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Quantitative Aspect of Identifying of Fe(II) Moieties in Zeolites ZSM-5 with Various Pore Hierarchy

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Abstract

This work was attempted to provide new and well-established approach for the quantification of Fe²⁺ sites in zeolites. The experimental procedure was based on carbon monoxide and nitrogen monoxide sorption in Fe-exchanged zeolites ZSM-5 of different pore hierarchy and followed by IR spectroscopy. The values of the absorption coefficients of the respective IR monocarbonyl Fe²⁺(CO) and mononitrosyl Fe²⁺(NO) bands were attained. In turn, the concentrations of Fe(II) moieties of various kinds were calculated and discussed with regard to the composition (Si/Al and Fe/Al) of studied zeolites.

1. Introduction

The iron moieties dispersed in aluminium poor pentasil zeolites are of a great attention due to their exclusive activity in oxidation reactions.¹⁻⁵ Depending on the nature of the reducing or oxidizing agent, extraframework Fe cations may adopt II, III and even IV of valency states.⁶ They are able to decompose N_2O , giving highly reactive adsorbed oxygen radicals, which selectively attack the hydrocarbons.⁷ An important example of the catalytic activity associated with an unusual redox behaviour of oxidation states of iron (mainly in MFI zeolite) is the partial oxidation of benzene to phenol using the N_2O as an oxidizing agent.⁷⁻⁹ The process of selective reduction of NO_x on zeolites, with iron in ion-exchange position is mediated by complex reaction. It consists of a disproportionation of NO_2 into nitrite or nitrate and in the final stage of ammonia chemisorption, to obtain nitrogen and water. The essence of the understanding SCR process is step associated with the adsorption and desorption of NO and NO_2 on Fe-zeolite, and a key step the oxidation of NO to NO_2 .¹⁰

It is unfortunately not clear, which of the active sites are in fact active in catalytic processes, especially in the SCR process. The subject of many discussions is zeolite Fe-ZSM-5, for which is reported the presence of many forms of iron. One of them are isolated and/or binuclear Fe ions in the ion-exchange positions, small oligonuclear clusters Fe_xO_y inside and/or outside the pores and large particles of Fe_2O_3 on the external surface.¹¹⁻¹⁴ Joyner and Stockenhuber¹⁵ reported the presence of the isolated iron cations and nanoclusters with average composition of Fe_4O_4 . The results obtained from catalytic studies correlated with infrared studies (sorption of NO) indicated that Fe_4O_4 nanoclusters were more active in the SCR process by propene than the isolated cations. Other literature data¹⁶⁻¹⁸ reported a significant catalytic activity of binuclear oxygen-bridged Fe sites. Yuli Wang et. al.¹⁹ demonstrated in the studies of NO and N_2O adsorption on Fe-BEA and H-BEA zeolites, that NO_x can be adsorbed on the Fe^{3+} sites and Brønsted acid sites. The energetically more favourable is bonding of NO_x with iron species than with protonic ones. Sorption of NO and O_2 on Fe-FER with different content of iron, carried out by Malpartida et. al.²⁰ showed the presence of mononitrosyls, behaving as intermediate compounds of the oxidation of NO to NO_2 . The test materials were proved to be active not only in the oxidation of NO to NO_2 , but also in the selective catalytic reduction of NO_x by ammonia.

As evidenced a detailed recognition of the nature of active iron species is key problem in elucidation of the mechanism of the particular catalytic process. One of the criteria that ion exchanged zeolite must meet to qualify for promising catalytically performance is not only the nature of the material, but also the position of the cation in the framework of the zeolite. There are many favourable methods for obtaining iron cations in extraframework positions. Among them, the iron ions exchange from Fe(III) salt solutions is not trivial procedure for high silica zeolites due to a low concentration of Al atoms thus the insufficient local negative framework charge to balance a bare trivalent cation. The Fe(III) ions in aqueous solutions are present in broad spectrum of complexes: from single-ion aqua-complexes $[Fe(H_2O)_6]^{3+}$ via $[Fe(H_2O)_5(OH)]^{2+}$ and $[Fe(H_2O)_4(OH)_2]^+$ hydroxycomplexes to dimeric forms present as oxo-bridged $[Fe_2(\mu-O)(H_2O)_8]^{4+}$ and di-oxo-bridged $[Fe_2(\mu-O)_2(H_2O)_8]^{4+}$ complexes.

Furthermore, the Fe ion polymerisation leads to $\alpha\text{-Fe}_2\text{O}_3$ or $\alpha\text{-FeO(OH)}$ ⁵ and in high silica zeolites isolated Fe ions at various oxidation state, oxo- and hydroxo-complexes and iron oxide species coexist. Similar situation has been recognized for zeolites ion-exchanged from Fe(II) salt solutions.²¹ Such variety of possibly formed active species requires detailed speciation analysis to identify the Fe-sites active in particular catalytic process.

IR spectroscopy gives the possibility to characterize the state of coordination, electrophilic properties and availability of cations in the zeolite. The numerous of carried out studies included sorption CO and NO as a probe molecules on Fe-zeolites. Most authors have used NO to characterize iron centers^{22,23} on Fe-FER, studies concerned using CO were not such extensive.²⁴⁻²⁷ In this respect, present work is aimed to quantify individual Fe(II) species in zeolites ZSM-5 of different micro- and micro/mesopore topology on basis of well-established approach of IR spectroscopy studies with reagent molecules adsorption, i.e. CO and NO. The effect of zeolite mesopore topology on the ion-exchange rate, thus the speciation of Fe species has been also investigated.

2. Results and Discussion

2.1. Structural and Textural Characterization

The XRD patterns (Figure 1) of both parent and desilicated materials present the typical diffraction pattern of zeolite ZSM-5. Desilication with NaOH solution did not perturb the crystallinity (% cryst, Table 1) of resulting hierarchical material. Also both mesoporous zeolites have shown the XRD patterns typical of ZSM-5 structure (Figure 1); however the lowered crystallinity was evidenced for M1-ZSM-5 of narrower mesopores.

In spite of the same ion-exchange procedure the resulting samples revealed significant differences in Fe amount accommodated. Undeniably a deciding factor in ion-exchange is the number of negatively charged AlO_4^- tetrahedra. After ion-exchange procedure zeolites under the study accommodated the Fe amounts corresponding Fe/Al in the range 0.15-0.26. The only exception is zeolite M1-ZSM-5 that hosted the highest Fe amount (0.44). However, as revealed XRD studies the crystallinity was not retained in this zeolite. It is supposed that a sorption of Fe(III) hydroxycomplexes took place on partly amorphous or/and non-perfect zeolitic surface. It has been known that the surface in silica at $\text{pH} > 3$ is negatively charged which is appropriate to not only sorbed positively charged complexes and even to incorporate electron-deficient metals to the silica surfaces, e.g. Fe(III) or Ti(IV).²⁸

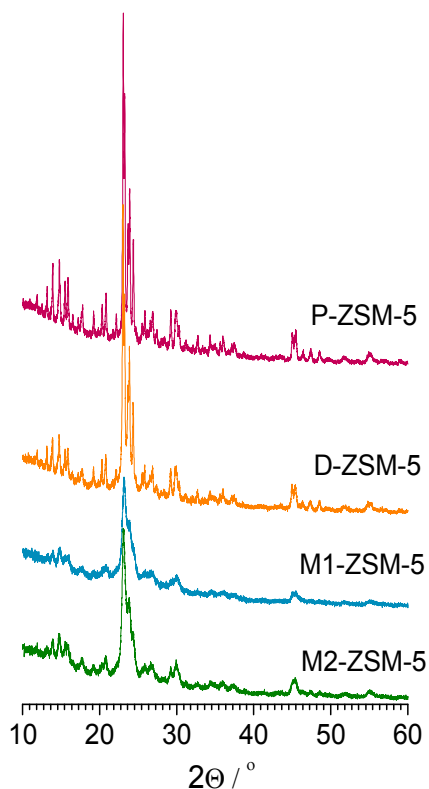


Figure 1. XRD patterns of bulk zeolite ZSM-5 and hierarchical analogues.

Table 1. The Al and Fe Concentration Obtained from XRF Analysis (Al_{XRF} and Fe_{XRF}). Relative Crystallinity Values (% cryst) Derived from XRD.

Sample name	Si/Al	Al_{XRF}	Al_{XRF}	Fe/Al	Fe_{XRF}	Fe_{XRF}	% cryst
		[$\mu\text{mol/g}$]	[-/u.c.]		[$\mu\text{mol/g}$]	[-/u.c.]	
P-ZSM-5	32	472	2.91	0.20	94	0.58	100
D-ZSM-5	21	698	4.36	0.15	104	0.64	99
M1-ZSM-5	27	549	3.43	0.44	242	1.51	66
M2-ZSM-5	27	549	3.43	0.26	143	0.89	85

2.2. IR Characterization of the Interaction of Probe Molecules with Iron Moieties in Zeolites of Different Hierarchical Structure

The nature of the iron sites is still not clarified. In general two types of transition metal ion (TMI) centers have been distinguished: isolated mononuclear TMI cations located in the exchangeable positions^{29,30} and TMI mono- and polynuclear clusters bearing extra-lattice oxygen of poorly defined stoichiometry.^{31,32} The concentration of centers of both types, i.e. the isolated and clustered ones can be controlled, to some extent, by adjusting the zeolite type, its Si/Al ratio, TMI concentration and the ion-exchange procedure. The extraframework cations balancing the negative charge of the framework can occupy various positions and their population within those positions is dependent on their ionic radii, coordination requirements, and the aluminum distribution in the framework. It has been recognized that isolated exchangeable cations are highly populated in zeolites of relatively low Si/Al (<20) while clustered oxo-centers are dominant species in Al-poor zeolites (Si/Al>30).

As mentioned earlier, Fe moieties hosted in zeolites are active in many catalytic processes of great importance, e.g. oxidation of benzene with N_2O ,^{1,2} N_2O decomposition, and SCR- NO_x with alkanes.³⁻⁵ Detailed recognition of the nature of active iron species is key problem in reaction mechanism elucidation in the particular catalytic process, especially when a broad spectrum of Fe moieties can coexist in zeolite. The isolated exchangeable Fe^{2+} and Fe^{3+} cations, oxo-species of various dispersion extent and oligomeric $\alpha-Fe_2O_3$ and/or $\alpha-FeO(OH)$ oxides⁵ can be populated dependent on the type of zeolite topology, Si/Al and Fe/Al ratios and the type of Fe-salt used for ion-exchange procedure.

2.2.1. Interaction of CO with Iron Species

Carbon monoxide is a probe widely employed to elucidate the electron donor properties of TMIs in zeolites both in a qualitative and in a quantitative aspect.³³⁻³⁶

The spectra of CO adsorbed at -130 °C on studied zeolites are presented in Figure 2. Interaction of the carbon monoxide molecules with the Si(OH)Al acid centers leads to the appearance of the 2177 cm^{-1} band associated with the formation of OH-CO adducts (Figure 2). While CO is engaged into

interaction with TM ions the position of TMI carbonyls strongly depends on two competitive effects: σ -donation (strengthening of C–O bond) and π -back donation (weakening of C–O bond). The extent of the weakening of the bond in ligated CO molecule is reflected in the downshift of the respective monocarbonyl bands. Thus it could be easily anticipated that the carbonyls of TM ions of lower oxidation degree will cover lower frequency C–O region in comparison to the sites of higher valences. The same rule relates to the isolated cations and clustered oxo-species.

Many spectroscopic studies have been devoted to characterize iron species in zeolites.^{37,38} The iron carbonyl bands at 2200–2194 cm^{-1} in zeolites BEA,³⁹ FER,⁴⁰ MFI⁴¹ have been widely reported. Carbon monoxide adsorption on a ferrisilicalite resulted in the formation of 2180, 2174 and 2157 cm^{-1} bands assigned to CO ligated to small iron oxide clusters.⁴² Additionally in Fe-silicalite, a band at 2215 cm^{-1} , thus unusual high frequency, has been assigned to Fe^{3+} monocarbonyls formed on highly electrophilic extraframework Fe^{3+} cations.⁴³ Comprehensive investigations of Fe ions speciation in FeFER have been delivered by Ivanova et al.⁴⁴ The Fe species in zeolites FeFER prepared from a ferrous solution was found to be mainly in Fe^{2+} forms. The accessibility of Fe^{2+} cations for CO molecules was dependent on the geometry of the positions that allowed one or two probe molecules to approach the Fe^{2+} site from different cages. It has been well recognized that the ability to form polycarbonyls is diverse for different zeolite positions.⁴⁵ Thus, Fe^{2+} ions forming monocarbonyls at 2195 cm^{-1} were easily converted into dicarbonyls (2188 cm^{-1}) at low temperatures. Additionally, this type of Fe^{2+} cations showed a little tendency to oxidation thus they hardly yielded Fe^{3+} cations. Another type of Fe^{2+} ions when ligated CO produced exclusively monocarbonyls (the band at 2189 cm^{-1}), was easily oxidized to Fe^{3+} ions most probably associated to the formation of α -oxygen species. With increasing Fe content an additional site is occupied. Iron ions in this position altered easily and reversibly their oxidation state $\text{Fe}^{2+}/\text{Fe}^{3+}$. Neither Fe^{2+} nor Fe^{3+} ions in Fe_2O_3 clusters were supposed to be revealed by IR spectroscopy of adsorbed probe.⁴⁴

In this work, an interaction of carbon monoxide at -130 °C with Fe species in vacuum only treated zeolites led to the development of the 2188 and 2200 cm^{-1} monocarbonyl bands (Figure 2). When the 2188 cm^{-1} band was unquestionably assigned to $\text{Fe}^{2+}(\text{CO})$ monocarbonyls formed by the exchangeable Fe^{2+} cations, the upshifted 2200 cm^{-1} band was tentatively attributed to exchangeable Fe^{2+} cations in framework location guaranteeing greater electron acceptor properties than Fe^{2+} of lower frequency monocarbonyls (2188 cm^{-1})⁴⁵ or to Fe^{3+} ions in exchange positions (Figure 2).⁴³ The intensity of both 2190 and 2200 cm^{-1} bands increased after reduction by hydrogen (Figure 2) and this process was not followed with the consumption of any monocarbonyl band indicating that newly formed Fe^{2+} cations originated from the Fe(III) species not detectable with CO as probe.

Subsequent re-oxidation resulted in the transformation of isolated Fe^{2+} cations, detected as the 2188 and 2200 cm^{-1} bands consumption, into species not represented by any monocarbonyls band (Figure 2).⁴⁴ Therefore, the Fe^{3+} oxo-species are believed to be formed upon O_2 -treatment. Additionally, the

facility to oxidation depended on electron donor properties of Fe(II) species. The cationic sites represented by a higher frequency monocarbonyl band (the 2200 cm^{-1}) were consumed in the first order and they were absent in oxidised samples.

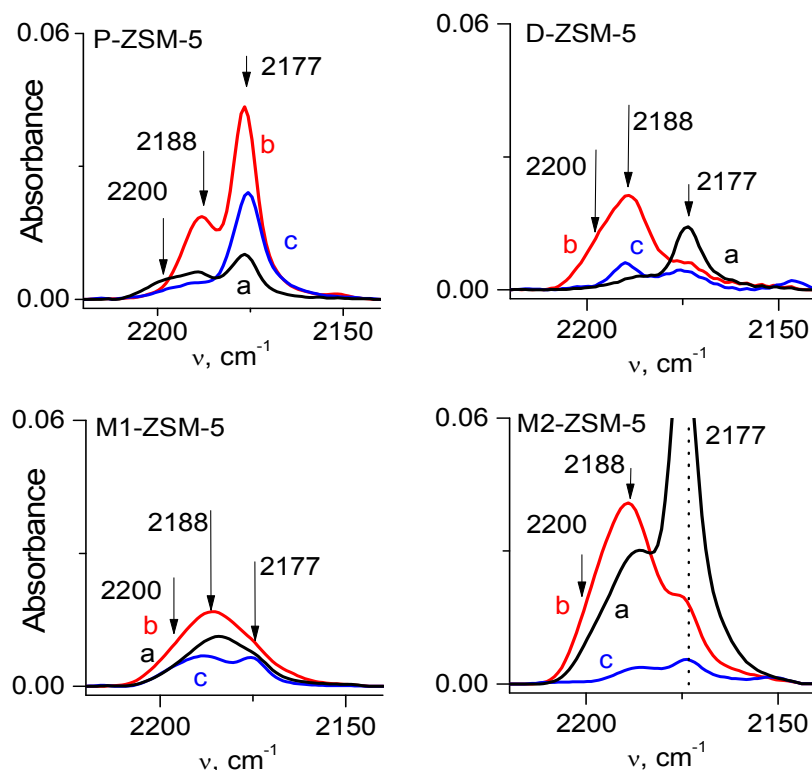


Figure 2. Maximum intensities of the $\text{Fe}^{2+}(\text{CO})$ bands recorded for vacuum treated (a – black line), H_2 -reduced (b – red line) and O_2 -treated (c – blue line) zeolites ZSM-5 of different hierarchy.

2.2.2. Absorption Coefficient of the $\text{Fe}^{2+}(\text{CO})$ Band

The sensitivity of the frequency of $\text{C}\equiv\text{O}$ band on the electron donor/electron acceptor properties of adsorption sites makes the carbon monoxide molecule particularly designated to quantitative studies of adsorption species. The main output of such quantitative investigations is the receiving of the concentration of all possible TMI sites dispersed on zeolite matrix independently. In the quantitative IR experiments the most demanding task is the determination of the absorption coefficient of the band of adducts formed by the interaction of probe molecules with adsorption site. The most desired is the situation when each probe molecule reacts selectively with only one kind of adsorption site and the stoichiometry of this interaction is perfectly known. The elaboration of exact experimental conditions allows for fulfilling the selectivity requirement. Sorption of CO was performed on H_2 treated samples revealing the highest intensity of $\text{Fe}^{2+}(\text{CO})$ band at $2190\text{--}88\text{ cm}^{-1}$, thus hosting the highest amounts of isolated Fe^{2+} cations.

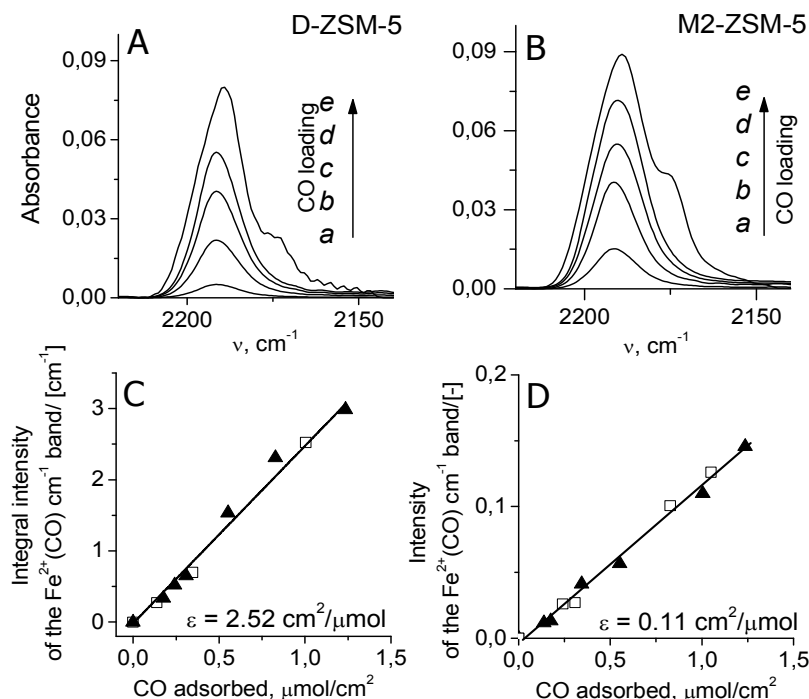


Figure 3. The spectra recorded at $-130\text{ }^\circ\text{C}$ upon the sorption of CO doses in H₂-reduced Fe-exchanged zeolites D-ZSM-5 (A) and M2-ZSM-5 (B) and then used for the determination of the absorption coefficient of the Fe²⁺(CO) band. The plots of the calibration lines, (C) based on the integral intensity (area) and (D) the intensity (height) of the 2200–2188 cm⁻¹ Fe²⁺(CO) band, used in determination of the Fe²⁺ cation concentrations (D-ZSM-5 – squares, M2-ZSM-5 – triangles).

The sorption of relatively small amounts of CO performed at $-130\text{ }^\circ\text{C}$ on H₂-reduced zeolites fulfilled the requirement for the selective reaction of CO with Fe²⁺ cations. The iron moieties were the only species enabled to interact with probe and, when the first doses of CO were adsorbed, the possibility of the interaction of the Si(OH)Al groups with carbon monoxide was totally eliminated due to a higher value of the adsorption heat of CO on Fe²⁺ sites than on the Si(OH)Al groups. The spectra in Figure 3 were recorded upon the sorption of small known doses of CO at $-130\text{ }^\circ\text{C}$ in zeolites D-ZSM-5 and M2-ZSM-5 previously H₂-reduced thus accommodating the highest amount of Fe²⁺ species. At low loading carbon monoxide reacted selectively with exchangeable Fe²⁺ which was exhibited by the development of the 2200–2188 cm⁻¹ monocarbonyl Fe²⁺(CO) band as the only species (Figure 3A and 3B, Spectra a-d). Neither the spectrum of gaseous CO nor the bands of dicarbonyls Fe²⁺(CO)₂ were noticed. At higher CO loading the 2177 cm⁻¹ band attributed to CO hydrogen bonded to Si(OH)Al groups started to develop (Figure 3A and 3B, Spectrum e). In this case the rule of the selective reaction of CO with Fe²⁺ sites was not obeyed thus this spectrum was excluded from further analysis. The integral intensities (Figure 3B) of the Fe²⁺(CO) bands at 2200–2188 cm⁻¹ in the spectra recorded upon the sorption of the first CO doses in H₂-reduced zeolites D-ZSM-5 and M2-ZSM-5 were measured and plotted against the concentration of CO sorbed. The points attained in three independent experiments

were represented by the same linear dependence (Figure 3 C and D). The slope of the line taken as the integral absorption coefficient of the $\text{Fe}^{2+}(\text{CO})$ band was equal to $2.52 \pm 0.07 \text{ cm}/\mu\text{mol}$ (Figure 3C), while the value obtained from the band height was $0.11 \pm 0.01 \text{ cm}^2/\mu\text{mol}$ (Figure 3D). In our earlier works regarding the evaluation of quantitative procedure for cobalt,⁴⁶ silver,⁴⁷ copper,³³ and nickel³⁶ sites in zeolites we have evidenced that the value of the absorption coefficient of respective carbonyls were independent of the structure type of zeolite regardless of the various CO stretching frequencies found in these structures. Consequently, it is believed that such assumption can be spread on the iron-exchange zeolites ($2200\text{--}2188 \text{ cm}^{-1}$ for Fe-ZSM-5 and FeBEA, $1889\text{--}1873 \text{ cm}^{-1}$ and $1855\text{--}1850 \text{ cm}^{-1}$ for FeY,⁴⁸ etc.)

2.2.3. Concentration of Iron Moieties Detected by Carbon Monoxide

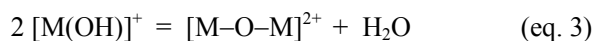
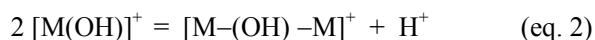
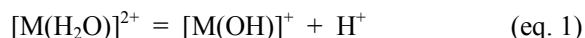
Determination the concentration of the iron(II) species in the studied zeolites required the saturation of all Fe^{2+} species with monocarbonyls. Therefore, the doses of carbon monoxide were sorbed until the maximum intensities of the $\text{Fe}^{2+}(\text{CO})$ monocarbonyl bands were achieved in zeolites non-treated as well as previously H_2 -reduced and subsequently reoxidised (Figure 2). The spectra recorded upon the saturation of all Fe^{2+} sites with CO molecules revealed the presence of two bands of $\text{Fe}^{2+}(\text{CO})$ adducts: the 2200 and 2188 cm^{-1} bands of CO bonded to Fe^{2+} in the form of an exchangeable cations. Besides, the 2177 cm^{-1} band of CO hydrogen bonded to $\text{Si}(\text{OH})\text{Al}$ groups was distinguished. As the bands originating from sites of different nature the integral intensities of the carbonyl bands were calculated upon the deconvolution.

The concentrations of respective Fe^{2+} sites were calculated from the maximum intensities (Figure 2) and their absorption coefficients. The value of the $\text{Fe}^{2+}(\text{CO})$ band absorption coefficient concerns 2200 and 2188 cm^{-1} bands of carbonyls formed on Fe^{2+} exchangeable cations. In earlier investigation on Ni exchanged zeolites Y and ZSM-5³⁶ it has been recognized that the same value of absorption coefficient could be applied for the bands of CO interacting with Ni^{2+} both in the various exchange positions and those in the oxo-forms. Accordingly, it was assumed that the value of the absorption coefficient was independent on the Fe^{2+} cations location, thus their electron donor properties. The same value of the absorption coefficient was used for all monocarbonyl bands of all Fe^{2+} species: the bands at 2200 and 2188 cm^{-1} . The values of the concentration of the Fe^{2+} sites in studied zeolites gathered in the Table 2. The amount of iron moieties detected with CO in non-treated samples reached the highest values for M2-ZSM-5 (57% of total Fe concentration) confirming the highest dispersion of Fe(II) species in mesostructured zeolite. In spite of hosting the smallest Fe amount ($70 \mu\text{mol/g}$), thus presumably the highest expected dispersion, the D-ZSM-5 was found to be zeolite of the poorest Fe(II) species accessibility for CO molecules. This small amount of Fe(II) centers measured for desilicated zeolite could result from the presence of Fe(III) oxides not detectable with CO and/or from highly clustered nature of Fe oxide species of both oxidation states.

Table 2. Results of XRF Analysis and Quantitative Studies of Carbon Monoxide Sorption.

Sample name	Fe [$\mu\text{mol/g}$]			
	XRF	Fe ²⁺ from CO sorption		
		non-treated	H ₂ -reduced	O ₂ -oxidised
P-ZSM-5	94	20	75	10
D-ZSM-5	104	10	99	20
M1-ZSM-5	242	40	50	25
M2-ZSM-5	143	82	122	10

Upon the contact with hydrogen at 600 °C the amount of Fe cations accessible for CO significantly increased. The highest dispersion of Fe(II) species was evidenced for zeolites of the most efficient mesoporosity and with preserved crystallinity. For mesoporous M2-ZSM-5 dispersion of Fe reached 85% while in desiccated zeolites D-ZSM-5 95% of Fe cations was detected with probe. This noticeable dispersion of Fe²⁺ cations can originate from the optimal values of the Si/Al and Fe/Al ratios that assist the occurrence of isolated Fe²⁺ cations. The contribution of TMI oxide-like-species was found to increase with both the Si/Al ratio and TMI content (TMI/Al). Large distances between AlO₄⁻ tetrahedral favour the hydrolysis (eq. 1) process resulting in the formation of oxide-like TMI species:



Hydrolysis is followed by the condensation of MOH⁺ species in ololation (eq. 2) and oxolation (eq. 3) processes finally leading to the oxide forms of different dispersion extent. This process occurs at elevated temperatures, i.e. during thermal pre-treatment of TMI-exchanged zeolites and ensures the neutralization of AlO₄⁻ tetrahedra by protons while the majority of the TMI bears the oxide forms. This is a case of zeolite M1-ZSM-5 where both lowered crystallinity and high Fe/Al value promoted the existence of Fe-oxide forms even after the H₂-treatment. In contrast, in zeolite D-ZSM-5 of Si/Al = 21 the relatively high density of AlO₄⁻ stabilizes the divalent Fe²⁺ cations that, due to low Fe/Al ratio (0.15), are formed by reduction in small amounts.

Subsequent re-oxidation process provoked by the contact of H₂-treated zeolites with oxygen at 600 °C resulted in vital drop of the amount of Fe(II) species able to interact with CO molecules. The consumption of Fe²⁺ species both from the exchangeable cations and oxo-forms in oxidation process can be related to the formation of oxide Fe(III) moieties. The CO ligation to extraframework Fe(III) species hosted in zeolites have been excluded, however such possibility for Fe(III) ions in tetrahedral framework positions is still under discussion.^{43,44,49} The lack of interaction between CO and extraframework Fe³⁺ species benefits in quantitating Fe²⁺ sites solely.

The elaborated methodology has been also verified for zeolites of various type topologies. Concentration of Fe^{2+} sites in zeolites Fe-BEA and Fe-FER presented in the Table 4. In aluminium rich zeolite Fe-BEA the amount of Fe^{2+} species detected with CO consists of ca. 13 % of total Fe species hosted in zeolite. Upon reduction process the number of Fe^{2+} sites detectable with CO noticeably increased, nevertheless, only half of total Fe amount existed as Fe^{2+} exchangeable cations. The rest of Fe species bears the form of oxides of Fe(II) and/or Fe(III). For zeolite Fe-BEA of lower aluminum content the number of Fe^{2+} sites dramatically decreased evidencing the influence of Si/Al ratio on Fe ions speciation. As mentioned earlier, in zeolites of high Al concentration where the distances between AlO_4^- tetrahedral are relatively close, almost all divalent ions are located in cation-exchange positions. The contribution of oxide species increases with the Si/Al ratio and with Fe/Al content, both these factors favour hydrolysis. Also the presence of high amounts of Al extraframework species in zeolite BEA results in lower ability of framework to balance the divalent cations, thus higher amount of oxide species is facilitated. Stabilization of the isolated Fe^{2+} cation is ensured in zeolite with low values both Si/Al and Me/Al ratios. This condition is obeyed for Fe-FER where 93 % of Fe species are exchangeable cations.

Table 3. The Fe(II) Moieties Concentration Derived from Quantitative Studies of Carbon Monoxide Sorption for Zeolites of Different Topology.

Sample	Si/Al	Al [$\mu\text{mol/g}$]	Fe/Al	Fe [$\mu\text{mol/g}$]		
				chemical analysis	CO sorption	
					non-treated	H ₂ -reduced
Fe-BEA	11	1156	0.59	687	85	355
Fe-BEA	19	694	0.94	654	105	195
Fe-FER	8.5	1418	0.14	194	80	180

2.2.4. Interaction of NO with Iron Species

Sorption of nitrogen monoxide can provide valuable information of the status of TMI species in zeolites. Low energy of the SOMO (π^* antibonding) orbital facilitates the donation of electrons to this orbital distinctly weakens the N–O bond resulting in an important red shift of the nitrosyl band in comparison to NO in gas phase. Consequently NO molecules are widely applied as a sensitive probes for characterization electron-donor properties of TMI adsorption sites.

The ligation of NO to Fe^{n+} species dispersed on zeolitic matrixes has been extensively studied.⁵⁰ While the NO adsorption on oxidized Fe-zeolites has been found to be negligible⁵⁰⁻⁵² the mono- and dinitrosyls are believed to be formed solely on Fe^{2+} ions. However, Guglielminotti et al.^{51,53} reported the $\text{Fe}^{3+}(\text{NO})$ nitrosyl bands at frequencies higher than 1805 cm^{-1} . Consequently, a band at 1930 cm^{-1} has been attributed to $\text{Fe}^{3+}(\text{NO})$ mononitrosyls in $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{2+}$ fragments.⁵⁴

Interaction of NO with studied ZSM-5 samples (Figure 4) resulted in the appearance of the 1880 and 1890 cm^{-1} bands of the $\text{Fe}^{2+}(\text{NO})$ mononitrosyls formed by isolated Fe^{2+} cations.⁵⁵ At higher concentration of NO adsorbed the set of bands of the $\text{Fe}^{2+}(\text{NO})_2$ dinitrosyls were developed at 1920 and 1812 cm^{-1} . In zeolite FeZSM-5 (Figure 4A) H_2 -treatment resulted in the noticeable increase of 1890 cm^{-1} band. It is also clearly seen that the sites detected by NO at 1890 cm^{-1} were remarkably less populated in the vacuum treated and oxidized sample, i.e. the respective iron sites are the most sensitive ones towards O_2 treatment. For hierarchical zeolites (Figure 4B–D) the susceptibility to O_2 -treatment is also observed, however, the Fe^{2+} sites detected by NO at lower frequencies were formed.

2.2.5. Absorption Coefficient of the $\text{Fe}^{2+}(\text{NO})$ Band

Sorption of small measured doses of NO on H_2 -reduced zeolites D-ZSM-5 and M2-ZSM-5 resulted in the appearance of 1890 cm^{-1} band of $\text{Fe}^{2+}(\text{NO})$ mononitrosyls obeying the rule of the selective reaction of NO with Fe^{2+} sites (Figure 5A and 5B, Spectra a-d). At higher NO loading the $\text{Fe}^{2+}(\text{NO})_2$ dinitrosyl bands started to develop, mainly for zeolite M2-ZSM-5 (Figure 5B, Spectra d-e), thus these spectra were excluded from further analysis. It should be also mentioned, that sorption of NO was performed up to achieving the $\text{Fe}^{2+}(\text{NO})$ nitrosyls solely. When simultaneous absence of the NO transformation products, e.g. N_2O , NO^+ ions were detected, the spectra were also excluded from further consideration. Finally, the integral intensities (Figure 5B) of the $\text{Fe}^{2+}(\text{NO})$ bands at 1890-1880 cm^{-1} were measured and plotted against the concentration of NO sorbed. The points attained in two independent experiments were represented by the same linear dependence (Figure 5C and 5D). The slope of the line taken as the integral absorption coefficient of the $\text{Fe}^{2+}(\text{NO})$ mononitrosyl band was found to be equal to $13.80 \pm 0.06 \text{ cm}^2/\mu\text{mol}$ (Figure 5C) when analysis was based on integral intensities of the bands and $0.39 \pm 0.02 \text{ cm}^2/\mu\text{mol}$ (Figure 5D) when the height of the mononitrosyl bands were considered.

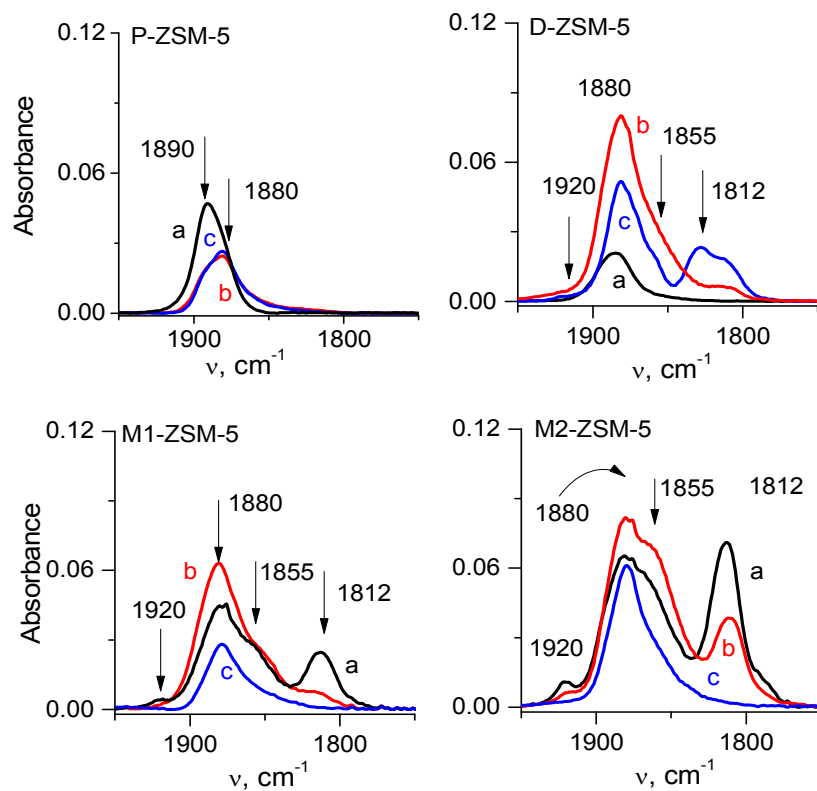


Figure 4. Maximum intensities of the Feⁿ⁺(NO) bands recorded for vacuum treated (a), H₂-reduced (b) and O₂-treated (c) zeolites ZSM-5 of different hierarchy.

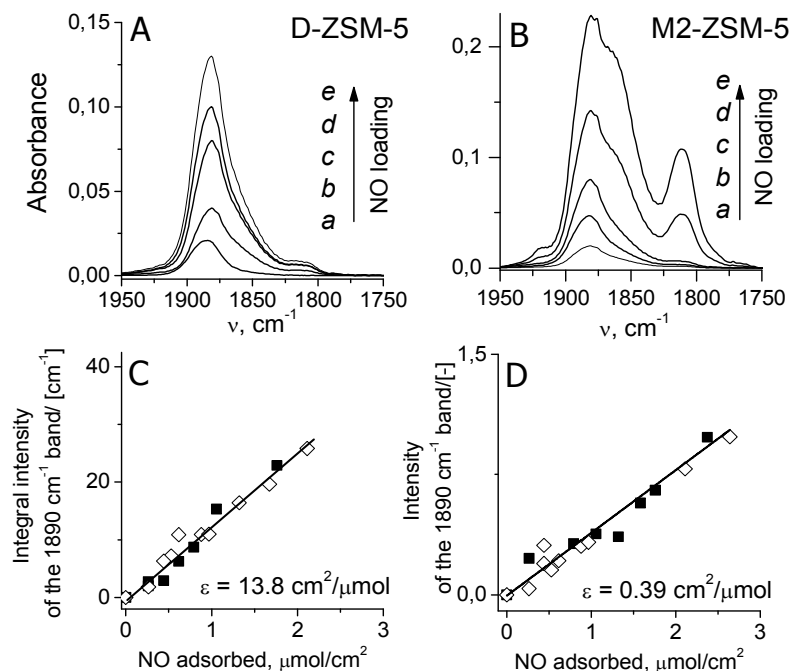


Figure 5. The spectra recorded at RT upon the sorption of NO doses in H₂-reduced Fe-exchanged zeolites D-ZSM-5 (A) and M2-ZSM-5 (B) and then used for the determination of the absorption coefficient of the Fe²⁺(NO) band. The plots of the calibration lines, based on (C) the integral intensity (area) (D) and the intensity (height) of the 1890–1880 cm⁻¹ Fe²⁺(CO) band, used in determination of the Fe²⁺ cation concentrations (D-ZSM-5 – squares, M2-ZSM-5 – diamonds).

2.2.6. Concentration of Iron Derived from NO Sorption

Sorption of NO was performed up to achieving the maximum intensities of Fe²⁺(NO) mononitrosyls with simultaneous absence of the NO transformation products, e.g. N₂O, oxo-compounds of nitrogen in oxidation states +3 and +5 (Figure 5). The spectra revealing the presence of NO⁺ ions were also excluded from further analysis once Kefirov et al.⁵⁶ proposed interaction of NO with the Fe³⁺-OH centers yielding Fe²⁺ and HNO₂. Consequently, the Fe²⁺(NO) concentration determined was typical of “fresh” catalyst and not perturbed by the additional Fe²⁺ species formed in reaction of NO with Fe(III) sites.

As the sorption of NO revealed the presence of three mononitrosyl species (NO bands at 1890, 1880 and 1855 cm⁻¹) the bands were subjected to deconvolution analysis that allowed calculating the concentration of the Fe²⁺ mononitrosyls of various types (Table 4). Scrutiny of the data revealed that the concentration of all mononitrosyls adducts, that corresponded to the concentration of Fe²⁺ moieties able to bond NO, was equal to the Fe²⁺ cations concentrations detected with carbon monoxide. This consistency was found for vacuum and H₂-treated zeolites. For oxygen-treated samples the mononitrosyl Fe²⁺(NO) concentration was noticeably higher than the amount of Fe²⁺(CO)

monocarbonyls adducts formed upon CO sorption due to high reactivity of Fe^{3+} -OH centers towards reduction to Fe^{2+} cations.

Table 4. The Fe Moieties Concentration Derived from Quantitative Studies of Nitrogen Monoxide Sorption and Obtained from XRF Analysis.

Sample name	Fe [$\mu\text{mol/g}$] from NO sorption									
	XRF	non-treated			H_2 -reduced			O_2 -oxidised		
		1880 & 1890 cm^{-1}	1855 cm^{-1}	Σ	1880 & 1890 cm^{-1}	1855 cm^{-1}	Σ	1880 & 1890 cm^{-1}	1855 cm^{-1}	Σ
P-ZSM-5	94	5	20	25	50	15	65	50	15	65
D-ZSM-5	104	17	0	17	80	15	95	40	10	50
M1-ZSM-5	242	30	15	45	45	10	55	27	5	32
M2-ZSM-5	143	50	30	80	70	40	120	55	10	60

3. Conclusions

This work evidenced that IR spectroscopy offers a well-established approach for the quantification of Fe^{2+} sites in zeolites. The experimental procedure was based on carbon monoxide and nitrogen monoxide sorption in Fe-exchanged zeolites ZSM-5 of different pore hierarchy and followed by IR spectroscopy. The values of the absorption coefficients of the respective IR monocarbonyl $\text{Fe}^{2+}(\text{CO})$ and mononitrosyl $\text{Fe}^{2+}(\text{NO})$ bands were attained. In turn, the concentrations of Fe(II) moieties of various kinds were calculated and discussed with regard to the chemical composition (Si/Al and Fe/Al) of studied zeolites. The values of the absorption coefficients were found to be valid also for zeolites of BEA and FER topologies thus proposed method is supposed to be finely adapted to quantify Fe^{2+} sites in zeolites of other structures.

4. Experimental

4.1. Studied materials

Parent ZSM-5 of Si/Al=32, hereafter denoted as P-ZSM-5, was purchased from Zeolyst Company (CBV 5524G). Zeolite D-ZSM-5 was obtained from P-ZSM-5 by alkaline leaching in the 0.2 M NaOH solution at the temperature of 65 °C for 0.5 h. After desilication, the suspension was cooled down in ice-bath, filtered, and washed with distillate water until neutral pH. Next fourfold $\text{Na}^+/\text{NH}_4^+$ ion-exchange with 0.5 M NH_4NO_3 was performed at 60 °C for 1 h. Finally, the resulting sample were again filtrated, washed, and dried at room temperature.

Zeolites M1-ZSM-5 and M2-ZSM-5 of tuneable mesoporosity were obtained via a direct synthesis route using the amphiphilic organosilanes as a mesopore-directing agent. For the synthesis of mesoporous zeolite M1-ZSM-5 of Si/Al = 27, the TPOAC (3(trimethoxysilyl)-propyloctadecyldimethyl-ammonium chloride) was added to a conventional alkaline mixture containing TPABr (tetrapropylammonium bromide), NaOH, tetraethylorthosilicate, sodium aluminate and distilled water. The molar composition of the mixture was 43 Na_2O : 5 Al_2O_3 : 200 SiO_2 : 20 TPABr : 10 TPOAC : 15 H_2SO_4 : 18000 H_2O . This mixture was heated with stirring at 130 °C for 240 h in an autoclave. For synthesis of mesoporous zeolite M2-ZSM-5 (Si/Al = 20) the same procedure was adapted, however, the reaction was performed at 130 °C for 72 h. After a reaction the precipitated products were filtered, washed with distilled water, dried at 110 °C and calcined at 550 °C.

All zeolites were subjected to two-fold ion-exchange procedure with 0.5 M $\text{Fe}(\text{NO}_3)_3$ that was performed at 60 °C for 1 h. Finally, the resulting Fe-sample were again filtrated, washed, and dried at room temperature. The notation applied for native Na or H-form zeolites was preserved for their iron-analogues.

In some experiments iron form in Fe-ZSM-5 zeolites undergone the reduction in H_2 atmosphere (60 Torr in gas phase) at 600 °C for 1 h. Otherwise, the iron forms were reoxidised by the treatment in O_2 atmosphere (60 Torr in gas phase) at 600 °C for 1 h.

4.2. Characterisation Techniques

The powder X-ray diffraction (XRD) measurements were carried out using a X'Pert Pro Philips (PANalytical Cubix diffractometer), with CuK_α radiation, $\lambda=1.5406 \text{ \AA}$ and a graphite monochromator in the 2θ angle range of $5\text{-}40^\circ$. X-ray powder patterns were used for structural identification of the relative crystallinity value (%Cryst) for all the zeolites. The determination of the relative crystallinity value was based on the intensity of the peaks in the range between 10° to 60° .

The content of Si and Al concentrations in studied materials investigated in this work were determined by the XRF method using an Energy-Dispersive XRF spectrometer (Thermo Scientific, ARL QUANT'X with the Rh anode, the X-rays of 4-50 kV (1 kV step), 1mm size beam). A 3.5 mm Si(Li) drifted crystal with a Peltier cooling ($\sim -88^\circ\text{C}$) was used as a detector.

Prior to FTIR studies, the materials were pressed into the form of self-supporting wafers (ca. $5\text{-}10 \text{ mg/cm}^2$) and pre-treated in situ in an IR cell at 500°C under vacuum conditions for 1 h. Spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a MCT detector with the spectral resolution of 2 cm^{-1} . All the spectra presented in this work were normalized to 10 mg of sample.

Sorption of the measured doses of carbon monoxide (Linde Gas 99.95%) was performed at -130°C while nitrogen monoxide (Linde Gas 99.5%) was sorbed at room temperature.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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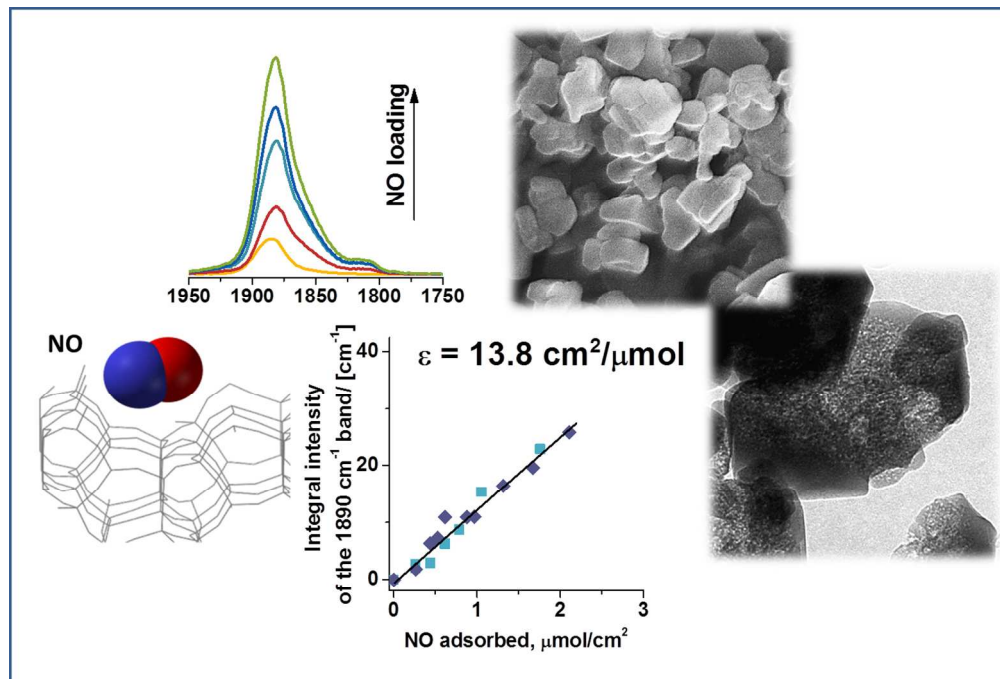
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