Selective catalytic reduction of NO with NH_3 over Fe-ZSM-5 catalysts prepared by sublimation of $FeCl_3$ at different temperatures

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Fe-ZSM-5 catalysts were prepared by subliming $FeCl_3$ into H-ZSM-5. The method used allowed Fe-ZSM-5 catalyst preparation by $FeCl_3$ exchange at a desired sublimation temperature and was found to be more precise. The sublimation of $FeCl_3$ into H-ZSM-5 was carried out at 320 and 700 °C. Fe-ZSM-5 prepared by sublimation of $FeCl_3$ at 320 °C followed by rapid heating to 700 °C and the catalyst prepared by subliming $FeCl_3$ at 700 °C were found to be more active for NO reduction with NH_3 in the presence of simulated exhaust gases containing water vapor than catalysts prepared by subliming $FeCl_3$ at 320 °C. To determine the active sites, the catalysts were characterized by H_2-TPR, *in situ* DRIFTS of NO adsorption, NH_3-TPD, XRD and chemical analysis methods. The observed NO conversion differences in selective catalytic reduction using NH_3 could be correlated to the iron cation species present at different locations determined from diffuse reflectance infrared spectroscopy. Enhanced NO reduction activity was obtained when γ positions in Fe-ZSM-5, corresponding to $Fe^{2+}(NO)$ band at 1877 cm^{-1} in DRIFTS, were preferentially occupied.

KEY WORDS: sublimation; $FeCl_3$; Fe-ZSM-5; selective catalytic reduction; NO; NH_3; infrared spectroscopy.

1. Introduction

Selective catalytic reduction (SCR) of NO with hydrocarbons and NH_3, and N_2O decomposition over Fe-ZSM-5 catalysts have been widely studied in recent years due to the catalysts' superior stability and high activity [1–11]. Various preparation methods of Fe-ZSM-5, however, led to different activities and occasionally were not very reproducible in SCR applications [1,4,5,7,12]. The group of Sachtler [7] has developed a method for the preparation of Fe-ZSM-5 catalysts by subliming $FeCl_3$ into H-zeolites; this method is very effective in obtaining high weight percentage Fe-zeolite catalysts in a reproducible way. Moreover the catalysts were very stable in the various reactions involving NO reduction [1,7–10]. The authors proposed an iron oxo complex to be the active site supported by characterization and reaction studies [13–15]. An Fe-ZSM-5 catalyst prepared by the sublimation method was found to be more active than a catalyst prepared by the ion exchange method in selective catalytic reduction of NO with NH_3 [1]. Long and Yong [4] have reported that Fe-ZSM-5 prepared by an improved ion exchange method showed relatively higher activity than catalysts prepared by the sublimation method in SCR of NO with NH_3. The observed differences by various researchers in conversion of NO over Fe-ZSM-5 in SCR with NH_3 [1–4,11] or hydrocarbons could be due to the nature and population of the active species at different locations in the pore network. The pretreatment conditions also had a strong influence on the activity of Fe-ZSM-5. It was shown that the hydrolysis process, extra-framework aluminum and the crystallite size of the zeolite affected different iron species observed in Fe-ZSM-5 [16]. N_2O conversions, even in the presence of water and oxygen, were higher over Fe-ZSM-5 calcined at 800 °C than catalysts calcined at 500 °C [10]. FTIR spectroscopy studies suggested that most of the Brønsted sites after calcination at 800 °C had disappeared. The reaction was thought to mainly occur on Lewis acidic sites. A recent study proposes a reaction between FeO_x nanoclusters and zeolite protons, resulting in iron at cationic positions, when Fe-ZSM-5 is treated at 700 °C [17,18]. This relocation of iron oxide to cationic positions leads to improved N_2O decomposition. Lobree *et al.* have also shown a redispersion of FeO_x to the cationic sites [19]. In conclusion a small change in catalyst preparation method could result in catalysts having very different activities. Fe-zeolite catalysts were characterized by FTIR NO adsorption studies to find out the nature and location of these active sites [19–25]. A few reports also tried to correlate the active species determined with IR spectra to the observed NO reduction with hydrocarbons and N_2O decomposition [9,21,23]. Not many studies were found in correlating the observed iron species or its location with the resulting NO conversions in SCR with NH_3. $FeCl_3$ is present as a dimer at 320 °C and as a monomer around 700 °C [26]. It is possible that the dimer may not react with all the

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protons, as the protons in the zeolite are not at a particular distance [27,28]. This could lead to ion exchanged iron species, which forms FeO_x on washing and calcination. $FeCl_3$ monomer on the other hand can reach all the protons of the zeolite and should result in a better ion exchange.

In this paper we studied how this monomer and dimer precursor species affects the ion exchange process and its catalytic activity in SCR of NO with NH_3. A modified preparation method of $FeCl_3$ sublimation is discussed, which results in a catalyst with an improved performance in SCR of NO with NH_3. We also discuss a correlation of the NO conversions to the location of the iron species in Fe-ZSM-5, as determined by diffuse reflectance infrared spectroscopy (DRIFTS) of NO adsorption.

2. Experimental

2.1. *Catalyst preparation*

Na-ZSM-5 (Si/Al = 11, TOSOH), crystallite size ~2 μm, was ion exchanged with NH_4NO_3 solution to obtain NH_4-ZSM-5, which was subsequently calcined at 600 °C in air to obtain H-ZSM-5. The sublimation of $FeCl_3$ (99.99%, Aldrich) in to H-ZSM-5 was carried out in a set up as shown in figure 1. The powdered H-ZSM-5 was placed in a U-shaped quartz reactor between two quartz wool plugs. One end of the reactor is connected to He flow (100 ml/min) with a thick, flexible plastic tube. The other end of the "U" reactor is connected to the exhaust. The glass vial containing anhydrous $FeCl_3$, corrugated at one end, is placed inside the flexible plastic tube, with the corrugated end facing the zeolite sample (as shown in figure 1). The glass vial containing $FeCl_3$ could be easily held in its place, without restricting the He flow. The "U" tube containing zeolite sample is placed in a programmable furnace and heated at 600 °C for 2 h (or 700 °C for 1 h) in He flow and cooled/maintained at a sublimation temperature of 320 or 700 °C. After attaining the stable temperature the corrugated end of the glass vial is broken so that the $FeCl_3$ falls on the quartz wool above the H-ZSM-5 sample. In this method during the whole experiment the complete system is maintained under inert He flow thus avoiding any contamination of the activated zeolite or $FeCl_3$ during the transfer process, which might be possible in the conventional way. Three different Fe-ZSM-5 samples were made by the above method. (1) H-ZSM-5 was heated at 600 °C for 2 h in a He flow and cooled to 320 °C. $FeCl_3$ is transferred over the activated zeolite at 320 °C and maintained for 3 h in a He flow and cooled to room temperature. This sample is called Fe-ZSM-5-69. The last two digits indicate the ion exchange percentage of the catalyst as determined from chemical analysis after washing, drying and calcination. (2) The H-ZSM-5 was activated at 700 °C for 1 h in a He flow and the $FeCl_3$ is added to the activated H-ZSM-5 at the same temperature and maintained for 1 h before cooling the sample to room temperature. This leads to sample Fe-ZSM-5-51. (3) The H-ZSM-5 is activated at 600 °C for 2 h in a He flow and cooled to 320 °C. $FeCl_3$ sublimation is carried out for 30 min at 320 °C. The iron chloride exchanged

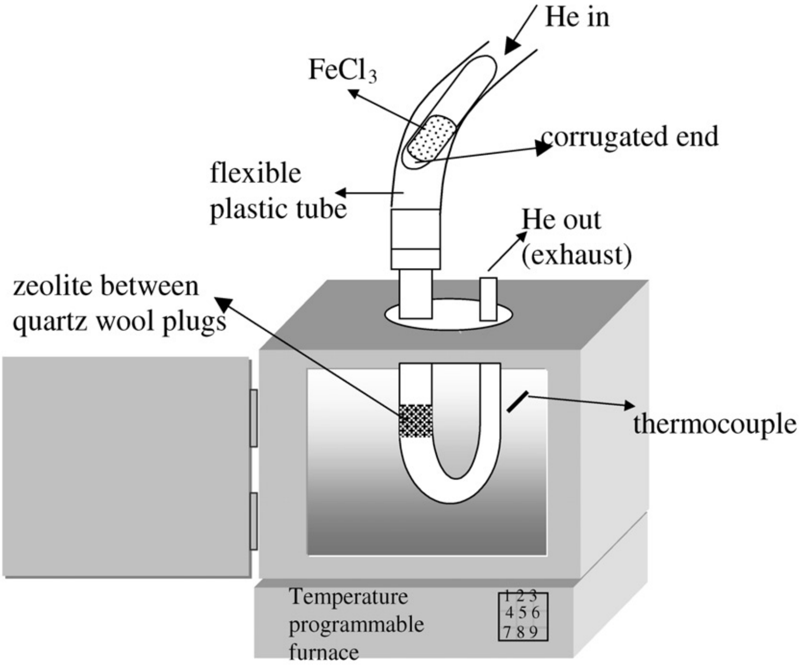

Figure 1. $FeCl_3$ sublimation set up.

Table 1
Catalyst preparation conditions and Fe ion exchange percentage[a]

Catalyst	Activation in He (°C/h)	$FeCl_3$ sublimation (°C/h)	Treatment after sublimation (in He)	Fe content (wt%)	Ion exchange (%)	TOF[b] ($\times 10^3$/s)
Fe-ZSM-5-69	600/2	320/3	Cooling to RT	3.9	69	10
Fe-ZSM-5-51	700/1	700/1	Cooling to RT	2.9	51	19
Fe-ZSM-5-67	600/2	320/0.5	Heated to 700 °C for 1 h and cooling to RT	3.8	67	17
Fe-ZSM-5-80	600/2	320/3	Cooling to RT	4.5	80	7

[a] Determined from chemical analysis after washing, drying and calcinations. Based on Fe^{3+}/Na.

[b] Turnover frequency (TOF) is defined as the number of NO molecules converted per iron ion per second (NO conversion at 300 °C).

zeolite ($FeCl_2$-ZSM-5) is heated at a rate of 1000 °C/h to 700 °C in a He flow and maintained at 700 °C for 1 h before cooling to room temperature. This is named Fe-ZSM-5-67.

A fourth catalyst was prepared by the conventional method of sublimation. The zeolite is activated at 600 °C for 2 h in a He flow, in a "U" tube, and cooled to room temperature. This tube is sealed off in a He flow and transferred to a glove box maintained under inert atmosphere. $FeCl_3$ is transferred over to the H-ZSM-5 sample and the "U" tube is transferred back to the furnace. The temperature is raised at a rate of 5 °C/min to 320 °C and maintained for 3 h before cooling to room temperature.

All the $FeCl_2$-zeolite samples were washed with plenty of deionized water until free of chloride ions ($AgNO_3$ test). The washed samples were dried at 100 °C overnight and finally calcined at 600 °C for 5 h in air. Table 1 gives an overview of the preparation conditions and the ion exchange percentages of different Fe-ZSM-5 catalysts. For comparison of TPR results ~5.5 wt% Fe_2O_3/H-ZSM-5 catalyst (Fe content not analysed) was prepared by pore volume impregnation of $FeCl_3$ and calcined at 600 °C for 5 h in air.

2.2. NH_3-TPD and H_2-TPR

NH_3-TPD and H_2-TPR were carried out using a Micromeritics pulse chemisorb (2900) TPD-TPR instrument. For NH_3-TPD the samples (20 mg) were activated at 600 °C for 1 h in He flow and cooled to 200 °C. NH_3 is adsorbed at 200 °C for 30 min and flushed with He for 30 min to remove any physically adsorbed NH_3. Desorption is carried at a heating rate of 10 °C/min to 600 °C.

For H_2-TPR the samples (20 mg) were activated at 600 °C for 1 h in air flow and cooled to room temperature. The flow through the sample tube is switched over to 5 vol% H_2 in Ar mixture at room temperature. After stabilizing the base line TPR was carried out with a heating rate of 10 °C/min to 900 °C and maintained for 30 min at 900 °C. A dry ice-cooled trap was placed before the TCD detector.

2.3. XRD

The crystallinity of the samples was checked using a Philips X-ray diffractometer, PW 1840, with Ni-filtered CuKα radiation ($\lambda = 1.541$ Å). Data were collected at $2\theta = 6$–$70°$ with a step size of 0.02° (total collection time 4 h).

2.4. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS studies were carried out with a Nicolet Magna IR 860 spectrometer equipped with a liquid nitrogen-cooled MCT detector. A spectratech DRIFT high-temperature cell, equipped with CaF_2 windows, was filled with the powdered catalyst (approximately 15–20 mg). The required gas flow (He or 5% NO in He) of 30 ml/min was maintained by mass flow controllers. Prior to adsorption measurements with NO, the catalyst samples were activated at 450 °C for 1 h in a He flow and cooled in the same flow to 50 °C. The adsorption of NO was carried out at 50 °C. A total of 64 scans were collected with a spectral resolution of 4 cm^{-1}. The spectra obtained after NO adsorption are displayed after subtraction of the features of the zeolite, recorded at 50 °C in He. The sample chamber was connected to a mass spectrometer to monitor the concentration of the different gases during activation, and adsorption and desorption of NO.

2.5. SCR of NO_x with NH_3

The catalysts (0.1 g, sieve fraction 300–500 μm) were screened for SCR of NO_x in a tubular quartz reactor (7 mm internal diameter) between 300 and 550 °C. The gas hourly space velocity (GHSV) was maintained at 7.5×10^5 or 1.4×10^6/h, based on a catalyst bulk density of 0.5 g/cm^3. The SCR synthetic exhaust gas mixture contained 1000 ppm NO, 1000 ppm NH_3, 10 vol% O_2, 9 vol% H_2O (when used) and balance N_2. The gas lines before and after the reactor were heated (150–180 °C) to avoid condensation of any reactants or products. NH_3 and water were removed by placing phosphoric

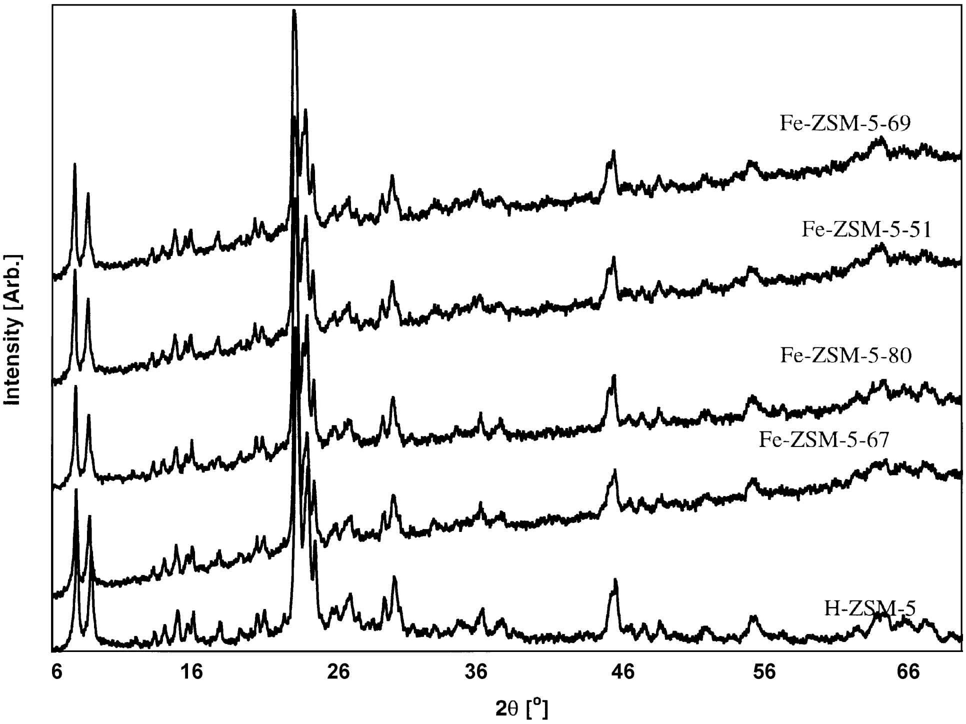

Figure 2. XRD patterns of samples as indicated.

acid and water traps before the analyzers. The concentration of NO_x and N_2O was monitored with a chemiluminescence detector and gas chromatography, respectively. The NO_x conversion was calculated after 1 h of time on stream at each reaction temperature. The conversion to N_2O over the catalysts was negligible (<4 ppm observed over Fe-ZSM-5-80) and will not be further discussed. The stability of the catalysts was tested by taking ~50 mg of the catalyst in a reactor and heated to 700 °C for 3 h in a flow containing 10 vol% O_2, 10 vol% H_2O and balance N_2 (flow rate 2 l/min). The NO conversions before and after this high-temperature treatment were compared.

3. Results and discussion

Figure 2 shows the XRD patterns of different materials studied. The XRD patterns of Fe-ZSM-5 catalysts prepared at different temperatures are identical to the parent H-ZSM-5. No detectable iron oxide was found from XRD. The zeolite structure was maintained even after the harsh treatment of catalysts at 700 °C. HCl, which is produced during the sublimation exchange procedure at high temperature, apparently did not affect the crystal structure of ZSM-5.

In figure 3 NH_3-TPD for different materials is presented. H-ZSM-5 shows a broad peak with a shoulder at 310 °C and a maximum desorption rate at 405 °C. Fe-ZSM-5-80 and Fe-ZSM-5-69 show a broad peak with a decreased intensity of the peak at the higher-temperature side due to the replacement of protons by Fe^{3+}. Fe-ZSM-5-51 and Fe-ZSM-5-67 show relatively more acidity compared to the above two catalysts which is in agreement with the lower ion exchange percentages. Careful comparison of Fe-ZSM-5-69 and Fe-ZSM-5-67 indicates more acidity in the latter catalyst, despite the similar ion exchange percentages leading to the following order in acidity: H-ZSM-5 > Fe-ZSM-5-51 > Fe-ZSM-5-67 > Fe-ZSM-5-80 > Fe-ZSM-5-69.

Figure 4 shows the NO_x conversion with NH_3 reductant at high space velocities in the presence of water vapor. All the catalysts showed better NO_x conversions, compared to conventional catalysts [29]. The activity of these materials was similar to some of the most active Fe-ZSM-5 catalysts reported in the literature [1,4]. Comparison among the different Fe-ZSM-5 catalysts suggests that the NO_x conversion is not determined by the iron content of the catalysts but the method of catalyst preparation determines the performance obtained. A maximum NO_x conversion of ~90% is observed above 450 °C. The catalysts Fe-ZSM-5-69 and Fe-ZSM-5-80 prepared by subliming $FeCl_3$ at 320 °C, in spite of having higher ion exchange percentage showed considerably lower NO conversion (e.g. 38 and 29%, respectively, at 300 °C) in the temperature range 300–450 °C. The catalyst that was prepared by 320 °C sublimation followed by rapid heating to 700 °C had similar or less iron content (67% ion exchange) compared with that of Fe-ZSM-5-69 and Fe-ZSM-5-80 prepared at 320 °C. However, the NO_x conversion over this catalyst was much higher (61% at 300 °C)

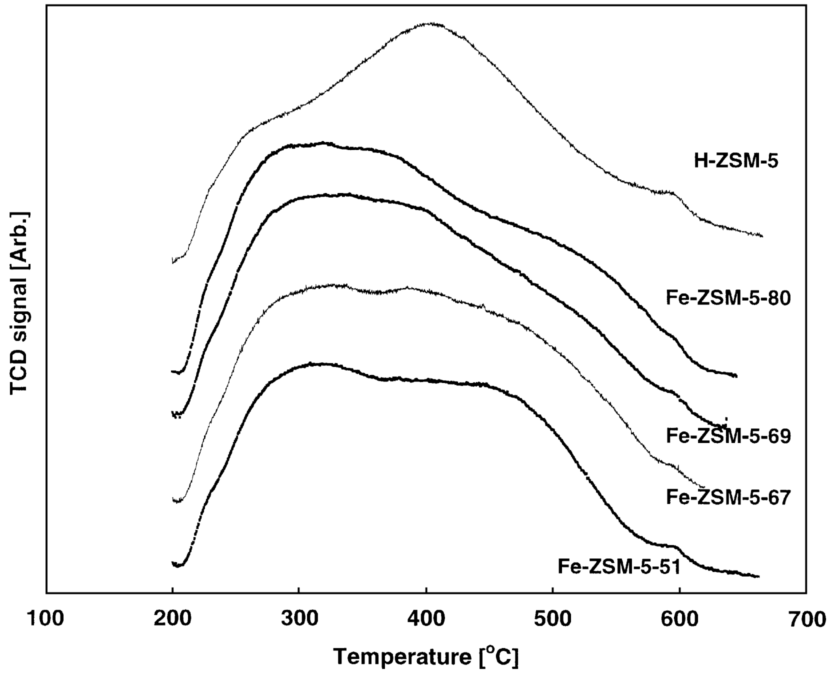

Figure 3. NH_3-TPD over H-ZSM-5 and Fe-ZSM-5 catalysts.

than Fe-ZSM-5-80 and Fe-ZSM-5-69. In spite of the low iron content, Fe-ZSM-5-51 prepared by sublimation of $FeCl_3$ at 700 °C, was very active (54% NO_x conversion at 300 °C). The catalyst Fe-ZSM-5-80, which had the highest ion exchange percentage of iron cations, prepared by conventional sublimation, showed much lower NO_x conversions at all the temperatures studied. Table 1 gives the turnover frequency (TOF) on Fe-ZSM-5, based on Fe content, at 300 °C reaction temperature. It is clearly seen that the catalyst Fe-ZSM-5-51 prepared by sublimation of $FeCl_3$ at 700 °C and Fe-ZSM-5-67 prepared at 320 °C followed by heating to 700 °C show the highest TOF, indicating that these catalysts contain the most active iron species.

Figure 5 shows NO_x conversion in the presence and absence of water vapor over Fe-ZSM-5 catalysts, before and after aging at 700 °C in 10 vol% H_2O and 10 vol% O_2. The NO_x conversion was always higher in the absence of water vapor at all reaction temperatures, over both fresh and aged catalysts. The NO_x conversion levels over Fe-ZSM-5-51 were higher than over the Fe-ZSM-5-69 catalysts at all reaction temperatures, before and after the aging treatment. A similar observation was made over Fe-ZSM-5-80 catalyst prepared by the

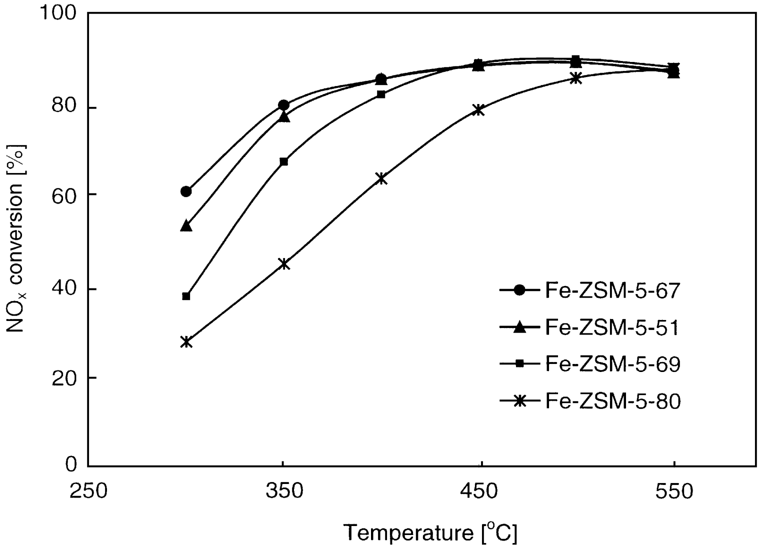

Figure 4. NO_x conversion over Fe-ZSM-5 catalysts as indicated. Reaction conditions: $NO = NH_3 = 1000$ ppm, $O_2 = 10$ vol%, $H_2O = 9$ vol%, balance $= N_2$, catalyst weight = 0.1 g, GHSV $= 7.5 \times 10^5$/h.

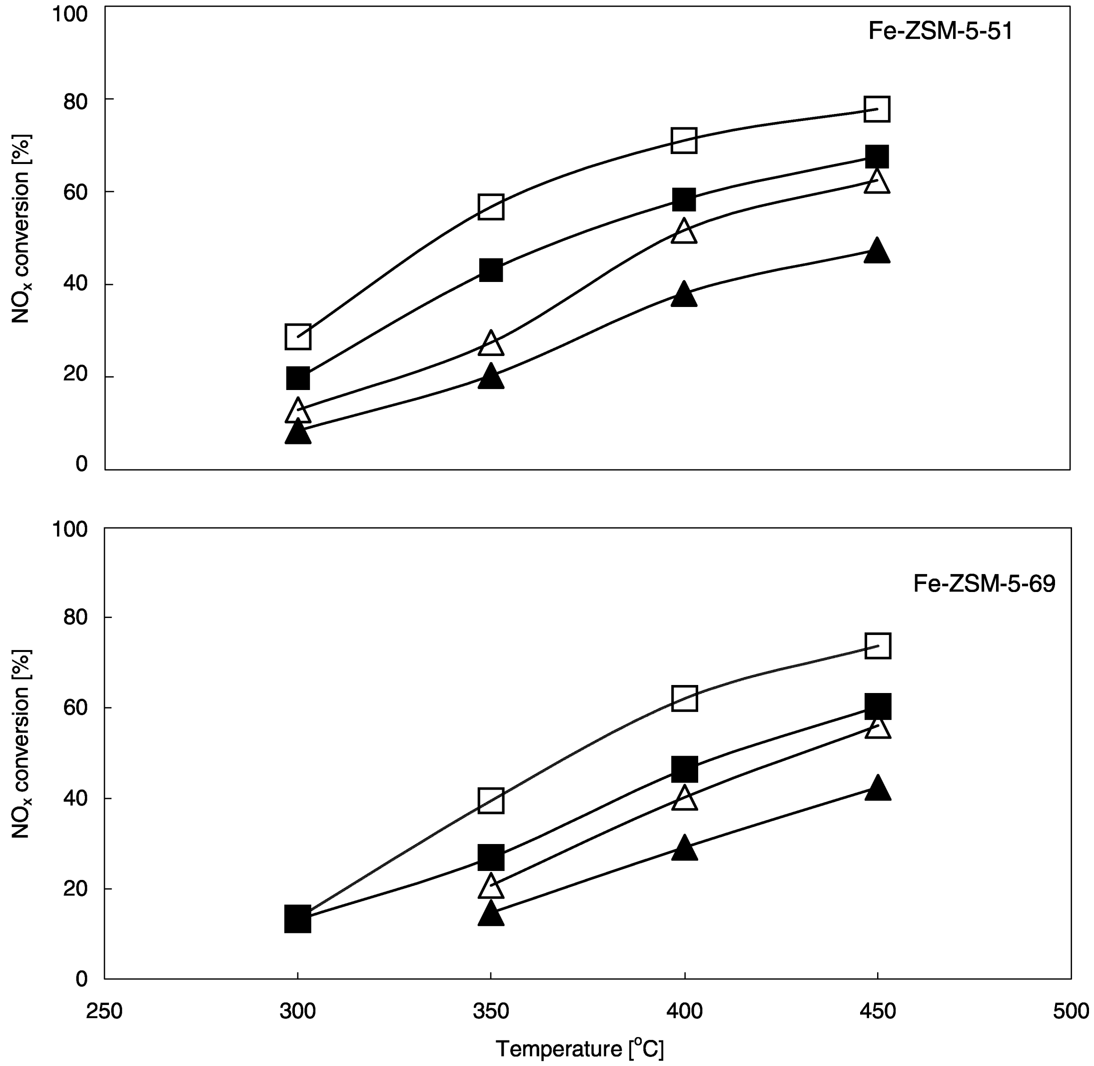

Figure 5. NO$_x$ conversion before and after aging over Fe-ZSM-5 catalysts: □ and ■, NO$_x$ conversion before aging; △ and ▲, NO$_x$ conversion after aging; open symbols, in the absence of H_2O; solid symbols, in the presence of H_2O. Aging conditions: $O_2 = 10$ vol%, $H_2O = 10$ vol%, balance = N_2, flow rate = 2.0 l/min, aged at 700 °C for 3 h. Reaction conditions: NO = NH_3 = 1000 ppm, $O_2 = 10$ vol%, H_2O (when used) = 9 vol%, balance = N_2, GHSV = 1.4×10^6/h.

conventional method. The NO conversion decreased considerably over the aged catalysts under both reaction conditions used. Recently, Zhu *et al.* [17,18] have shown that due to relocation of FeO$_x$ to the framework exchange positions on calcination and steam treatments at 700 °C, the N_2O decomposition over Fe-ZSM-5 increased. The opposite behavior in NO reduction with NH_3 might be related to: (i) due to the relatively lower ion exchange percentages of iron, most of the iron is already attached to the framework [19] and no FeO$_x$ nanoparticles are present in the catalysts for relocation; (ii) FeO$_x$, present at the outside of the zeolite crystal surface, is difficult to redisperse into the zeolite pores/cationic sites [30]; (iii) the active sites responsible for the N_2O decomposition and NO reduction with NH_3 are different; and (iv) the slightly different aging procedures could have caused deactivation due to dealumination of the catalysts which results in removal of Fe^{3+} attached to the framework. H_2-TPR spectra of Fe-ZSM-5-69 (figure 6) after aging and reaction in fact showed a H_2 consumption peak around 900 °C due to FeO$_x$ species, which is not observed for the fresh catalyst.

The process during the catalyst preparation can be described as follows. It is known that $FeCl_3$ at 320 °C will be present as a dimer (Fe_2Cl_6) [18,26]. For the dimer to be ion exchanged with zeolite protons, all the protons should be accessible at a particular distance. There is a possibility that some of the protons could be too close or too far from each other [27,28]. Therefore the ion exchange could proceed according to the following equations [18]:

$$Fe_2Cl_6 + \text{H-ZSM-5} \xrightarrow{320\,^{\circ}\text{C/He}} Fe_2Cl_5\text{-ZSM-5} + HCl \quad (1)$$

$$Fe_2Cl_5\text{-ZSM-5} \xrightarrow{H_2O/\text{calcination}} \text{Fe-ZSM-5} + FeO_x + 5HCl. \quad (2)$$

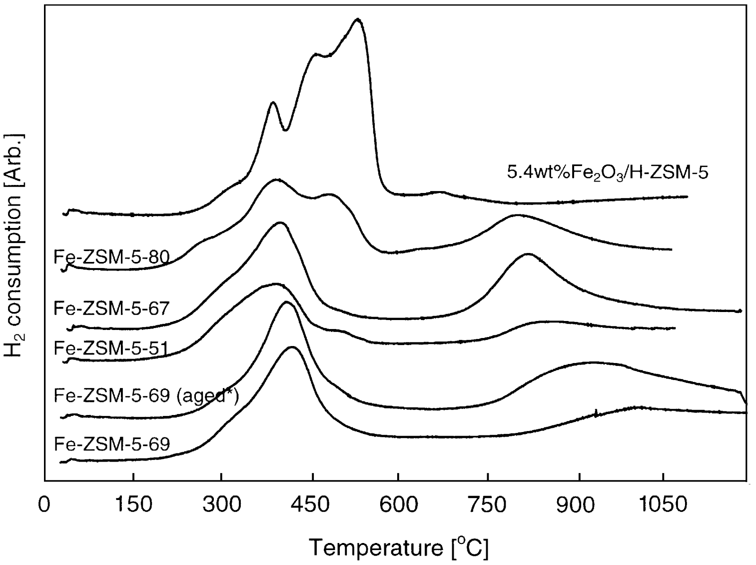

Figure 6. H_2-TPR spectra of Fe-ZSM-5 catalysts as indicated. * Fe-ZSM-5-69 aged at 700 °C for 3 h and used for reaction of figure 5.

In the above sample FeO_x species can be formed upon washing and calcination. However, when Fe_2Cl_5-ZSM-5 is heated in He to 700 °C (as in the case of Fe-ZSM-5-67) the extra $FeCl_3$ will either exchange with another protonic site or migrate out to form larger particles. By looking at the similar ion exchange percentages of Fe-ZSM-5-69 and Fe-ZSM-5-67 it can be said that the extra $FeCl_3$ from Fe_2Cl_5-ZSM-5 does not leave the zeolite. The material on subsequent washing and calcination results in FeO_x particles:

$$\text{Fe}_2\text{Cl}_5\text{-ZSM-5} \xrightarrow{700\,^\circ\text{C/He}} \begin{array}{l}\text{FeCl}_2\text{-ZSM-5 (FeCl}_3\\ \text{not attached to framework)}\\ \text{or } 2\text{FeCl}_2\text{-ZSM-5} + \text{HCl}\end{array} \tag{3}$$

$$\text{FeCl}_2\text{-ZSM-5(FeCl}_3) \xrightarrow{\text{H}_2\text{O/calcination}} \text{Fe-ZSM-5(FeO}_x) + 5\text{HCl}. \tag{4}$$

$FeCl_3$ will be present as a monomer around 700 °C. When the ion exchange is carried out at 700 °C the monomeric $FeCl_3$ can access all the protonic sites equally. At 700 °C, $FeCl_3$ could also decompose to $FeCl_2$ and Cl_2 [26]. Since the ion exchange process is quite fast at 700 °C, the above decomposition of $FeCl_3$ may not be very crucial for the preparation of the catalyst. The low iron content of the Fe-ZSM-5-51 catalyst can be expected due to rapid ion exchange process at 700 °C:

$$\text{FeCl}_3 + \text{H-ZSM-5} \xrightarrow{700\,^\circ\text{C/He}} \text{FeCl}_2\text{-ZSM-5} + \text{HCl}. \tag{5}$$

H_2-TPR spectra of Fe-ZSM-5 catalysts are shown in figure 6. Fe_2O_3/H-ZSM-5 prepared by impregnation showed three reduction peaks typical of bulk or large FeO_x particles. The first peak corresponds to reduction of Fe_2O_3 to Fe_3O_4 followed by reduction to FeO and at 550 °C the complete reduction of FeO_x to Fe^0 [7,19]. Different iron species were observed in Fe-ZSM-5 catalysts by TPR [7,19,31]. In general the reduction proceeded in two stages. The first reduction peak around 410 °C corresponds to the reduction of Fe^{3+} to Fe^{2+} and the second peak at higher temperatures corresponds to the reduction of FeO_x to Fe^0. When Fe^{3+} is present at the ion exchanged positions, the complete reduction to Fe^0 occurs at temperatures >1000 °C due to the collapse of the zeolite structure [32,33]. The larger particles of FeO_x can be reduced to Fe^0 around 540 °C as seen from TPR of Fe_2O_3/H-ZSM-5. The reduction peaks observed around 900 °C in Fe-ZSM-5 catalysts can be attributed to the reduction of FeO_x nanoparticles [33]. Fe-ZSM-5-69 showed the reduction of Fe^{3+} to Fe^{2+} at 420 °C and a broad peak above 900 °C (after maintaining at 900 °C for ~12 min), due to the slow reduction of Fe^{2+} in ion exchanged positions to Fe^0. The Fe-ZSM-5-69 catalyst, which was aged at 700 °C and used for reaction, showed a peak around 900 °C corresponding to the reduction of FeO_x nanoparticles. This oxide phase is obviously formed due to the dealumination of the zeolite framework, which leads to the detachment of Fe^{3+} from ion exchanged positions. Fe-ZSM-5-51 showed a main reduction peak at 410 °C and a very small peak at high temperatures around 830 °C attributable to the reduction of the oxide phase. A prominent peak corresponding to reduction of FeO_x to Fe^0 around 830 °C in Fe-ZSM-5-67 indicates the presence of a considerable amount of oxide in the catalyst. Fe-ZSM-5-80 showed a shoulder at 500 °C corresponding to the reduction of larger FeO_x particles. The small differences observed in the maxima of H_2 consumption points to the presence of different iron species and FeO_x particle sizes in the catalysts.

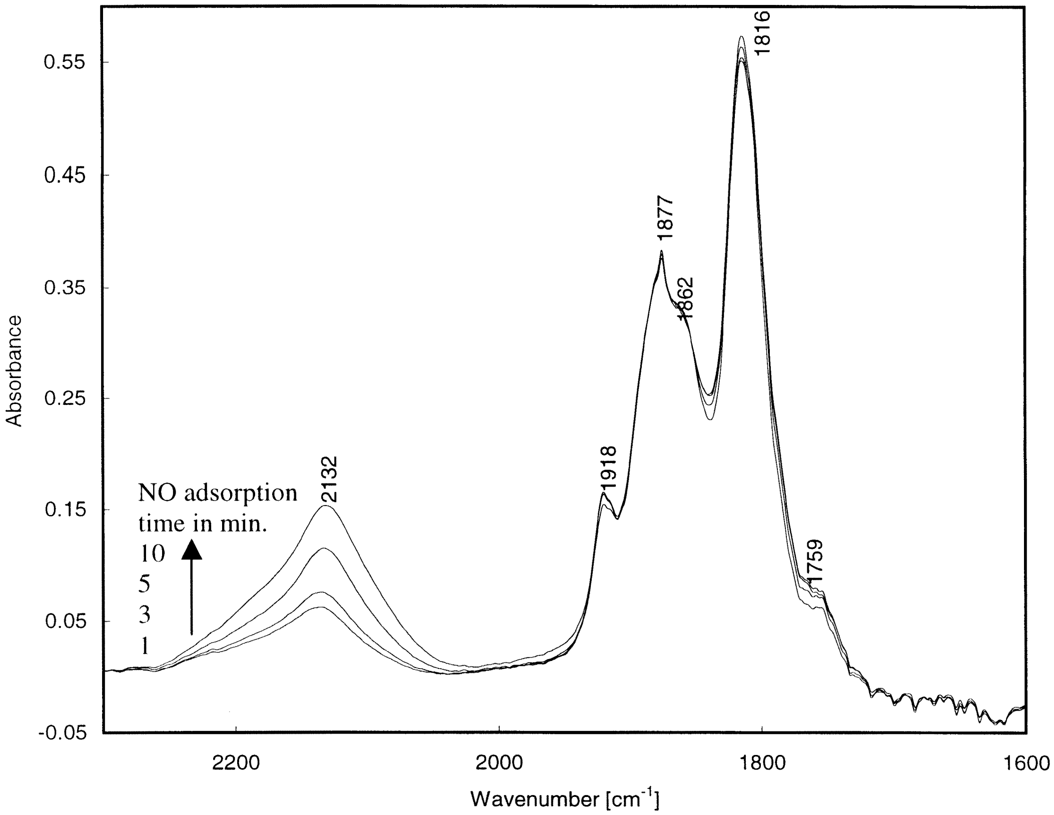

Figure 7. Evolution of DRIFT spectra of NO adsorbed over Fe-ZSM-5-69 at 50 °C in flowing 5% NO in He.

Figure 7 shows the DRIFTS spectra of Fe-ZSM-5-69 at 50 °C in a flow of 5% NO in He. The He pre-treatment at 450 °C for 1 h, before adsorption of NO, results in auto-reduction of Fe^{3+} to Fe^{2+} [12,21–23]. The observed IR bands were assigned to Fe^{2+}/FeO_x species at α, β and γ (I, II and III) locations in zeolite, which are present in straight channels of ZSM-5 and sterically hindered six- and five-membered rings, respectively [19–22,34–38]. The band appearing at 2132 cm^{-1} was assigned to NO_2^+ or NO^+ adsorbed at Brønsted acidic sites of the zeolite [25,39–42]. A recent paper strongly supports the band for NO^+ at the Brønsted acid sites [39]. The intensity of this band increased with increase in adsorption time with a relative decrease in the intensity of the band at 3609 cm^{-1} (not shown), corresponding to Brønsted hydroxyl groups. This phenomenon is observed for all the Fe-ZSM-5 catalysts studied (e.g. see figure 10, inset). Observing the different spectra of NO adsorbed on Fe-ZSM-5-based catalysts (figures 7–10) the relative intensity of the 2132 cm^{-1} band seems to depend the amount of Brønsted hydroxyl groups. The bands at 1877 and 1862 cm^{-1} were assigned to the mono nitrosyl groups over Fe^{2+}/FeO_x [19–25]. Segawa *et al.* [20] have shown that the bands at 1876 and 1862 cm^{-1} in Fe^{2+}-Y zeolite correspond to iron ions present in sterically hindered and sites of intermediate accessibility, respectively. These iron cations in ZSM-5 were present at γ and β positions, respectively [19,34–38]. The bands at 1918 and 1816 cm^{-1} were assigned to $Fe^{2+}(NO)_2$, at α sites, and the shoulder at 1759 cm^{-1} to $Fe^{2+}(NO)$ species adsorbed on the same structural unit responsible for the dinitrosyl species.

A similar IR spectrum (figure 7) was observed by Lobree *et al.* [19,22] for the Fe-ZSM-5 having 56% ion exchange. It was suggested that below an Fe/Al ratio of 0.56, iron occupies cationic positions [19]. Considering the similar IR spectra and Fe/Al ratio of Fe-ZSM-5-69 with the spectra reported in the literature [19,22], we can speculate that most of the iron ions in our catalyst must be present as framework charge compensating ions with iron distributed in all the three α, β and γ positions. H_2-TPR also did not show a reduction peak corresponding to iron oxide phase, supporting the above IR results. The observed band intensities indicate that the relative population of iron in α sites was more than in β and γ sites.

Significant differences are observed between the spectra of Fe-ZSM-5-69 (figure 7) and Fe-ZSM-5-51 prepared by sublimation of $FeCl_3$ at 700 °C (figure 8). The band at 2132 cm^{-1} was more intense compared to the spectra in figure 7. With increasing NO adsorption time, there was a very small increase in the intensity of this band and a corresponding decrease in the band at 3609 cm^{-1} (not shown). The higher intensity of the NO^+ occupying the Brønsted sites is in agreement with the lower ion exchange percentage of this catalyst (51% vs. 69%). The acidity as measured from NH_3-TPD of this catalyst (above 360 °C) was also greater

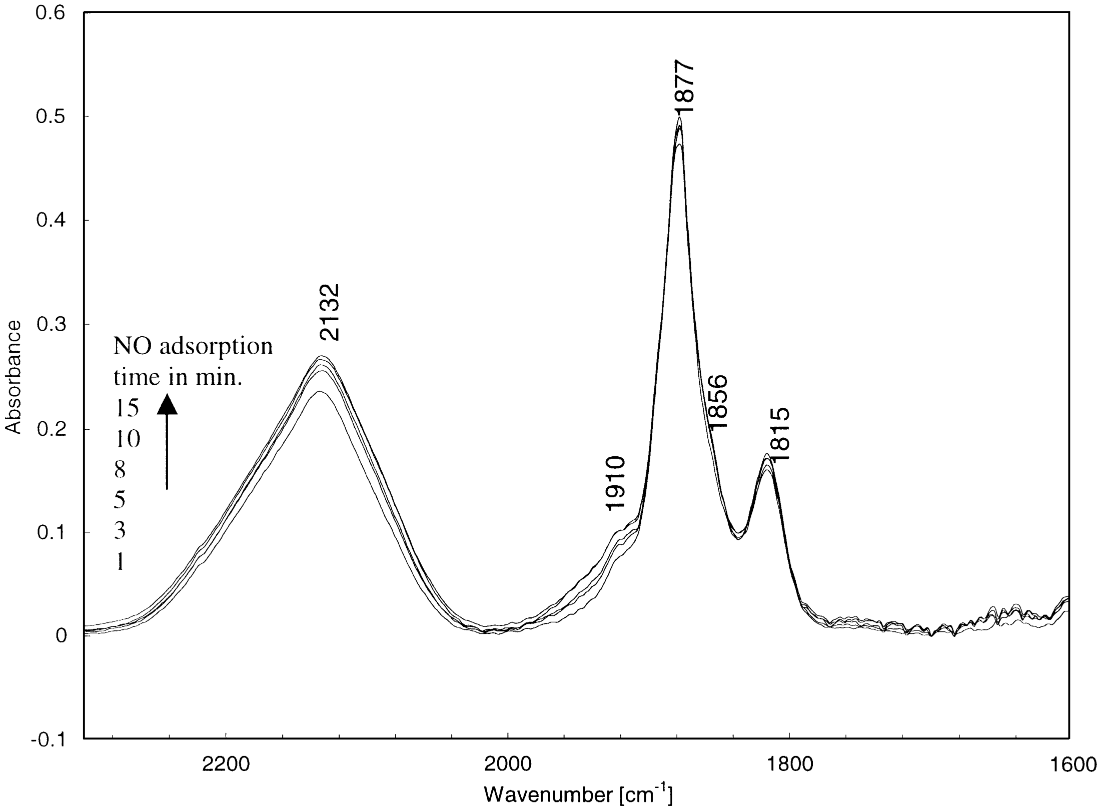

Figure 8. Evolution of DRIFT spectra of NO adsorbed over Fe-ZSM-5-51 with time at 50 °C in flowing 5% NO in He.

compared with Fe-ZSM-5-69, further supporting the above observations. A large decrease in the intensity of the bands at 1910 and 1815 cm^{-1} is observed (compared to figure 7), while the intensity of the band at 1877 cm^{-1} increased. The changes in the intensity of the bands in DRIFT spectra over Fe-ZSM-5-51 due to the concentration of NO can be ruled out as a high NO concentration is used in the present study (5% NO in He). The above observations indicate that the number of iron ions occupying α and β sites in Fe-ZSM-5-51 have decreased enormously and most of the iron ions are present at γ positions. The catalyst also has relatively more Brønsted acidic sites compared to Fe-ZSM-5-69.

Figure 9 shows the DRIFT spectra of NO adsorption recorded over Fe-ZSM-5-67 prepared by subliming $FeCl_3$ at 320 °C and heated to 700 °C at a rate of 1000 °C/h in a He flow. The spectra are similar to those obtained over Fe-ZSM-5-51 prepared by sublimation at 700 °C. The major difference is that the band corresponding to NO^+ ions at Brønsted acidic sites (band at 2132 cm^{-1}) is more intense compared with Fe-ZSM-5-51. Increased acidity was also found in NH_3-TPD especially in the high-temperature region, which is in agreement with the above observation. The band corresponding to iron ions at γ sites (1877 cm^{-1}) was sharp with a very small shoulder corresponding to iron species at the β position.

The relatively high ion exchange percentage of Fe-ZSM-5-67, the acidity as indicated by NH_3-TPD and the IR band at 2132 cm^{-1} prompt us to suggest the presence of FeO_x particles along with the predominantly occupied γ sites. The TPR spectra showed a prominent peak at 830 °C indicating the presence of iron oxide phase in Fe-ZSM-5-67 and supporting the above IR observations. Although the sublimation is carried out at 320 °C, which should result in the iron cations at α and β positions (as seen in figure 7), due to rapid heating to 700 °C they have migrated to γ sites and also formed larger aggregates in the zeolite which resulted in iron oxide particles in the zeolite after washing and calcination.

Diffuse reflectance spectra of NO adsorbed over Fe-ZSM-5-80 prepared by conventional sublimation are shown in figure 10. Bands at 2132, 1920, 1880, 1875, 1815 and a shoulder at 1762 cm^{-1} were observed in the spectra. The band at 2132 cm^{-1} corresponding to NO^+ ions adsorbed at Brønsted sites is much more intense than for all the other catalysts studied. The band corresponding to α sites was found to be more intense than γ and β sites and increased gradually with time. The relative intensity of the band at 1815 cm^{-1} is less for Fe-ZSM-5-80 compared with Fe-ZSM-5-69 prepared by sublimation at 320 °C. Lobree *et al.* [19] have shown that with an increase in the ion exchange percentage of above 56% in ZSM-5, the band corresponding to α sites decreased and ion exchanged iron cations will be mostly present as FeO_x species. The high ion exchange percentage of Fe in this catalyst with a relatively large

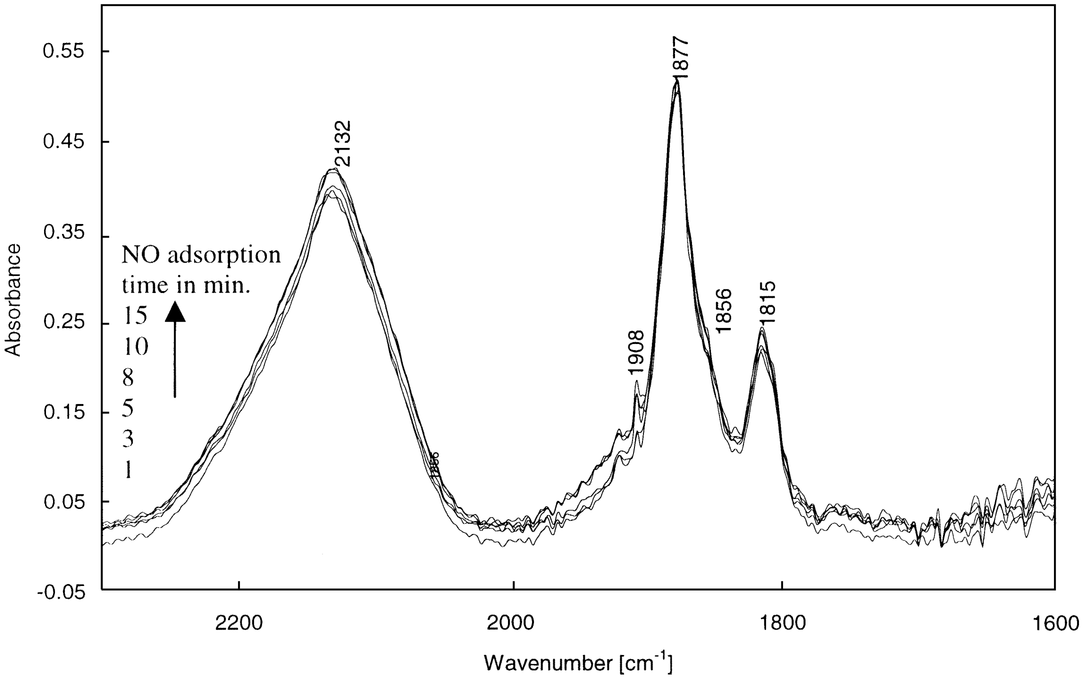

Figure 9. Evolution of DRIFT spectra of NO adsorbed over Fe-ZSM-5-67 at 50 °C in flowing 5% NO in He.

band corresponding to NO^+ adsorbed at Brønsted sites indicate that many of the framework acidic sites were not occupied by iron cations. Therefore, an extensive amount of Fe is present as FeO_x species in agreement with previous studies [19]. TPR spectra of Fe-ZSM-5-80 show the presence of a shoulder at 500 °C corresponding to the reduction of larger FeO_x particles supporting the above IR observations.

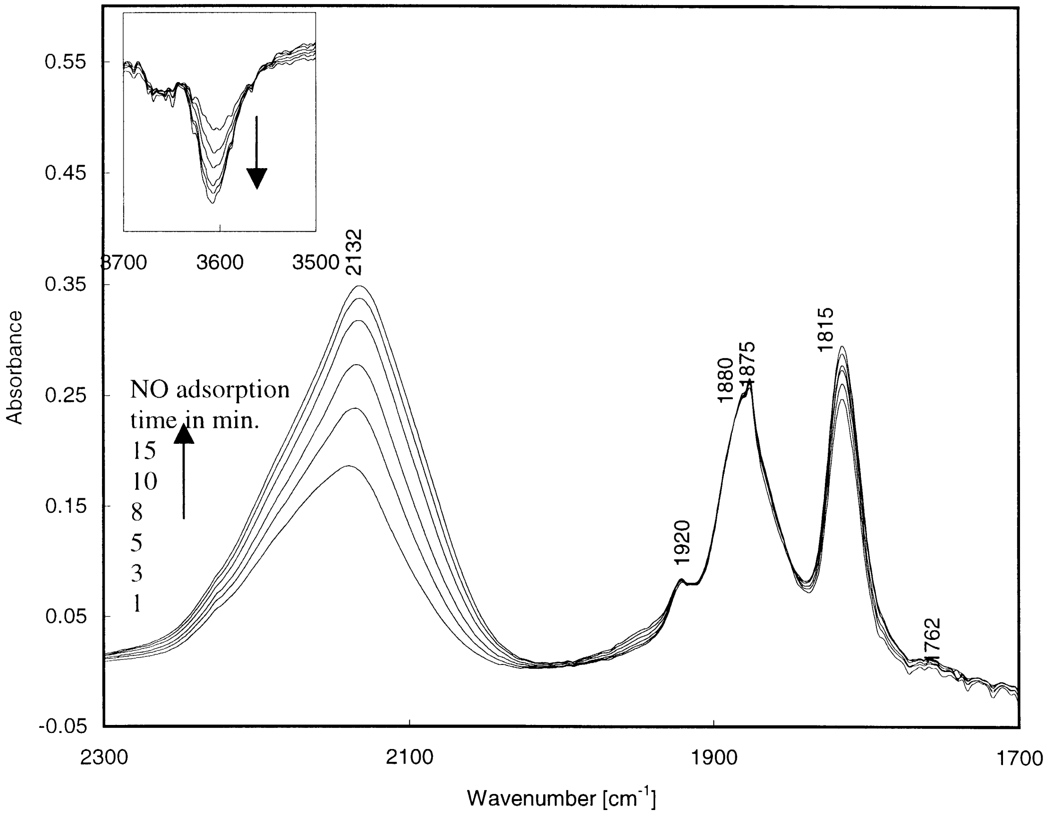

Figure 10. Evolution of DRIFT spectra of NO adsorbed over Fe-ZSM-5-80 at 50 °C in flowing 5% NO in He. The inset shows the evolution with time of the band at 3609 cm^{-1} corresponding to zeolite hydroxyl group.

Wichterlova *et al.* [34–38] have proposed the presence of α, β and γ sites in ZSM-5 which are located at straight channels, at the intersection of the straight and sinusoidal channels, and in a boat-shaped site in sinusoidal channels, respectively. The H_2-TPR and DRIFTS studies showed that Fe-ZSM-5 prepared by changing the sublimation conditions had a strong influence on the nature and distribution of Fe cations at different positions in ZSM-5. The presence of FeO_x in the catalysts speculated from the IR spectra is complemented by H_2-TPR. The Fe_2Cl_6 dimer present at 320 °C sublimation temperature, in the preparation of Fe-ZSM-5-80 and Fe-ZSM-5-69, resulted in iron species preferentially occupying the α positions along with β and γ positions. Due to steric hindrance the Fe_2Cl_6 may not efficiently reach the γ sites resulting in lower occupation of this position [20,34–38]. When the ion exchange was done at 700 °C, $FeCl_3$ monomer could reach all the sites of ZSM-5 more efficiently. Although the α and β sites present in straight channels and intersections are easily available, these positions were not extensively occupied when the materials were prepared by sublimation or treated at 700 °C. We think that $FeCl_2$ is bound weakly at this position and migrates to more stable γ positions or migrates out to the crystal surface. This is further supported by the fact that $FeCl_3$ sublimation at 320 °C, which is supposed to have α positions occupied, when heated to 700 °C did not show a significant amount of iron ions occupying α positions. Similarly the β positions in Fe-ZSM-5-51 and Fe-ZSM-5-67 prepared or treated at 700 °C were occupied to a lesser extent. Fe-ZSM-5 catalysts prepared at high temperatures resulted in preferential occupation of γ positions. Kaucky *et al.* have proposed that, in Co-ZSM-5, the α-type Co ions exhibit the weakest bonding followed by β sites of medium strength of bonding to framework oxygens [38]. The γ sites showed highest strength Co ions bound to the framework oxygens, similar to the above observation.

In SCR of NO with hydrocarbon Joyner *et al.* [23] have associated the catalytic activity with the 1880 cm^{-1} band. Similarly the most populated β sites were indicated to be the active sites in Co-ZSM-5 for CH_4-SCR of NO [35]. We can correlate the activity of NO_x reduction with NH_3 (table 1 and figure 4) with the iron species present at different locations of ZSM-5. When all the positions were occupied, as in the case of Fe-ZSM-5-80 and Fe-ZSM-5-69, the resulting NO_x conversion and TOF of the catalysts was low due to relatively inactive iron cations present at α and β positions. The iron cations occupying γ positions efficiently reduced NO_x with NH_3 as evident from superior NO_x conversion and high TOF (figure 4 and table 1) over Fe-ZSM-5-51 and Fe-ZSM-5-67. The effect of Brønsted acidity in determining the catalytic activity of Fe-ZSM-5 catalysts should be further studied. The catalysts Fe-ZSM-5-51 and Fe-ZSM-5-69 aged at high temperature showed deactivation. The most probable cause of deactivation is dealumination, which removes Fe^{3+} from the ion exchanged positions.

4. Conclusions

We have shown that a modified sublimation technique for preparing Fe-ZSM-5 at different temperatures results in improved conversion in NO reduction with NH_3 under simulated exhaust gas conditions. Fe-ZSM-5 prepared at 700 °C and the catalyst prepared at 320 °C followed by heating to 700 °C have high NO_x reduction capacity. The most active iron species responsible for NO_x reduction are the iron cations located at γ positions of ZSM-5 as observed from DRIFT studies. Iron ions in α and β sites possess relatively low activity compared to the iron in γ sites. The influence of Brønsted acidity on NO_x conversion and catalyst deactivation should be further studied.

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