 143.
[15] A.A. Ivanov, V.S. Chernyavsky, M.J. Gross, A.S. Kharitonov, A.K. Uriarte, G.I. Panov, Appl. Catal. A 249 (2003) 327.
[16] V.I. Sobolev, K.A. Dubkov, O.V. Panna, G.I. Panov, Catal. Today 24 (1995) 251.
[17] G.I. Panov, V.I. Sobolev, K.A. Dubkov, V.N. Parmon, N.S. Ovanesyan, A.E. Shilov, A.A. Shteinmen, React. Kinet. Catal. Lett. 61 (1997) 251.
[18] R. Joyner, M. Stockenhuber, J. Phys. Chem. B 103 (1999) 5963.
[19] A.A. Battiston, J.H. Bitter, D.C. Koningsberger, Catal. Lett. 66 (2000) 75.
[20] A.A. Battiston, J.H. Bitter, D.C. Koningsberger, J. Catal. 218 (2003) 163.
[21] P. Marturano, L. Drozdová, A. Kogelbauer, R. Prins, J. Catal. 192 (2000) 236.
[22] P. Marturano, L. Drozdová, G.D. Pirngruber, A. Kogelbauer, R. Prins, Phys. Chem. Chem. Phys. 3 (2001) 5585.
[23] J. Jia, Q. Sun, B. Wen, L.X. Chen, W.M.H. Sachtler, Catal. Lett. 82 (2002) 7.
[24] K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon, G.I. Panov, J. Catal. 207 (2002) 341.
[25] L.J. Lobree, I.C. Hwang, J.A. Reimer, A.T. Bell, J. Catal. 186 (1999) 242.
[26] S.H. Choi, B.R. Wood, J.A. Ryder, A.T. Bell, J. Phys. Chem. B 107 (2003) 11843.
[27] S.H. Choi, B.R. Wood, A.T. Bell, M.T. Janicke, K.C. Ott, J. Phys. Chem. B., submitted for publication.
[28] E.M. Flanigen, R.L. Patton, US patent 4,073,865 (1976).
[29] J.A. Ryder, A.K. Chakraborty, A.T. Bell, J. Phys. Chem. B 106 (2002) 7059.
[30] W.-Z. Liang, A.T. Bell, M. Head-Gordon, A.K. Chakraborty, J. Phys. Chem. B, in press.
[31] A.L. Yakovlev, G.M. Zhidomirov, R.A. van Santen, Catal. Lett. 75 (2001) 45.
[32] J.A. Ryder, A.K. Chakraborty, A.T. Bell, J. Catal. 220 (2003) 84.