FTIR Study of the Interaction of Nitric Oxide with Fe-ZSM-5[1]

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Abstract—The temporal behavior of infrared spectra obtained during NO adsorption on oxidized and reduced Fe-ZSM-5 at –100, 0°C, and ambient temperature is reported. The band assignment is made based on the adsorption of labeled molecules. Bands near 1838 and 1886 cm^{-1} (mononitrosyl Fe^{2+}(NO) species) form quickly and remain invariant. Bands at 1922 and 1813 cm^{-1} (dinitrosyl Fe^{2+}(NO)$_2$) together with a band at 1750 cm^{-1} (another mononitrosyl species) gradually become more intense for hours. Purging with He at 0–500°C leads to a gradual decrease in the intensity of all the bands. Mononitrosyl bands near 1886 and 1838 cm^{-1} are the most stable. The features of the IR spectra of adsorbed NO suggest the presence of dispersed Fe oxide clusters in the zeolitic pore network in addition to Fe^{2+} ions in cationic positions of ZSM-5.

INTRODUCTION

Many infrared investigations have been conducted to understand the interaction of NO with the transition metal-exchanged ZSM-5. Most of the studies have focused on Cu-ZSM-5 [1–9] because of its good performance in the selective catalytic reduction (SCR) of NO_x with C_{2+} hydrocarbons [10–18] and high activity for NO decomposition [4, 10, 19–25] and on Co-ZSM-5 [6, 26–28] because this material is active in NO_x SCR with CH_4 [6, 26, 27, 29–32]. However, it was reported that an Fe-ZSM-5 catalyst can be prepared that is very active in the NO_x SCR with *iso*-C_4H_{10} [33–37] and its catalytic performance is unaffected by the presence of high levels of water and sulfur dioxide [33, 34]. Fe-ZSM-5 has also shown superior activity and selectivity in NO SCR with NH_3 [38] and with C_3H_6 [39], N_2O SCR with C_3H_6 [40, 41], direct N_2O decomposition [28, 41–43], and benzene hydroxylation [44, 45]. Nevertheless, little spectroscopic information is available regarding the interaction of NO with adsorption sites in Fe-ZSM-5 [28, 46, 47].

Several studies have been conducted with FeY [46, 48–51] and FeMor [46]. The infrared spectra of NO adsorbed on FeY consist of bands assigned to mononitrosyl and dinitrosyl complexes of Fe^{2+}. Bands of mononitrosyls form quickly and remain invariant, whereas the bands of dinitrosyls increase in intensity over periods of hours. These observations were rationalized in terms of the different accessibility of Fe^{2+} ions at different sites of zeolite Y to gaseous NO [46, 51]. Those Fe^{2+} cations of low coordination, which were accessible to gaseous NO (at sites II and II'), formed mononitrosyl complexes. Ferrous cations of high coordination formed dinitrosyl complexes by migrating to sites of high accessibility.

The present work is an infrared investigation of NO adsorbed upon Fe-ZSM-5. Since the goal of this paper is to assign nitrosyl complexes of Fe-ZSM-5 associated with bands in the 1920–1750 cm^{-1} range, only assignment of these bands is considered. The origin of the band at 2133 cm^{-1} was discussed by Hadjiivanov *et al.* [52] and assigned to NO^+ species occupying cationic positions of the zeolite. The bands at 1602 and 1547 cm^{-1} have been previously assigned to the nitrate species with a different coordination to the metal cation [53–57]. The band near 1640 cm^{-1} of varying intensity present in all spectra belongs to water accumulated on the sample wafer from flowing gases. This assignment is supported by the absence of a band shift when labeled NO was adsorbed.

EXPERIMENTAL

An Fe-ZSM-5 zeolite that was prepared by ion exchange of Na-ZSM-5 (Grace Davison, lot. no. SMR5-6758-1296) with iron(II) oxalate was used for the present investigation. The material was provided by Professor W. Keith Hall (Department of Chemistry at the University of Pittsburgh), and details of the preparation procedure are provided elsewhere [34]. The ion-exchanged zeolite is denoted as Fe-ZSM-5-11-50, where the numbers are the cation-type of zeolite, Si/Al ratio, and Fe exchange percentage. The percentage of Fe exchanged is based on the assumption that one Fe^{2+} is incorporated at the expense of two Na^+. The final catalyst was analyzed for Fe, Si, Al, and Na at Galbraith Laboratories. This established a unit cell composition of $(FeOH)_2Na_{0.24}H_{5.76}Al_8Si_{88}O_{192}$.

Infrared spectra were recorded using a Research Series II FTIR spectrometer (Mattson, Inc.) equipped with a liquid N_2 cooled MCT detector. The resolution

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[1] This article was submitted by the authors in English.

was 4 cm^{-1} and 33 scans were accumulated per spectrum. The IR cell has been previously described in the literature [2]. It was equipped with CaF$_2$ windows and operated in the temperature range from –100 to 500°C.

A self-supporting wafer of approximately 10–20 mg/cm^2 was prepared by pressing the powdered material at 850 kg/cm^2 for 1 min. It was then placed onto a tungsten mesh located on a nickel sample holder in the cell.

The sample was pretreated *in situ* with flowing He (20 cm^3/min) while heating at a rate of 6°C/min from 25 to 400°C, and holding at that temperature for 2 h. Then, the sample was cooled in flowing He to a temperature at which NO was adsorbed. This pretreatment was repeated between each experiment. The spectrum of the pretreated sample in the presence of He was used as a background. In addition, both the oxidized and reduced forms of Fe-ZSM-5 were investigated. The former was obtained by exposure of the He-pretreated sample to 10% O$_2$/He at 500°C for 2 h and then cooled to room temperature before flushing with He for 1 h. The latter was prepared by H$_2$ treatment of the He pretreated sample at 300°C for 2 h, cooling to room temperature and subsequently flushing with He for 1 h.

To confirm the assignment of the IR bands, labeled NO was used. The gaseous mixture contained 0.1% ^{14}NO and 0.1% ^{15}NO in He.

All spectra were obtained while the adsorbate stream was flowing continuously at 20 cm^3/min through the IR cell at the desired temperature.

RESULTS

The temporal behavior of infrared spectra obtained from NO adsorbed on Fe-ZSM-5 during the continuous flow of 0.1% NO in He at –100°C is shown in Fig. 1. This low temperature was chosen to probe only the adsorption process and minimize the rate of possible reactions that could take place concomitantly. The adsorption of NO at –100°C resulted in intense bands at 2136, 1886, and 1813 cm^{-1}, less intense bands at 1838 (not completely resolved from the band at 1886 cm^{-1}), 1922, and 1750 cm^{-1}, a shoulder at 1787 cm^{-1}, and a low-intensity band at 1638 cm^{-1}. The latter band is probably due to a trace amount of water present in the NO + He mixture that accumulated on the zeolite surface during the course of the experiment. The bands at 1886 cm^{-1} (initially at 1889 cm^{-1}) and 1838 cm^{-1} reached a maximum intensity after 15 min and the former band remained invariant thereafter. The band at 1838 cm^{-1} was gradually obscured by an increase in the intensity of the absorption band at 1813 cm^{-1} and was not observed after 15 min on stream. The band is still present thereafter, as indicated by the lower wavenumber "tail" of the band at 1886 cm^{-1}. It is worth noting that the latter band is more asymmetric on the higher wavenumber side, viz, a less intense band near 1900 cm^{-1} may be encompassed by the intense band at 1886 cm^{-1}.
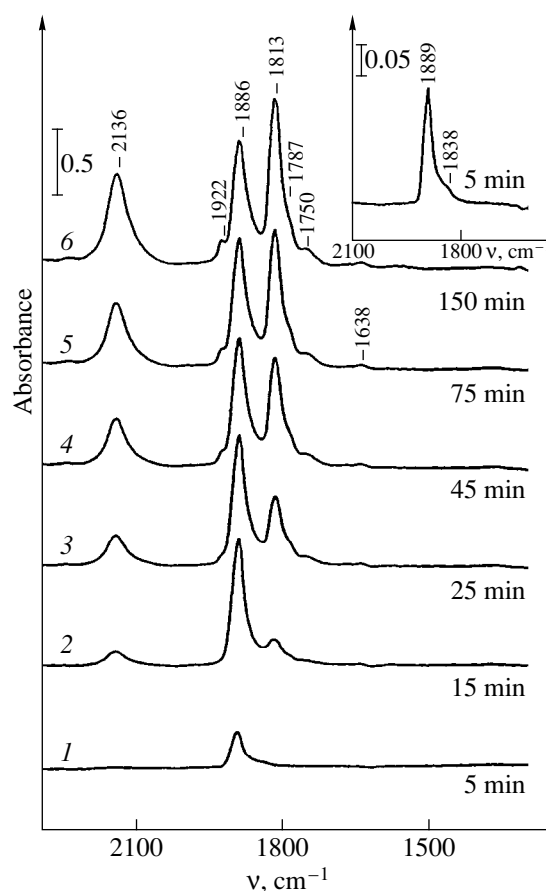

Fig. 1. The time evolution of infrared spectra obtained from NO adsorbed on Fe-ZSM-5-11-50 from 0.1% NO in He flow at –100°C: (*1*) 5, (*2*) 15, (*3*) 25, (*4*) 45, (*5*) 75, and (*6*) 150 min.

The intensities of the remaining bands at 2136, 1813, 1922, and 1750 cm^{-1} increased during the 150 min experiment. The intensities of the bands at 1922 and 1750 cm^{-1} both increased at the same rate. The intensities of the bands at 1922 and 1813 cm^{-1} also varied linearly, however, the intensity of the 1813 cm^{-1} band was 9 times greater than the 1922 cm^{-1} band. The relationship among the intensities of 1922 with 1813 and 1750 cm^{-1} bands as a function of time is shown in Fig. 2.

The infrared spectra obtained during NO adsorption on Fe-ZSM-5 at –100°C in a flow of 0.05% NO in a He mixture had the same set of bands and similar time evolution as in the case of the higher concentration of NO. However, a longer time was required for the bands to reach their maximum intensity.

An increase in the NO concentration in flowing He to 1% and in the adsorption temperature to 0°C led to the splitting of the band that was observed at 1886 cm^{-1} during NO adsorption at –100°C into bands at 1891 (shoulder), 1882, 1873, and 1867 (shoulder) cm^{-1}. Less intense bands at 1602 and 1547 cm^{-1} also emerged (Fig. 3, spectrum *1*). A comparison of the spectra pre-
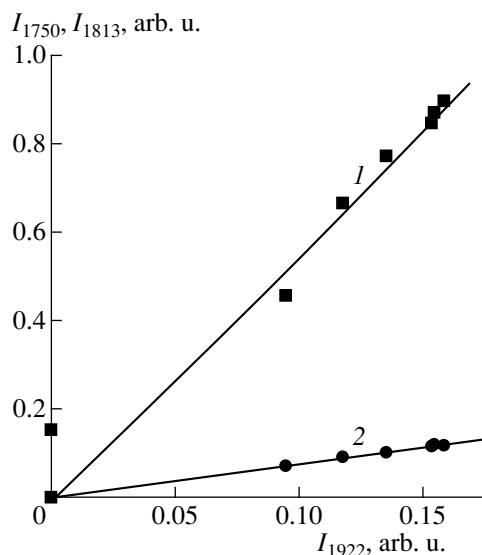
I_{1750}, I_{1813}, arb. u.

Fig. 2. Intensities of the bands at (*1*) 1813 and (*2*) 1750 cm^{-1} vs. the intensity of the band at 1922 cm^{-1} in the course of NO adsorption on Fe-ZSM-5-11-50 from a flow of 0.1% NO + He at –100°C.
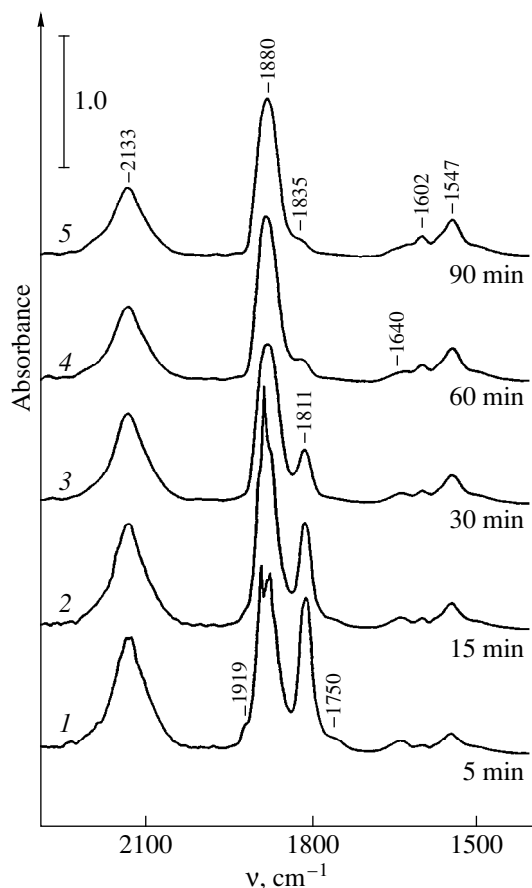

Fig. 3. Effect of the time of purging Fe-ZSM-5 wafer with He at 0°C on the intensities of bands in the infrared spectrum obtained after 2 h flow of the 1% NO in He mixture at the same temperature: (*1*) 5, (*2*) 15, (*3*) 30, (*4*) 60, and (*5*) 90 min.

sented in Fig. 1, and Fig. 3 shows that, for temperatures higher than –100°C and NO concentration above 0.1%, several bands shifted to lower wavenumbers, e.g., 2136 cm^{-1} shifted to 2133 cm^{-1}, 1886 to 1880 cm^{-1}, and 1813 to 1811 cm^{-1}.

Infrared spectra obtained upon switching the flow of 1% NO in He after 2 h to pure He are presented in Fig. 3. The bands at 1640, 1602, and 1547 cm^{-1} slightly increased during purging. The bands at 2133, 1919, 1813, and 1750 cm^{-1} decreased gradually after 90 min of purging; the latter three bands disappeared completely, while the intensity of the former band was halved. However, after 90 min a shoulder near 1835 cm^{-1} emerged. The intensity of the group of bands centered at approximately 1880 cm^{-1} first increased to a maximum during 15 min of purging and then decreased to 90% of their initial intensity, with the bands and shoulders forming a single broad band centered at 1880 cm^{-1}. The band at 1880 cm^{-1} was the most thermally stable. It disappeared completely only after a 15-min purging with He at 500°C in contrast to bands at 2136, 1602, and 1547 cm^{-1} that were eliminated after a 15-min purging at 200°C (Fig. 4).

Regardless of whether the sample was oxidized for 2 h with 10% O$_2$ in He at 500°C or reduced with pure H$_2$ at 300°C for 2 h before NO adsorption, the spectra were essentially the same. Figure 5 illustrates the results obtained with the oxidized and reduced samples after a 30-min NO exposure. Interestingly, the same bands were present in both spectra. However, the intensities of the 1880 and 1811 cm^{-1} bands were higher for the reduced sample than for the oxidized. In contrast, the bands at 2133, 1605, and 1555 cm^{-1} were more intense for the oxidized than for the reduced sample.

Figure 6 shows the time evolution of infrared spectra obtained for NO adsorbed on an Fe-ZSM-5-11-50 wafer from a 0.1% ^{14}NO and 0.1% ^{15}NO in a He mixture at room temperature and ambient pressure. Three intense overlapped bands at 1883, 1847, and 1804 cm^{-1} were present in the spectrum after 1 min. With an increase in exposure, less intense and poorly resolved bands at 1778, 1747, and 1712 cm^{-1} emerged. In addition, two broad overlapped bands at 2133 and 2100 cm^{-1} and a small band at 1640 cm^{-1} were also observed.

DISCUSSION

Iron has two stable oxidation states, Fe^{2+} and Fe^{3+} [58]. The reduction of Fe^{3+} to Fe^{2+} in zeolites Y, Mor, and ZSM-5 occurs readily, even by simple evacuation at elevated temperatures. The reverse process takes place in oxidizing media [48, 59–63]. However, Fe^{2+} cations are present in both reduced and oxidized materials [46, 62, 64, 65]. Aside from the band at 1910–1930 cm^{-1} assigned to a symmetric stretch of dinitrosyl Fe^{2+}(NO)$_2$ species, nitrosyl complexes of Fe in zeolites do not have vibration above 1900 cm^{-1} [28, 46, 48–51]. The same is true for iron oxide supported on silica [66] and

alumina [67]. Moreover, the pretreatment of these Fe-containing materials in oxygen at elevated temperatures followed by NO adsorption at ambient temperature results in a significantly lower intensity of all bands belonging to nitrosyl complexes [28, 51, 66–67].

The low intensity band at 1870 cm^{-1} of NO adsorbed on oxidized FeY was previously assigned to Fe^{3+}(NO) species [51]. There is good reason to question this assignment because a band in the same position is observed for the initial FeY with a much higher intensity [51]. Moreover, stoichiometric nitrosyl complexes of Fe^{3+} are known to have a greater than 1900 cm^{-1}. For example, NO in $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ absorbs at 1944 cm^{-1}, but few other examples are present in the literature [68]. This suggests that Fe^{3+} ions in zeolites are incapable of adsorbing NO. The results of the present investigation are consistent with the statement that coordinatively unsaturated Fe^{2+} ions are the sites for NO adsorption; the same set of absorption bands at the same position was observed in both reduced and oxidized Fe-ZSM-5 samples with band intensities in the vNO region being lower in case of the latter sample (Fig. 5).

The assignment of the bands observed during NO adsorption on different Fe-containing catalysts together with those of the present work is listed in the table. The spectra of adsorbed NO on zeolites Y, Mor, and supported Fe oxide consist of five bands: 1890–1870, 1845–1830, 1778–1750, 1930–1910, and 1822–1810 cm^{-1} [46, 48–51]. The first three bands are assigned to mononitrosyl species, with the band at 1890–1870 cm^{-1} absent in the case of non-zeolitic Fe-containing material. The last two bands are assigned to dinitrosyl complexes of adsorbed NO. Surprisingly, from the comparison of the results of the present investigation (Fig. 1 and the table) with spectra obtained by others for NO adsorbed on FeY, FeMor, and even on silica-supported iron oxide, all of the main bands (1922, 1880, 1838, 1813, and 1750 cm^{-1}) were almost at the same position. In contrast, Cu exchanged in ZSM-5 and Y zeolites shows a different behavior in their interaction with NO [2].

The adsorption of the $^{14}N^{16}O$ and $^{15}N^{16}O$ mixture (further NO + ^{15}NO) on Fe-ZSM-5 (Fig. 6) was employed to confirm the band assignments. At a short time-on-stream the spectrum of NO adsorbed on Fe-ZSM-5 at –100°C consists of two bands near 1889 and 1838 cm^{-1} (Fig. 1). One could expect that, at a short time, the spectrum of adsorbed NO + ^{15}NO mixture consists of at least four bands, two for NO and two for ^{15}NO complexes. This is observed (Fig. 6), but the band at 1838 cm^{-1} was obscured by the absorption band at 1847 cm^{-1}. Thus, the band at 1883 cm^{-1} in Fig. 6 for the unlabeled NO corresponds to the band at 1886–1889 cm^{-1} in Fig. 1, the band at 1847 cm^{-1} (Fig. 6) is the corresponding band for ^{15}NO. The band at 1804 cm^{-1} of ^{15}NO corresponds to the NO band at 1838 cm^{-1} in Fig. 1. Good agreement between the isotopic shifts of these bands and gaseous ^{14}NO and ^{15}NO (33 cm^{-1}) [69, 70]
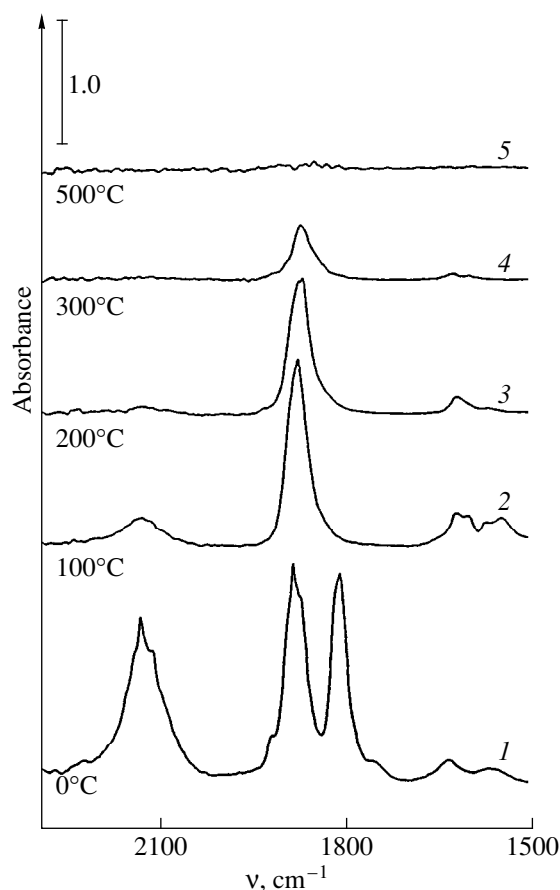

Fig. 4. Effect of temperature on the band intensities of the NO adsorbed on Fe-ZSM-5-11-50 wafer. After 2 h, a flow of 1% NO in He was switched to He only and spectrum *1* was recorded after 15-min He flow at the set up temperature followed by increasing temperature to the next set up value: (*2*) 100°C, (*3*) 200°C, (*4*) 300°C, and (*5*) 500°C.

allows these bands to be assigned to mononitrosyl complexes. The fact that the position of the band at 1889–1886 cm^{-1} in Fig. 1 is similar to the band position for FeY and FeMor [46, 49, 51, 71] provides evidence that this band belongs to NO adsorbed on Fe^{2+} occupying cationic positions of ZSM-5. Then, the band at 1838 cm^{-1} can be assigned to NO adsorbed on dispersed Fe oxide clusters formed during the calcination of Fe-ZSM-5 from either Fe^{2+} in the cationic position or from the traces of iron oxalate occluded in the zeolite pore network. The fact that the FeO_x species can exist in Fe-ZSM-5 was proven elsewhere [72, 73] by means of TPR, TEM, and EXAFS. It is worth noting that the mononitrosyl species for silica-supported iron oxide was observed at 1830 cm^{-1} [62].

The frequency difference between the less intense bands at 1747 and 1712 cm^{-1} that appeared at a longer time of contact of the NO + ^{15}NO mixture with Fe-ZSM-5 (Fig. 6) is 35 cm^{-1}. This difference of 35 cm^{-1} is almost the same as that observed for vNO of gaseous NO and ^{15}NO [69–70]. Hence, we can conclude that the
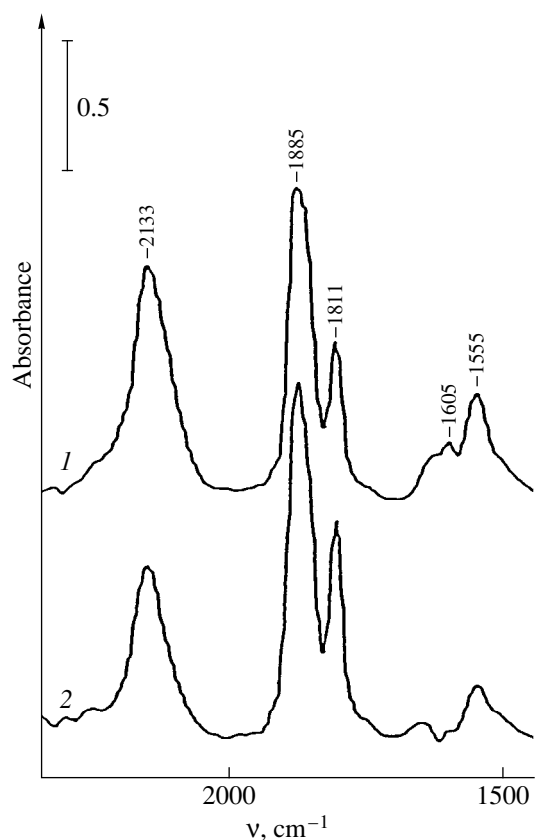
Fig. 5. IR spectra of NO adsorbed from a flow of 0.1% NO + He for 30 min at room temperature on (*1*) the oxidized (2 h at 500°C in a flow of 10% O_2 + He) and (*2*) reduced (2 h at 300°C in a flow of H_2) samples of Fe-ZSM-5-11-50.

Fig. 6. The time evolution of infrared spectra obtained from NO adsorbed on Fe-ZSM-5-11-50 wafer from a 0.1% ^{14}NO and 0.1% ^{15}NO in He mixture at room temperature and ambient pressure: (*1*) 1, (*2*) 8, (*3*) 15, (*4*) 25, and (*5*) 45 min.

band at 1750 cm^{-1} in Fig. 1 (an analog of the band at 1747 cm^{-1} in Fig. 6) belongs to another mononitrosyl complex of NO with Fe^{2+} in the cationic position of ZSM-5. Most likely it is low-spin complex, as it was proposed by Jermyn *et al.* for FeY [49].

Due to the overlapping of several bands in the spectra and to the high number of NO oscillators involved, experiments carried out with ^{14}NO/^{15}NO isotopic mixtures (Fig. 6) were not helpful in assigning the bands belonging to dinitrosyl species. Segawa *et al.* [51] assigned the bands at 1917 and 1815 cm^{-1}, which were present for NO adsorbed on FeY zeolite, to the symmetric and asymmetric stretching modes of iron dinitrosyl complexes. They based this assignment on the observation that the intensities of the 1917 and 1815 cm^{-1} varied linearly at different NO partial pressures, labeled NO experiments and the fact that upon evacuation the intensities of both bands associated with the dinitrosyl species decreased similarly. In the present work, the intensities of the 1922 and 1813 cm^{-1} bands varied linearly with increasing NO coverage (Fig. 2). Following the assignment of Segawa *et al.* for FeY, it is reasonable to suggest that the bands at 1922 and
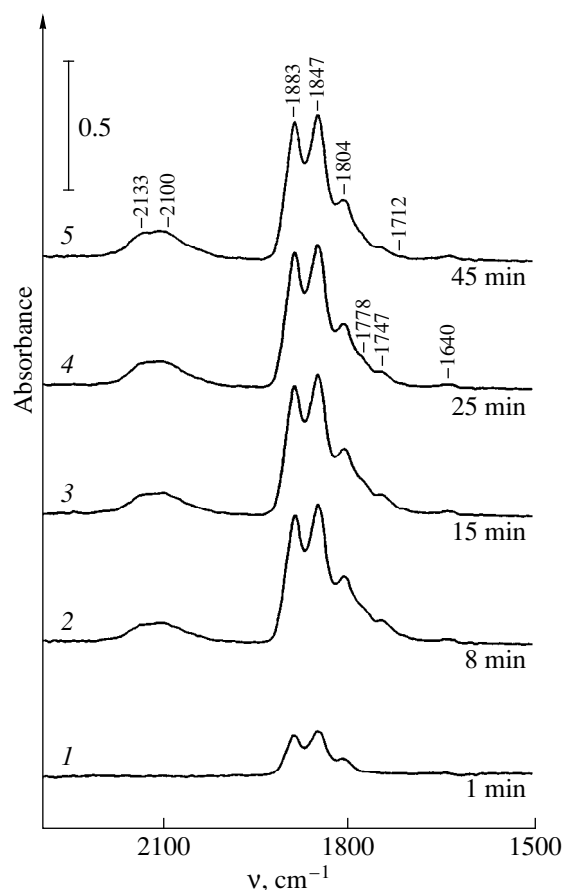
1813 cm^{-1} represent symmetric and asymmetric stretching vibrations of dinitrosyl species. In this regard, the shoulder at 1787 cm^{-1} (Fig. 1) may belong to the asymmetric vibration of dinitrosyl complexes of Fe^{2+} in oxide clusters with the symmetric band obscured by the 1886 cm^{-1} band.

The assignment of the shoulder at 1778 cm^{-1} (Fig. 6) can be made on the basis of the work of Segawa *et al.* [51]. After the adsorption of ^{15}NO on FeY the band at 1815 cm^{-1} observed with ^{14}NO and assigned to the asymmetric stretch of dinitrosyl shifted to 1778 cm^{-1}. Thus, most likely the shoulder 1778 cm^{-1} (Fig. 6) belongs to the asymmetric vibration of Fe^{2+}(^{15}NO)$_2$.

Figure 2 shows that the intensities of the bands at 1922, 1813, and 1750 cm^{-1} increased linearly with coverage. One could conclude that these bands belong to the same species, namely to trinitrosyl. Although trinitrosyl complexes of transition metal ions in zeolites have not been detected, Cu(I) in ZSM-5 forms tricarbonyls at temperatures below –100°C [3, 9, 74] and even a tetranitrosyl stoichiometric complex has been reported for Fe [75]. However, the linear correlation between the intensities of the bands at 1922, 1813, and

Frequencies of IR bands of NO adsorbed on Fe-containing zeolitic and oxide materials

Species	Catalyst	νNO, cm^{-1}	Reference
$Fe^{2+}(NO)$ (high spin complex)	FeY	1890	[49]
	FeY	1870	[51]
	FeY	1882	[46]
	FeY	1880	[71]
	FeMor	1882	[46]
	Fe-ZSM-5	1878	[37]
	Fe-ZSM-5	1880–1886	This work
	FeY	1845	[51]
	FeY	1850	[46]
	Fe-ZSM-5	1838	This work
	$Fe_2O_3(Fe_3O_4)/SiO_2$	1830	[66]
$Fe^{2+}(NO)_2$	FeY	1930, 1822	[49]
	FeY	1917, 1815	[51]
	FeY	1918, 1815	[46]
	FeMor	1918, 1815	[46]
	Fe-ZSM-5	1922, 1813	This work
	$Fe_2O_3(Fe_3O_4)/SiO_2$	1910, 1810	[66]
$Fe^{2+}(NO)$ (low spin complex)	FeY	1778	[49]
	FeY	1767	[51]
	FeY	1760	[46]
	FeMor	1760	[46]
	Fe-ZSM-5	1750	This work
	$Fe_2O_3(Fe_3O_4)/SiO_2$	1750	[66]

1750 cm^{-1} is likely a coincidence for several reasons. First, when ^{14}NO is substituted for the $^{14}NO + {}^{15}NO$ mixture, the band at 1750 cm^{-1} exhibits a shift characteristic of mononitrosyl (Fig. 6). Second, trinitrosyl species are not expected to be very stable, however, the band at 1750 cm^{-1} is still present in the spectra after a 30-min purging of the Fe-ZSM-5 sample with preadsorbed NO with He at 0°C (Fig. 3). Lastly, following simple logic, the decomposition of trinitrosyl species should result in the formation of dinitrosyl complexes and then mononitrosyl ones, but purging the Fe-ZSM-5 sample with preadsorbed NO with He at 0°C resulted in neither the emergence of new bands nor an increase in the intensity of existing bands. Instead, all bands decrease in intensity with time with the bands near 1880 and 1835 cm^{-1} (mononitrosyls) being the most stable (Fig. 3). It is worth noting that unlike in the present study, the purging or evacuating of Fe exchanged zeolites Y, mordenite, ZSM-5, or silica-supported iron oxide led to an increase in the intensity of the band near 1750 cm^{-1} [46, 47, 49, 51, 66]. Such behavior is understood in terms of the suggestion that the band near 1750 cm^{-1} is a mononitrosyl complex with Fe ions capable of forming dinitrosyl species. Evacuation or purging resulted in the decomposition of dinitrosyl species to form mononitrosyl ones.

CONCLUSION

The NO adsorption from an NO + He flow on Fe-ZSM-5 at –100, 0°C, and room temperature, as well as thermal stability of the adsorption complexes were studied with FTIR spectroscopy. The band assignment was performed using labeled NO. Analyses of the infrared results reported in the present work together with those reported in the literature suggest that, in ion-exchanged Fe-ZSM-5 zeolites, only a fraction of the cations occupying the framework exchanged position, while the remaining cations form small surface iron oxide particles. Both the Fe^{2+} ions exchanged in the zeolite lattice and the coordinatively unsaturated Fe^{2+} ions in oxides clusters interact with NO forming two sets of mono- and dinitrosyl species.

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