Interaction of N₂O at low temperatures (473–603 K) with Fe-ZSM-5 zeolites (Fe, 0.01–2.1 wt %) activated by steaming and/or thermal treatment in He at 1323 K was studied by the transient response method and temperature-programmed desorption (TPD). Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) of NO adsorbed at room temperature as a probe molecule indicated heterogeneity of surface Fe(II) sites. The most intensive bands were found at 1878 and 1891 cm⁻¹, characteristic of two types mononitrosyl species assigned to Fe²⁺(NO) involved in bi- and oligonuclear species. Fast loading of atomic oxygen from N₂O on the surface and slower formation of adsorbed NO species were observed. The initial rate of adsorbed NO formation was linearly dependent on the concentration of active Fe sites assigned to bi- and oligonuclear species, evolving oxygen in the TPD at around 630–670 K. The maximal coverage of a zeolite surface by NO was estimated from the TPD of NO at ~700 K. This allowed the simulation of the dynamics of the adsorbed NO formation at 523 K, which was consistent with the experiments. The adsorbed NO facilitated the atomic oxygen recombination/desorption, the rate determining step during N₂O decomposition to O₂ and N₂, taking place at temperatures ≥563 K.

1. Introduction

\[ \text{N}_2\text{O} + (\text{Fe})_{\text{Fe}} \rightarrow \text{N}_2 + (\text{O})_{\text{Fe}} \]  

(1)

Recently, the evidence was presented that adsorbed NO and NO₂ species are also formed during N₂O interaction with Fe-ZSM-5 zeolites.¹⁻³ Thus, Grubert et al.³ by “in situ” FTIRS observed the formation of adsorbed NO on Fe(II) sites of Fe-ZSM-5 and Fe-MCM-41 during an interaction with N₂O at room temperature. El-Malki et al.²,⁴ also observed at 473 K surface nitro- and nitrate groups formation from N₂O similar to those obtained by direct interaction of a NO/O₂ mixture with the catalysts prepared by sublimation of FeCl₃ onto ZSM-5. The temperature-programmed desorption (TPD) of NO from the catalysts exposed to N₂O gave an NO peak with a maximum at around 653 K.² Mauvezin et al.⁵ observed an evolution of NO at around 600 K during the temperature-programmed reduction of Fe-β zeolites with hydrogen after their oxidation in N₂O. Novakova et al.⁹ observed the formation of NO and NO₂ in TPD performed after N₂O decomposition over Fe-ferrierite at 553 K. In line with all these results, we found¹ that adsorbed NO species are slowly accumulated on the surface of Fe-ZSM-5 catalyst with low iron content and strongly affect the dynamics of N₂O decomposition, leading to an increase of the reaction rate with time.

Reaction 2 is often considered as responsible for the formation of NO/NO₄ surface species:

\[ 2\text{N}_2\text{O} \rightarrow 2\text{NO} + \text{N}_2 \]  

(2)

The active sites are related to iron, but their nature is still not clear because of the complexity of the state of iron in zeolites. Framework Fe(III) species, surface extraframework isolated bi- and oligonuclear Fe(II) sites and bulk Fe₂O₃/Fe₃O₄ nanoparticles have been reported to be present in the samples, depending on iron content and zeolite pretreatment.

Fe-containing zeolites are not unique for the NO formation from N₂O. Evolution of gaseous NO/NO₂ was observed during the TPD after the contact of N₂O with Cu-ZSM-5 catalysts at 598 K. However, with Cu-mordenite and Cu-Y zeolites, this was not the case.⁶ Traces of gaseous NO/NO₂ were also detected during the N₂O decomposition to O₂ and N₂ over Cu-ZSM-5 zeolites.⁷⁻⁸

The formation of adsorbed NO from N₂O attracts much attention because this species promotes the N₂O decomposition to O₂ and N₂ over Fe-ZSM-5 catalysts.¹⁻¹⁻¹⁶ The decomposition involves the formation of surface atomic oxygen from N₂O (reaction 1), followed by its recombination with desorption as the rate-determining step

\[ 2(\text{O})_{\text{Fe}} \rightarrow \text{O}_2 + 2(\text{O})_{\text{Fe}} \]  

(3)

This step is facilitated by adsorbed NO, accelerating the overall reaction:¹⁻¹¹

\[ 2(\text{O})_{\text{Fe}} + [\text{NO}] \rightarrow \text{O}_2 + [\text{NO}] + 2(\text{O})_{\text{Fe}} \]  

(3a)

Recently, we proposed a kinetic model for N₂O decomposition by taking into account the formation of adsorbed NO promoting the N₂O decomposition to O₂ and N₂.¹⁷ The present work aims to clarify the regularities of the adsorbed NO formation on Fe-ZSM-5 zeolites from N₂O. The surface iron sites in Fe-ZSM-5 catalysts are characterized by the adsorption of NO as a probe molecule at room temperature controlled by DRIFTS. The total amount of surface Fe(II) sites is determined by the transient response method at 523 K. The amount of Fe-
TABLE 1: Main Characteristics of the Studied Fe-ZSM-5 Catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Fe loading wt %</th>
<th>Si/Al ratio</th>
<th>steaming</th>
<th>time of activation in He at 1323 K, h</th>
<th>iron active sites × 10⁻¹⁸, sites g⁻¹</th>
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<tbody>
<tr>
<td>ZSM-5₁₁₀</td>
<td>0.011</td>
<td>42</td>
<td>-</td>
<td>1</td>
<td>0.062</td>
</tr>
<tr>
<td>ZSM-5₁₁₀</td>
<td>0.011</td>
<td>42</td>
<td>-</td>
<td>20</td>
<td>0.021</td>
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<tr>
<td>ZSM-5₁₁₅</td>
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<td>25</td>
<td>20</td>
<td>1</td>
<td>0.55</td>
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<tr>
<td>ZSM-5₂₀₀</td>
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<td>42</td>
<td>+</td>
<td>20</td>
<td>2</td>
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<tr>
<td>ZSM-5₃₀₀</td>
<td>0.03</td>
<td>47</td>
<td>+</td>
<td>20</td>
<td>0.83</td>
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<tr>
<td>ZSM-5₅₅₀</td>
<td>0.035</td>
<td>42</td>
<td>-</td>
<td>1</td>
<td>2.8</td>
</tr>
<tr>
<td>ZSM-5₅₇₀</td>
<td>0.035</td>
<td>42</td>
<td>+</td>
<td>1</td>
<td>3.0</td>
</tr>
<tr>
<td>ZSM-5₅₉₅₀</td>
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<td>25</td>
<td>-</td>
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<td>2.1</td>
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<tr>
<td>ZSM-5₅₉₈₀</td>
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<td>25</td>
<td>+</td>
<td>1</td>
<td>3.9</td>
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<tr>
<td>ZSM-5₅₉₈₀</td>
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<td>25</td>
<td>+</td>
<td>11</td>
<td>11.3</td>
</tr>
<tr>
<td>2.1%Fe−ZSM-5₅₅₀</td>
<td>0.58</td>
<td>25</td>
<td>+</td>
<td>11</td>
<td>6.3</td>
</tr>
<tr>
<td>Activated by Steaming and Thermal Treatment in He at 823 K</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ZSM-5₅₉₅₀</td>
<td>0.035</td>
<td>42</td>
<td>+</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>ZSM-5₅₉₈₀</td>
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<td>25</td>
<td>+</td>
<td>0</td>
<td>7.3</td>
</tr>
<tr>
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<td>25</td>
<td>+</td>
<td>28.9</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Catalysts were characterized by "in situ" DRIFTS of adsorbed NO at 303 K. A Perkin-Elmer 2000 FTIR spectrometer with an MCT detector was used. The catalyst (~0.015 g) ground in an agate mortar was placed into a SpectraTech 003–102 DRIFTS cell with CaF₂ windows in a setup described earlier. The setup allowed quick switching between two flows, one with pure Ar, another containing 0.5 vol % of NO in Ar. The flow rate was equal to 20 mL (STP)/min. The spectra of the nitrosyl region (1740–1940 cm⁻¹) were almost identical during 2–6 min in NO. After 6 min, the flow passing through the catalyst was switched back to Ar. The DRIFT spectra obtained by averaging of 32 scans with a resolution of 4 cm⁻¹ were taken every 0.5 min. Before every run, the activated catalysts were pretreated in the cell in Ar at 823 K for 60 min. A single beam spectrum of the catalyst before introduction of NO into the cell at the interaction temperature was taken as a background. The contribution of the gaseous NO to the spectra was negligible, as shown by measuring the spectra of the mixture containing 0.5 vol % NO over KBr.

2.3. Transient Response and TPD Measurements. Transient response and TPD experiments were performed in a Micromeritics AutoChem 2910 analyzer. A ThermoStar 200 (Pfeiffer Vacuum) quadrupole mass spectrometer was used for gas analysis. Calibrations were carried out with gas mixtures of known compositions. The following peaks were controlled simultaneously by the mass spectrometer (4 (He), 18 (H₂O), 28 (N₂, N₂O), 30 (NO, N₂O), 32 (O₂), 40 (Ar), 44 (N₂O), and 46 (NO₂) m/z). The lines in the setup as well as a fused silica capillary connected to the mass spectrometer were heated to 383 K. Sometimes, a NO detector (EcoPhysics CLD 822) with a sensitivity of ±10 ppm of NO₃ was used to identify the nitrogen oxides at the reactor outlet.

The amount of a catalyst placed in a quartz plug-flow reactor was equal to 0.5–1.0 g. Before every run, the activated catalysts were pretreated in He (50 mL/min) at 823 or 1323 K for 1 h (Table 1), then cooled to the studied temperature.

In the transient response experiments, normally a 2 vol % N₂O/2 vol % Ar/96 vol % He mixture was used. Argon was introduced to the mixture as an inert tracer. Other mixtures containing 1.3 and 0.7 vol % of N₂O were created by dilution with He in the Micromeritics 2910 analyzer. The same total flow rate was used for all gas compositions (20 mL (STP)/min).

Two methods for the determination of the Fe(II) sites were
applied with a Micromeritics AutoChem 2910 analyzer as described elsewhere. They were based on the total amount of oxygen loaded from N_2O on a zeolite (N_2 formed in reaction 1, C_{Fe} in Table 1) and on the amount of oxygen desorbed at 630–670 K after the N_2O interaction for 5 min (reaction 3, C_{Fe}^{TPD}, Table 1). It was shown earlier that these two methods give different amounts of Fe sites: C_{Fe} > C_{Fe}^{TPD}.

NO interaction with a catalyst was performed for 5 min with a 0.5 vol % NO/0.5 vol % Ar/99 vol % He mixture. After N_2O or NO reacted with the catalyst, the reactor was purged by He for 10 min, and temperature-programmed desorption (TPD) was performed in He (20 mL/min, STP) with a 30 K/min ramp. Gas purities were higher than 99.998%, except for NO, which was >99.9%.

3. Results

3.1. NO Adsorption on the Surface Iron Sites. The iron sites were probed by infrared spectroscopy of adsorbed NO at room temperature. This is a developing method for the iron sites characterization in zeolites, which gives some hints concerning their oxidation state, nuclearity, and coordination. The DRIFT spectra presented in Figure 1a were obtained for the catalysts prepared by different methods, such as hydrothermal synthesis and postsynthesis iron deposition (2.1%Fe-ZSM-5) (Table 1). The spectra of the nitrosyl region obtained after 6 min of the NO (0.5 vol %) interaction with zeolites at 303 K in the presence of gaseous NO were similar. They showed two strong bands at 1891 and 1878 cm^{-1} with the same ratio of intensities and weak bands at 1819 and 1806 cm^{-1} (Figure 1a). Only the former species were stable in a flow of Ar at room temperature. The nitrosyl species characterized by the region of 1870–1890 cm^{-1} were found also stable in the presence of 0.5 vol % NO at a temperature as high as 603 K.

The two strong bands at 1870–1890 cm^{-1} were observed earlier for different Fe-ZSM-5 samples. However, two strong bands at 1856 and 1882 cm^{-1} or only one band at around 1880 cm^{-1} were also reported. The differences could be due to different NO partial pressures, time-on-stream, temperature, conditions of catalysts synthesis, activation, and pretreatments. The two species giving the bands at 1870–1890 cm^{-1} were reported to possess high, but quite similar thermal stability. In accordance with our data, the two species were found stable in the presence of 0.5% NO/He at 673 K and in He at 573 K. However different reactivity of these two species with oxygen was reported, indicating different species responsible for two bands.

The catalyst activation and pretreatments used in the present work implied the formation of extraframework iron, its autoreduction to the Fe(II) state, and dehydroxylation. It was observed that the intensity of the bands at 1870–1890 cm^{-1} increased after the thermal treatment of hydrothermally synthesized ZSM-5 samples in He at 1323 K as compared to the thermal treatment at 823 K. This suggests that the high-temperature treatment increases the amount of sites responsible for NO adsorption. The band intensities of adsorbed NO (1870–1890 cm^{-1}) increased with the number of active iron sites involved in the surface oxygen loading presented in Table 1 as C_{Fe}. Up to 80% of iron content in the sample ZSM-5 was able to load oxygen, indicating that iron in this sample was mainly in the Fe(II) state before the NO adsorption. Additionally, it is known that the adsorption of NO on Fe(III) sites is much weaker than on Fe(II) sites. Hence, the detected nitrosyl species are assigned to iron in the state Fe(II). In accordance, no band in the region 1870–1890 cm^{-1} was observed for the similarly treated Fe_2O_3 (Fluka, >99%) or Fe_2(SO_4)_3·aq (Fluka) dehydrated at 373 or 473 K.
A discrepancy is in the literature concerning the coordination and nuclearity of the iron sites responsible for the 1870–1890 cm⁻¹ region. These sites were assigned to isolated iron sites located in β positions of zeolite;²³,³⁰ however, a detailed analysis showed that oligonuclear species are more probable,²,²⁵,²⁶,³⁴ These species were also associated with the extraframework Fe species attached to Al cations via bridging oxygen atoms²⁵ because the bands in this region were not observed for Fe-silicalites without aluminum.²²,²⁵ Hence, the bands in this region were assigned to mononitrosyl Fe²+(NO) species involved in surface bidentonuclear iron species, probably with aluminum in vicinity.

As the species with the bands at 1891 and 1878 cm⁻¹ were stable without gaseous NO at room temperature, the unstable species could be distinguished. The spectrum after the subtraction of the stable species bands is very weak (Figure 1b). The species could be distinguished. The band assigned earlier to mononitrosyl Fe²+NO) species. It is evident that the iron species accepting two or three NO molecules should possess high coordinative unsaturation and are probably isolated,²²,²⁶,³⁵ The band at around 1770 cm⁻¹, accompanied²²,³⁵ or not accompanied²⁹,³⁰ by the 1845 cm⁻¹ band assigned earlier to dinitrosyls or mononitrosyls, respectively, was not observed in the present study.

The bands in the range of 1860–1840 cm⁻¹ seen on Figure 1b were assigned earlier to mononitrosyls Fe²+(NO)²⁴,²⁹,³⁰,³⁴ or trinitrosyl Fe²+(NO)³²²,²⁶,³⁴ species. It is evident that the iron species accepting two or three NO molecules should possess high coordinative unsaturation and are probably isolated,²²,²⁶,³⁵ The band at around 1770 cm⁻¹, accompanied²²,³⁵ or not accompanied²⁹,³⁰ by the 1845 cm⁻¹ band assigned earlier to dinitrosyls or mononitrosyls, respectively, was not observed in the present study.

From the DRIFTS experiments, it follows that Fe(II) species in the studied zeolites are not uniform. A comparison of the relative band intensities with the literature data²²,²⁹,³⁰,³⁵ shows that the intensity of the bands shown in Figure 1b are extremely weak with respect to the bands of 1878 and 1891 cm⁻¹. Hence, the concentration ratio of the isolated iron species responsible for the bands in Figure 1b to other species present (bi- and oligonuclear, probably with aluminum in vicinity) is small, if not negligible, for the studied samples.

### 3.2. NO Formation from N₂O

N₂O interaction with different Fe–ZSM-5 catalysts (Table 1) was studied by the transient response method, followed by the TPD in He. It is seen in Figure 2a that, after the N₂O introduction, the N₂O-concentration curve is shifted with respect to the inert tracer (Ar). This shift is due to N₂O reversible adsorption and its transformation to atomic surface oxygen and gaseous N₂.¹⁸ Nitrogen was the only gaseous product observed. No gaseous NO/NO₂ formation was detected by the NO₂ detector (± 10 ppm sensitivity). The amount of N₂ evolved was used to estimate the total amount of surface Fe(II) sites involved in oxygen loading (C³⁰Fe, Table 1). This assignment is formal: N₂ appears as an asymmetric peak with a tailing up to 200 s. This shape of the N₂ response could not be described by the rate of reaction 1 on a single type of sites. The response pattern suggests also another source of N₂ formation.

After 5 and 65 min of interaction of the gas mixture containing 2 vol % of N₂O with the ZSM-5 catalyst at 523 K and He purge, the TPD runs were performed (Figure 2b). It is seen that adsorbed NO and oxygen loaded during the N₂O interaction could be removed from the surface during the TPD with the peaks at around 700 K for NO and 630–670 K for oxygen. The amount of iron sites able to desorb oxygen (C³⁰Fe, Table 1) was lower than the total amount of iron sites involved in the oxygen loading from N₂O (C³⁰Fe, Table 1). This indicates that iron sites of a different nature are present. Some of them could accept oxygen from N₂O, but cannot evolve O₂ at 630–670 K in the TPD. Another reason for this difference could be due to N₂ release during the surface NO formation from N₂O:

\[ 2\text{N}_2\text{O}_{\text{ads}} \rightarrow \text{N}_2 + 2\text{NO}_{\text{ads}} \]  \hspace{1cm} (4)

It is seen from Table 1 that the thermal activation of the same zeolite synthesized by the hydrothermal method at 1323 K provides a higher amount of active sites as compared to the activation by steaming and heating at 823 K. The catalyst prepared by postsynthesis iron deposition (2.1%Fe/ZSM-5) is almost not sensitive to the activation temperature. The gap between C³⁰Fe and C³⁰TPD is bigger for these catalysts, indicating that some Fe(II) is present in the form of iron oxide particles, which can load some oxygen from N₂O, but do not desorb it at 630–670 K. Long time activation of the ZSM-5 catalyst at 1323 K results in a decrease of the amount of active sites, contrary to the catalysts with much lower concentration of iron (ZSM-5).¹⁸,¹⁹ This can be a result of agglomeration of iron to inactive iron oxide particles.

The amount of NO accumulated on the surface increased almost 1 order of magnitude when the interaction time with N₂O increased from 5 to 65 min (Figure 2b). This increase was concomitant with a ~30 K shift of the oxygen TPD peak to lower temperatures, indicating an easier desorption of oxygen due to NO in agreement with our earlier data.¹ It is important that the amount of O₂ desorbed in the TPD run remained independent of the time of N₂O interaction with the zeolite. The time dependences of the NO amount accumulated on ZSM-
5350 and ZSM-5200 catalysts during the interaction with N2O are shown in Figure 3. The ZSM-5350 catalyst possessing a higher amount of active iron sites than the ZSM-5200 (Table 1) accumulates more NO formed from N2O during the same period. This suggests that the sites active in the NO formation are related to iron.

The N2O interaction with the ZSM-5350 catalyst was also performed at different temperatures to determine the amount of the accumulated, adsorbed NO. For this purpose, after 65 min of the reaction at the selected temperature (>523 K), the reactor was quickly cooled in the reaction mixture to 523 K, purged with He for 10 min, and the TPD was performed. The NO amount produced from N2O and accumulated on the surface was calculated and plotted as a function of temperature (Figure 4). It is seen that the concentration increases, reaching a maximum value equal to 1.5 × 10^18 molecules g⁻¹, which does not change in the range 563–603 K. The maximum value may correspond to the saturation of the sites, which adsorb NO irreversibly because desorption of NO starts only at higher temperatures (>653 K). The NO adsorption was also performed directly from gas phase on the ZSM-5350 catalyst to obtain a maximal amount of the sites. For this purpose, a mixture containing 0.5 vol % of NO was contacted with the catalyst for 5 min at 523 K, and after He purge, the TPD was performed. The amount of NO desorbed was equal to the amount of NO produced from N2O at temperatures 563–603 K. This value was 2 times higher than the concentration of adsorbed NO formed from N2O at 523 K for 65 min (Figure 4). These data indicate that the maximal concentration of sites, which adsorbed NO is equal to 1.5 × 10^18 sites g⁻¹, and that, after 65 min at 523 K, the produced NO from N2O was not sufficient to cover all sites. The maximum number of NO sites (CNOmax) was taken for kinetic modeling of N2O decomposition in our previous publication.17 This value corresponds to ~75% of the active Fe(II) sites determined by the TPD (CFeTPD = 2.0 × 10^19 sites g⁻¹).

Figure 5 shows the effect of the initial N2O concentration on the NO formation. In these experiments, the catalyst was contacted with the reaction mixture containing different concentrations of N2O (2, 1.3, and 0.7 vol %) at 523 K for 5 min, and then heated in the reaction mixture at 10 K/min. It is seen

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**Figure 3.** Time dependence of the adsorbed NO accumulation (CNO_{TPD}) from N2O (2 vol %) at 523 K on the ZSM-5350 and ZSM-5200 catalysts activated in He at 1323 K.

**Figure 4.** Dependence of the concentration of adsorbed NO species (CNO_{TPD}) accumulated on the ZSM-5350 catalyst during 65 min of the interaction with N2O (2 vol %) on the temperature. A result of direct adsorption of NO (0.5 vol %, 5 min) is shown for comparison.
that NO evolved in different amounts (Figure 5, inset). The higher the concentration of N₂O, the higher the amount of the evolved NO. Roughly linear first-order dependence is observed for the NO formation on the concentration of N₂O, as shown in Figure 5.

### 3.3. Rate of NO Formation from N₂O.

The N₂O interaction with different ZSM-5 catalysts (Table 1) was performed for 5 min at 523 K, and the amounts of adsorbed NO and loaded oxygen from N₂O were determined from the TPD profiles (Figure 2b). As the adsorption of NO is irreversible and is far from saturation of adsorption sites, the amount of adsorbed NO during 5 min of reaction of N₂O is proportional to the initial rate of its formation from N₂O. Thus, the rates were calculated for the samples with different concentrations of the active Fe(II) sites (Table 1).

A correlation of NO formation was found between the rate and the concentration of the sites evolving oxygen during the TPD at 630–670 K (C_{Fe}^{TPD}) and is presented in Figure 6. Neither oxygen nor NO were observed in the TPD after the N₂O interaction with the Fe₂O₃/Al₂O₃ catalyst (0.20 g, Fe 5 wt %) pretreated in the same way as the Fe–ZSM-5 samples.

Thus, iron oxide particles were not responsible for the NO formation/accumulation. On the contrary, the amount of adsorbed NO increased with the amount of Fe sites evolving oxygen at 630–670 K. It is interesting that the temperature of the zeolite activation (823 or 1323 K) had no effect on the observed dependence (Figure 6, triangles and squares), showing that the same sites were formed after both activations. The straight line indicates that the formation/accumulation of NO takes place either with participation of the sites responsible for oxygen desorption or on the sites related to them. The latter seems more probable, as for the ZSM-5₃₅₀ sample, the maximum coverage by NO equals only 75% from C_{Fe}^{TPD}. Additionally, as is seen from Figure 2b, the adsorbed NO does not block the sites for the oxygen loading from N₂O, as the concentration of oxygen in the TPD peak does not decrease when the NO concentration increases considerably. This conclusion corresponds to the reported data¹,¹¹ on the effect of NO in N₂O decomposition to O₂ and N₂, confirming noncompetitive adsorption.

### 4. Discussion

Adsorbed NO was found to be formed from N₂O during its interaction with Fe-containing ZSM-5 catalysts at low temper-
Surface NO Formation during N₂O Interaction with Fe–ZSM-5


Figure 7. The dynamics (simulated and measured) of adsorbed NO formation from N₂O (2 vol %, 523 K) related to the maximal NO coverage on the ZSM-550 and ZSM-520 catalysts activated in He at 1323 K.

atures (473–603 K). The accumulated amounts of NO do not correspond to an impurity in N₂O; in order to accumulate the determined amounts of NO (3.5 × 10¹⁷ NO molecules g⁻¹) during 5 min of the N₂O reaction with the samples with high iron content, N₂O should contain up to 0.5% of NO. This concentration could be easily monitored by the NO/NO₂ detector, but it was not the case. This is also in line with the observed dependence of the adsorbed NO concentration on the temperature (Figure 4). Additional evidence that NO is not present as an impurity in N₂O was obtained by the comparison of the oxygen dynamics curves at different temperatures,¹⁷ which were found to be dependent on the temperature. The increase of the reaction rate was more marked for higher temperatures, confirming the chemical interaction of N₂O with the surface leading to adsorbed NO, but not accumulation of NO impurity.

The amount of active iron sites, on which NO accumulation takes place, is generally low and does not exceed 3·10¹⁹ sites g⁻¹ (Table 1).²¹ A slow increase of the adsorbed NO concentration takes place during more than 1 h of the N₂O interaction with zeolite at 523 K (Figure 3). These species desorb at temperatures higher than 643 K (Figure 2b). The formation of NO species in the Fe–ZSM-5 samples was proportional to the N₂O concentration (Figure 5). Hence, the adsorbed NO species are quite difficult to detect during or after the N₂O decomposition performed over the Fe–ZSM-5 catalysts with low iron content, at low N₂O pressures, low time-on-streams, or temperatures higher than 643 K.

DRIFTS of adsorbed NO at room temperature (Figure 1a) shows heterogeneity of iron sites. Adsorbed NO was mainly presented by the species characterized by the bands at around 1870–1890 cm⁻¹ (Figure 1a). These species possessed high thermal stability, indicating strong interaction of NO with iron. Assignment of these bands to Fe(II) involved in bi- and oligonuclear sites associated with aluminum extrawork framework cations seems possible; however, this point requires further studies. The contribution of the sites with high coordinative unsaturation (probably isolated) is low.

Insight concerning the sites involved in NO formation by measuring the NO amount formed from N₂O on activated ZSM-5 catalysts with different acidity, amount of iron, and concentration of active iron sites (Table 1) was also obtained. It was demonstrated that there is a relationship between the iron sites, which form oxygen from N₂O desorbing at 630–670 K and the sites, which may form adsorbed NO from N₂O (Figure 6). Desorption of oxygen from isolated iron sites is more difficult than from bi and oligonuclear iron sites. Diffusion of one oxygen atom to another over the ZSM-5 surface is necessary in this case. Hence, the iron sites evolving oxygen at 630–670 K were assigned to bi- and/or oligonuclear ones.¹⁸,²¹ Thus, the initial rate of the adsorbed NO formation is proportional to the N₂O concentration (C₆O) and concentration of the iron sites evolving oxygen Cₑ转移:

\[ r _ {NO} ^ {0} \sim C _ {NO} C _ {Fe} ^ {TPD} \]  \hspace{1cm} (5)

Nitrogen evolution during the N₂O interaction accompanied by oxygen loading is finished within ~2 min (Figure 2), but the accumulation of the strongly adsorbed NO species was slow and was observed for more than 60 min (Figure 3). Hence, the step of N₂O decomposition to surface atomic oxygen and gaseous nitrogen is much faster than the accumulation of surface NO species and the oxidized iron sites (O)Fe could participate in the formation of adsorbed NO.

A simplified kinetic scheme of the N₂O interaction with Fe–ZSM-5 at low temperatures (≤563 K) can be presented as:

\[ N _ {2} O _ {gas} \rightarrow N _ {2} O _ {ad} \]  \hspace{1cm} (reversible adsorption) instantaneous \hspace{1cm} (6)

\[ N _ {2} O _ {ad} + ( ) _ {Fe} \rightarrow N _ {2} + (O) _ {Fe} \]  \hspace{1cm} (deposition of oxygen) fast \hspace{1cm} (7)

\[ N _ {2} O _ {ad} + (O) _ {Fe} \rightarrow 2[NO] ^ {'} + ( ) _ {Fe} \]  \hspace{1cm} (formation of surface NO) relatively fast \hspace{1cm} (8)

\[ [NO] ^ {'} \rightarrow [NO] \]  \hspace{1cm} (accumulation of catalytic NO) slow \hspace{1cm} (9)

Step 6 corresponds to reversible adsorption of N₂O, followed by the surface atomic oxygen loading, accompanied by N₂ evolution (step 7). The adsorbed NO, [NO]′, is formed in step 8, followed by the reaction 7 with participation of the liberated ( )Fe sites, additionally giving N₂ in the gas phase. Evidence for the relatively fast step 8 could come from the pattern of the N₂ response. During the N₂O interaction, nitrogen appears as an asymmetric peak with a tail up to 200 s. This shape of the N₂ response could not be described by only the rate constant of
the reaction 7. The response pattern suggests also another source of the N₂ formation and was proposed via reactions 8 and 7 together. Another reason for the tailing of the N₂ peak may come from the heterogeneity of the iron sites (DRIFTS) involved in the oxygen loading on the surface presented by reaction 7. Because the accumulation of NO at temperatures T ≤ 600 K is a slow process (Figure 3), a slow transformation of the [NO⁺] species to the [NO] species was suggested and described by the step 9.

The transformation of the adsorbed NO to adsorbed NO₂ species via the oxidation by the loaded oxygen can also take place.²,4,12,17 All of these factors are difficult to take into account for simulation of the adsorbed NO accumulation in time (Figure 3). It is important that a satisfactory description of the dynamics of the accumulation was obtained for two samples (Figure 7) by using a simple equation:

\[ C_{\text{NO}}^{\text{TPD}}/C_{\text{NOmax}}^{\text{TPD}} = 1 - \exp(-kt) \]  

implying that the slowest step of the NO adsorption/formation takes place on unoccupied sites. In this equation, t is the time-on-stream, and k represents the initial rate of the adsorbed NO formation related to the maximal concentration of the sites, which can adsorb NO (\( C_{\text{NOmax}}^{\text{TPD}} \)):

\[ k = r^0_{\text{NO}}/C_{\text{NOmax}}^{\text{TPD}} \]

where \( C_{\text{NOmax}}^{\text{TPD}} \) was assumed to be 75% from the amount of the sites that evolved oxygen at 630–670 K, \( C_{\text{Fe}}^{\text{TPD}} \), and was 1.5 × 10¹⁸ sites g⁻¹ for the ZSM-5:350 and 0.9 × 10¹⁸ sites g⁻¹ for the ZSM-5:200 sample. The k value was determined from Figure 6 and related to 75% of the \( C_{\text{Fe}}^{\text{TPD}} \), being equal to 0.0049 min⁻¹.

In our previous publications¹¹,¹⁷ a considerable increase of the N₂O decomposition rate in time until reaching a steady state at 563–603 K was shown and assigned to the accumulation of surface NO species catalyzing the reaction. This was in accordance with the adsorbed NO formation dynamics (Figures 3, 7). Direct introduction of the NO pulse into the N₂O mixture reacting with the ZSM-5:200 catalyst at 603 K provided an immediate reaching of a steady state.¹ Thus, the observed rate increase was assigned to autocatalysis by NO. The adsorbed NO could lead to an increase of the N₂O decomposition rate via a promotion of the oxygen desorption (reaction 3a), which is the rate-determining step. This step is not elementary and will be considered in detail in a forthcoming publication.

5. Conclusions

DRIFTS of adsorbed NO as a probe molecule at room temperature indicated different Fe(II) sites with a roughly similar ratio of concentrations in the studied zeolites. Adsorbed NO formation from N₂O was found to take place on Fe-ZSM-5 catalysts at 473–603 K. The initial rate of the NO formation at 523 K was observed to be first order in N₂O partial pressure and was linearly dependent on the concentration of active bi- and oligonuclear Fe(II) sites. The amount of these sites, \( C_{\text{Fe}}^{\text{TPD}} \), was determined by desorbing oxygen at 630–670 K after Fe(II) loading by atomic oxygen from N₂O at 523 K. Adsorbed NO species could be desorbed at around 700 K. The simulated dynamics of adsorbed NO formation from N₂O was consistent with the experimental data.

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Note Added after ASAP Publication. This article was published ASAP on December 8, 2005. The citation of ref 16 was changed to a citation of ref 17 in the paragraph following eq 9. The correct version was reposted on December 12, 2005.

References and Notes