STUDY OF THE INFLUENCE OF WATER ON OXIDATIVE PROPERTIES OF Fe^{3+} IN ZSM-5 ZEOLITE CHANNELS

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The interactions of phenol and thiophene with Fe^{3+} ions have been studied in ZSM-5 zeolite channels in the presence of water. The Fe-ZSM-5 was prepared by the ion exchange of Fe^{3+} for Na^+. The Fe^{3+} ions in zeolite channels have unsaturated co-ordination spheres and oxidize organic substrates (phenol, thiophene) at room temperature. The interaction of Fe^{3+} with phenol gives rise to the stabilized cation-radical $PhOH^{\bullet+}$ and thiophene forms low oligomers (2–6 monomeric units). The oligomers are present in the neutral as well as oxidized form as cation-radicals (polarons). The formation of dications (bipolarons) has not been observed.

Keywords: Aluminosilicates; Zeolites; Molecular sieves; Heterogeneous catalysis; Transition metals; Cation-radicals; Oxidation; Phenol; Thiophene.

Transition metals incorporated in aluminosilicate molecular sieves have held considerable interest in past years due to potential by new catalytic properties of the modified materials. This results in different acidities and in new catalytic activities in dependence on the nature and loading of the incorporated transition metal ion.

Iron-doped zeolites are used as catalysts for the selective oxidation and removal of NO_x [1]. At low iron loading, Fe/MFI (ZSM-5) zeolite has been reported to be active in the partial oxidation of benzene to phenol and of methane to methanol with N_2O as the oxidant[2]. With high iron loadings, certain "over-exchanged" Fe/MFI catalysts have shown a high activity and remarkable stability in the selective catalytic reduction (SCR) of NO_x with hydrocarbons in presence of a large excess of oxygen and water vapour[3,4]. Generally Fe-ZSM-5 are materials, which are known to show catalytic activ-

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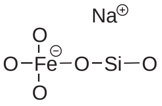
ity in a number of chemical processes. Among them isomerization, conversion, and dehydrogenation reaction[5–7], reduction of NO by hydrocarbons[8] and selective oxidation[9–11] can be mentioned. For most of these reactions, the catalytic activity is thought to be related to extra-framework iron species (iron oxides or oxohydroxide aggregates). A certain number of papers have been published concerning the characterization of Fe-exchanged zeolites, *i.e.*, of systems where iron is introduced in the zeolite channels and cavities from an external source (see for instance refs[12–16]). Information on the location, immediate environment and possible mobility of the active iron centres within the zeolite structure is of paramount importance for understanding its catalytic and adsorptive properties. The performance of zeolite catalysts depends on the method of their preparation. Whereas the conventional wet ion exchange results in catalysts with a low Fe/Al ratio and mediocre performance, the sublimation method was found quite effective for preparing selective catalysts with high durability and the Fe/Al ratio near the unity. However, the origin of iron sites and activity is still controversial[4]. On the basis of temperature-programmed reduction studies (TPR) with CO and H_2 and EPR data, an oxygen-bridged dinuclear iron complex $[HO–Fe^{3+}–O–Fe^{3+}–OH]^{2+}$ was proposed as an active centre in chemical (catalytic) processes[4,17]. This model has been recently supported by EXAFS and XANES results[18,19]. Extra-framework iron species can be formed also by "extraction" during the post-synthesis thermal treatments[20–22] of the as-synthesized Fe-ZSM-5 and acting either independently or in synergy with protonic – Fe–OH–Si – sites (Brönsted acid). Inter-framework iron species (Fe–OH–Si) can be also present in the zeolite crystallic lattice of the parent sample, where they are created as impurities in the process of synthesis. Concentration of Fe-species in the lattice can be increased directly in the process of zeolite synthesis by adding a ferric substrate into the reaction mixture. The structure of the created ferric centres has not been yet fully studied and is still a topic of discussions in literature.

For example, in the as-synthesized Fe-ZSM-5, Fejes *et al.*[24] proposed three types of lattice sites of iron (Fe^{3+}) denoted as follows:



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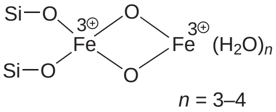

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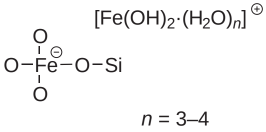

type III

From the above cited works it follows that various iron species have been identified in Fe-ZSM-5: isolated ions in framework positions or extra-framework at cationic positions in the zeolite channels and cavities, dinuclear and, in general, oligonuclear iron complexes in extra-framework positions, iron oxide nano-agregates (1–2 nm), and large iron oxide particles (>5 nm) in the surface of the zeolitic crystal, depending on the preparation method. But there is still controversy in the relation to the nature of the active Fe sites in different processes catalyzed by Fe-ZSM-5, due to heterogeneous nature of the Fe species in the material. However, from the analysis of the existing literature summarized above, it can be concluded that the real nature of the extra-framework species in Fe-ZSM-5 zeolites is not fully understood[25].

In our previous work[26], oxidative properties of Fe^{3+}-ZSM-5 prepared by the ionic exchange of Fe^{3+} for Na^+ were studied. As a model reaction, the oxidative oligomerization of thiophene in channels of the Fe-ZSM-5 zeolite, which was subjected before the reaction to thermal activation (500 °C, air atmosphere), was used. Under these conditions, the oligomers of thiophene with 2–9 thiophene units were formed. As it is already known that the catalytic activity of Fe-ZSM-5 depends in many cases on the amount of water present in zeolite channels we concentrated in this work on studying the influence of water on oxidative properties of Fe^{3+}. To avoid deeper changes in the zeolite crystallic microstructure we performed dehydration under milder conditions (temperature during dehydration did not exceed 110 °C). In the present work, the influence of a “higher” amount of water on oxidative properties of the Fe^{3+}-ZSM-5 zeolite prepared by ion exchange of Fe^{3+} for Na^+ was studied. Phenol and thiophene were used as organic substrates. Phenol (donor) was chosen as we anticipated the creation of a Fe–phenol complex under conditions when Fe^{3+} was co-ordinatively unsaturated with water. Thiophene can for the same reason undergo oxidative oligomerization, even if the zeolite sample was not calcined before the reaction.

The goal of this work was to study physicochemical properties of the iron-doped ZSM-5 zeolite and its ability to react with phenol and thiophene in the presence of water in the zeolite microstructure.

EXPERIMENTAL

The sodium form of ZSM-5 (Na-ZSM-5) was supplied by the VURUP Co., Slovakia (molar ratio SiO_2/Al_2O_3 43.7, BET area 303.22 $m^2\ g^{-1}$, volume of pores 0.393 $cm^3\ g^{-1}$, $p/p_o = 0.9999$; total absorption volume $304.59 \cdot 10^{-6}\ m^3\ g^{-1}$, Brönsted sites 0.140 mmol g^{-1}). Sorption properties were determined by physical adsorption of nitrogen at –196 °C in Sorptomatic 1800. Before measuring, sample was calcined at 500 °C for 3 h and evacuated at 300 °C and 2 Pa for 5 h. Specific surface area was calculated by BET-isotherm, volume of micropores was evaluated by t-plot method[27]. According to this method, the volume of nitrogen adsorbed is plotted against *t* (thickness of nitrogen layer) for the nitrogen on a non-porous reference solid (standard isotherm). Acidity was measured by TPD of ammonia in the range 220– 250 °C. Activation of the catalyst lasted 1 h at 500 °C.

Fe-ZSM-5 was prepared by ion exchange with an aqueous solution of 0.5 M $Fe(NO_3)_3$ (Fluka) according to ref.[10] After the 12-h ion exchange at room temperature under vigorous stirring, the product was filtered off, thoroughly washed out with deionized water, and dried in a desiccator. The basic characteristics of zeolite samples are indicated in Table I.

The reaction of Fe-ZSM-5 with phenol (Aldrich) was performed in a 1 M ethanol solution. 2 g Fe-ZSM-5 were added to 100 cm^3 of 1 M ethanol. The obtained mixture was stirred in a magnetic stirrer, at room temperature for 10 days. Finaly the zeolite was carefully washed on the filter with ethanol and dried in a desiccator.

The oligomerization of thiophene (Aldrich) in Fe-ZSM-5 zeolite channels was carried out using the procedure described in our previous work[26], but without thermal activation before the reaction. The reaction proceeded at room temperature for 5 days. In both reactions Fe-ZSM-5 with $7 \cdot 10^{-4}$ mole % Fe was used. Diffusion reflectance UV-VIS spectra were measured with an M-40 apparatus (Zeiss, Germany) and the data were transformed to Kubelka–Munk parameters ($F[R_\infty]$). Barium sulfate was used as a standard.

FT-IR spectra were measured in KBr tablets using a Magna 750 (Nicolet) apparatus with an accuracy of ±0.1 cm^{-1} in KBr tablets. All spectra were corrected for the water content in KBr. Dehydration of Fe-ZSM-5 present in KBr tablets was performed under an IR-lamp and lasted 4 h. Temperature of the sample did not exceed 110 °C. After the process of drying had been finished the sample was transferred into a FT-IR spectrometer and measured. 100 mg KBr and 4 mg of zeolite were used for the tablets.

A Bruker 200 D EPR spectrometer with an Aspect 2000 computer was used to measure the spectra. A typical setting for the series of EPR experiments was as follows: gains 10^4–10^5; time constant 50 or 100 ms; sweep time 20 or 50 s, modulation amplitude 0.005–0.05 mT, microwave power 10 mW. The *g*-value was determined with an uncertainty of ±0.0001 using a marker containing 1,1-diphenyl-2-picrylhydrazyl (DPPH) built into the spectrometer. The measurements of EPR spectra were accomplished in a 3-mm o.d. quartz EPR tube. Dehydration for the purpose of measuring EPR spectra was performed in an EPR tube with a closing

TABLE I
Basic characteristics of zeolites

Zeolite	Ion exchange time h	Fe content mole %	Fe/Al ratio	Fe content mmol g^{-1} of zeolite
Na-ZSM-5	–	2×10^{-4}	0.01	1.8×10^{-3}
Fe-ZSM-5	1	3×10^{-4}	0.02	3.5×10^{-3}
	4	6×10^{-4}	0.03	5.6×10^{-3}
	12	7×10^{-4}	0.04	7.2×10^{-3}

cock and lasted 1 h at temperature of 100 °C and pressure of 1 Pa. Height of the column of the zeolite sample was 1 cm. After dehydration the closing valve was closed and the tube was transferred to the EPR spectrometer. Under these experimental conditions the weight reduction of the zeolite samples was between 9–10 wt.%. Rehydration of the zeolite samples was done in the desiccator, where the open EPR tube with zeolite was placed and 150 cm^3 saturated water vapour was injected. Rehydration lasted 24 h.

X-Ray microanalysis of zeolite samples was conducted by scanning electron microscopy (SEM) with a JXA-840 A instrument (JEOL).

RESULTS AND DISCUSSION

Figures 1 and 2 (Table II) show the FT-IR spectra of zeolite samples (Na-ZSM-5, Fe-ZSM-5, Fe-ZSM-5-phenol, Fe-ZSM-5-thiophene) before and after IR drying. From the results it follows that both non-modified and modified zeolite samples show two absorption bands (3400–3500 and 3650–3700 cm^{-1}, respectively). On the second band, a shoulder can be identified at 3600–3610 cm^{-1}.

According to ref.[29], the absorption band in the 3400–3500 cm^{-1} range may be assigned to complexes of OH groups of water with isolated silanol groups present in the channels and on the external surface, and that at 3600–3700 cm^{-1} may be assigned to the interaction of the OH group with the oxygen in the SiOAl group. The shoulder at *ca* 3600 cm^{-1} belongs to the Brönsted acid of aluminium[30,31].

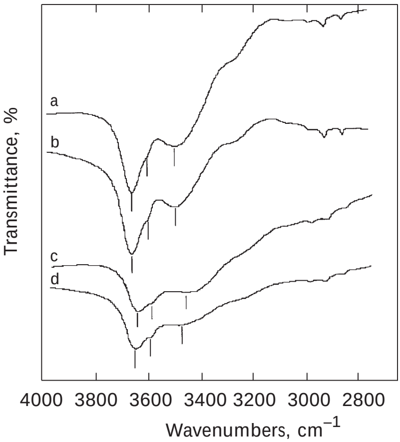

FIG. 1

FT-IR spectra of zeolites: a Na-ZSM-5 non-dried; b Na-ZSM-5 dried at 110 °C for 4 h; c Fe-ZSM-5 non-dried; d Fe-ZSM-5 dried at 110 °C for 4 h. Spectra are corrected for water adsorbed in KBr

It can be deduced from the FT-IR spectra (Table II) that the positions of absorption bands will change after the ion exchange of Fe^{3+} for Na^+, but also by drying. Table II indicates that after the ion exchange the bands with

TABLE II
Diffusion reflectance and FT-IR spectra of zeolites in KBr[a] tablets before and after drying

Sample		λ_{max}, nm	$\tilde{\nu}$, cm^{-1}		
Na-ZSM-5	non-dried	–	3 665	3 607 (shoulder)	3 501
	dried		3 666	3 607 (shoulder)	3 502
Fe-ZSM-5	non-dried	–	3 659	3 605 (shoulder)	3 467
	dried		3 662	3 605 (weak peak)	3 496
Fe-ZSM-5-Ph	non-dried	478[b]	3 649	3 605 (weak peak)	3 449
	dried		3 656	3 605 (shoulder)	3 492
Fe-ZSM-5-Pt	non-dried	300[b]	3 654	3 606 (shoulder)	3 449
	dried	402 486 (shoulder) 555 (shoulder)	3 656	3 606 (shoulder)	3 468

[a] All FT-IR spectra are corrected for water adsorbed in KBr. [b] After subtracting the Fe-ZSM-5 spectrum.

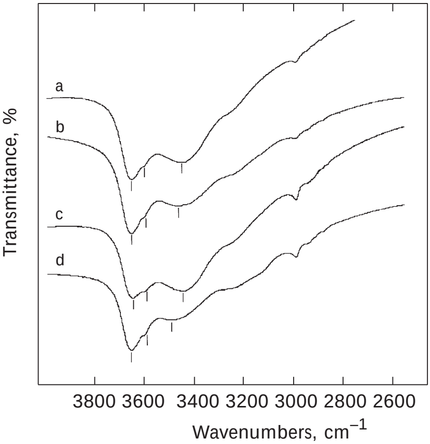

FIG. 2
FT-IR spectra of zeolites: a Fe-ZSM-5-phenol non-dried; b Fe-ZSM-5-phenol dried at 110 °C for 4 h; c Fe-ZSM-5-thiophene non-dried; d Fe-ZSM-5-thiophene dried at 110 °C for 4 h. Spectra are corrected for water adsorbed in KBr

the maximum at 3501–3665 cm^{-1} were shifted to lower wavenumbers (to 3467 or 3659 cm^{-1}); this is obviously caused by the presence of Fe^{3+} ions in channels which influence the interaction of water with zeolite OH groups. Taking a low content of Fe (7 × 10^{-4} mole %) into account it is not possible to disregard a possibility that the changes in IR spectra somehow depend on qualitative changes of the surrounding environment caused by migration of Fe^{3+} particles on the spots where Al sites are balanced with Na^+ or with H^+. After IR drying the samples (at temperature below 110 °C), major changes in the position of bands can be observed only in the Fe-ZSM-5 sample where the absorption of 3467 shifted to 3496 cm^{-1}. The position of the second band characterizing the complex of water and zeolite SiOAl and OH groups changed only slightly (from 3659 to 3662 cm^{-1}). In the parent zeolite (Na-ZSM-5), drying had almost no influence on this band. A possible explanation to this can be that the zeolite samples in KBr tablets were not measured after dehydration in the inert atmosphere but in the open air after being transferred into the spectrometer. Under these conditions the samples could acquire humidity from the air and this can also explain insignificant changes in IR spectra in the wavenumber area of 3500 cm^{-1} in the parent Na-ZSM-5 zeolite. Similar explanation can be used for wavenumbers 3600–3700 cm^{-1} in the sample of Na-ZSM-5 and Fe-ZSM-5. Table II also indicates that neither the ion exchange nor the influence of drying reflected in the position and in intensity change of bands characterizing Brönsted acid groups. A similar character of changes in the FT-IR spectra caused by drying can be observed also in Fe-ZSM-5-phenol and Fe-ZSM-5-thiophene samples (Table II). Considering the changes in the FT-IR spectra, it is possible to conclude that the oxidative properties of Fe^{3+} ions incorporated in ZSM-5 zeolite channels are affected by the presence of water which can enter into their co-ordination spheres under various conditions in dependence on the position of the ferric ion or on its embedding in the zeolite lattice. In this connection it can be assumed that Fe-ZSM-5 without thermal activation acquires oxidation properties only in the case when ferric ions in the zeolite microstructure remain co-ordinatively “unsaturated” also in the presence of water.

To confirm this assumption we studied changes in the EPR spectra before and after “dehydration” of the samples (at temperatures not exceeding 100 °C at 1 Pa) with subsequent rehydration by water vapour. Figure 3 shows EPR spectra of the parent Na-ZSM-5 zeolite before drying (at room temperature and at –196 °C), after drying, and after subsequent rehydration. From the character of the EPR spectra of the non-dried sample it follows that the signal in the region of $g \approx 2$ is very broad (about 100 mT) and consists at least of two signals with *g* = 2.24 and *g* = 2.01 (Fig. 3a). At –196 °C, the signal broadens to 500 mT (Fig. 3b). Furthermore, in the Na-ZSM-5 samples the signal of a relatively low intensity at *g* = 4.32 is observed. It is obvious that those signals are caused by the presence of a small amount of Fe incorporated in the zeolite lattice during the synthesis (2×10^{-4} mole % Fe; see the analysis in Experimental). The drying of the sample resulted in weakening and the rehydration in repeated strengthening of the signals (Fig. 3a, c, d).

On the basis of the facts known from literature about the presence of Fe^{3+} ions in the zeolite microstructure (in channels and cavities), it is possible to claim that the shape of the EPR spectra depends on the method of preparation of the sample and on the distortion of the co-ordination sphere of Fe associated with the ion location[17,23,30].

A typical X-band spectrum of the zeolite containing Fe^{3+} usually consists of three major absorptions which appear at *g* ≈ 4.3, *g* ≈ 2.2–2.3 and *g* ≈ 2.0. Of those, only the signal at *g* ≈ 2.2–2.3 showing the behaviour characteristic of ferrimagnetic or ferromagnetic interactions was unequivocally attributed to clustered iron species present in the oxide/oxide-hydroxide impurity phases. The signal at *g* ≈ 4.3, initially assigned to the iron-substituted silicon in the zeolite framework, has become well known as characteristic of such a substitution[17,24,30,32]. Wichterlová and Jírů[33] pointed out that this signal may be due, at least in part, to the extra-framework Fe^{3+} complex at

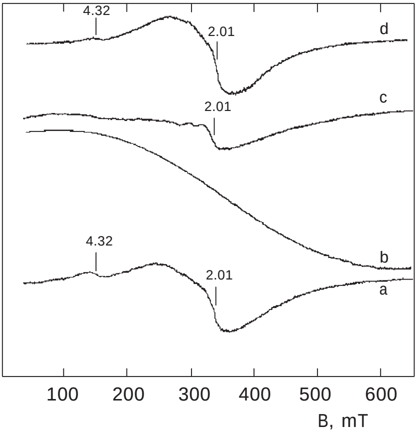

FIG. 3

EPR spectra of Na-ZSM-5: a before drying at room temperature; b before drying at –196 °C; c after drying at 100 °C (1 h); d after rehydration with water vapour at room temperature. Spectra a, c and d were measured at room temperature cationic sites. Other authors have found out that the signal at $g = 4.3$ can belong to Fe^{3+} ions in the exchanged cationic positions[34], or it can belong to two forms: $(Fe(H_2O)_{6-a}O_a)^{(3-2a)+}$ and $(Fe(OH)_nO_{4-a})^{(a-5)+}$ (ref.[23]). According to Goldfarb *et al.*[15], the commonly accepted assignment of EPR signals is the following: $g \approx 4.3$, framework iron; $g \approx 2.5–2.1$, iron in interstitial oxide and hydroxide phases; and $g \approx 2.03–1.98$, iron at cation exchange sites, respectively.

Changes in the EPR spectra of the parent Na-ZSM-5 sample observed by us can be explained on the basis of the accepted assumption that iron is embedded in the crystalline lattice (*e.g.* as "impurity" of type II – see above). Another dinuclear (similar) iron complex has been proposed by Dubkov[35].

Beran's calculations[36] made by the CNDO/2 method extended to transition metals show that the negative charge densities localized on the oxygen atoms co-ordinated to Fe^{3+} ions are significantly lower than the charge on the remaining oxygen atoms. This can be explained by donation of the electron density to Fe^{3+} ions, which exhibit the strongest electron acceptor ability of all the transition metal ions studied so far. Thereby the negative charge on the $\{FeO_{4/2}\}^-$ tetrahedron is reduced substantially.

Consequently, if we take into account this fact, we can state that in the process of "dehydration" the number of water molecules in the co-ordination sphere of Fe^{3+} must be reduced, which is, however, "effectively" compensated by interactions of the free electron pairs of adjacent oxygen atoms of the lattice. As a consequence (providing that Fe^{3+} is a part of the zeolite lattice), these changes will reflect also in the EPR signal intensity in such a way as was observed in our case (the EPR signal decreased after drying and again increased after rehydration).

Figure 4 shows EPR spectra (before and after drying, and also after rehydration) of the Fe-ZSM-5 sample which was obtained by the ion exchange of Fe^{3+} for Na^+. The shape of the spectrum of the Fe-ZSM-5 sample (Fig. 4a) is rather complicated. It consists of at least 4 lines with the g-factor values 2.01, 2.10, 2.80 and 3.57. From the shape of the EPR spectra it can be deduced that iron in the Fe-ZSM-5 exists in the environment with a different symmetry and various substituents in the co-ordination sphere. Moreover, these lines seem to be superimposed on the very wide line ($g \approx 2.2$; $\Delta H_{pp} \approx 150$ mT) which can be assigned to Fe^{3+} ions that are in the ferromagnetic or antiferromagnetic interaction. A temperature drop to –196 °C manifested itself in the EPR spectrum by disappearance of the lines with $g =$ 2.01, 2.10, 2.80, 3.57 and by a great growth of the initial wide line ($\Delta H_{pp} >$ 500 mT). In addition, a new signal appeared in the region with $g = 4.3$

(Fig. 4b). This signal can be assigned to Fe^{3+} ions in a strong rhombic distortion of the tetrahedral site. All the above described signals demonstrated in Fig. 4a are preserved also after drying the sample at 100 °C (Fig. 4c). After repeated rehydration of the Fe-ZSM-5 sample, the lines with $g = 3.57$ and 2.80 disappeared but those with $g = 2.10$ and 2.01 remained.

The dehydration causes a remarkable strengthening of the signal with $g = 2.80$ and after rehydration the intensity of all signals weakened considerably. In virtue of these facts it can be assumed that iron in Fe-ZSM-5 sample is co-ordinatively unsaturated. The same conclusions were found in the work of Kucherov and Slinkin[34] who studied the interactions of Fe^{3+} in the ZSM-5 zeolite with H_2O and *p*-xylene. The strengthening of the EPR signal (double signal) is apparently associated with dehydration of very fine particles (*e.g.* Fe_2O_3) and their transition to larger clusters in the same way as explained in refs[17,32]. The signal with $g = 2.10$ and the small signal with $g \approx 2.01$ are usually assigned to Fe^{3+} ions in the Fe_2O_3 phase occluded by zeolites and to the octahedral co-ordination of Fe^{3+} ions in the exchangeable sites having the C_{3v} symmetry. Signals in the low-field region ($g > 3$) are usually attributed to isolated Fe^{3+} ions in a different co-ordination environment, which can be observed in our case for signals with $g = 3.57$ and with $g = 4.3$. The signal at $g = 2.01$ can be assigned to a separate antiferromagnetic Fe–O–Fe phase[30]. This could consist of ferric oxide nanoclusters inside the zeolite channels; these clusters could exhibit super-

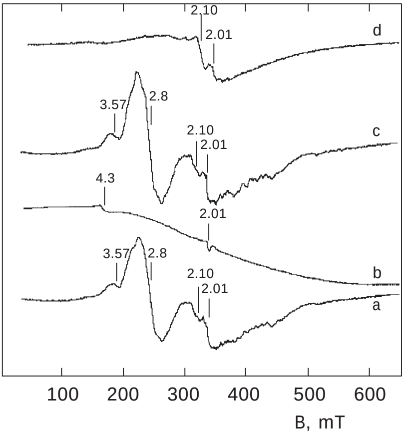

FIG. 4

EPR spectra of Fe-ZSM-5: a before drying at room temperature; b before drying at –196 °C; c after drying at 100 °C (1 h); d after rehydration with water vapour at room temperature. Spectra a, c and d were measured at room temperature paramagnetic and even ferromagnetic behaviour[37]. Another possibility is the dinuclear iron ions [HO–Fe^{3+}–O–Fe^{3+}–OH] at the exchange sites[30]. The iron ions in such a complex are co-ordinatively unsaturated; addition of water presumably replaces the bridging oxygen by two hydroxy groups thus increasing the co-ordination number. As a result, the two iron ions lose their mutual contact and the co-ordination in the second shell decreases, while the first shell co-ordination increases.

On the basis of the facts ascertained by us, the interactions of Fe^{3+} ions with phenol and thiophene in the ZSM-5 were also studied. Phenol was chosen on the assumption that it would form a complex with Fe^{3+} in zeolite channels (assuming that there exists co-ordinated unsaturation) and that thiophene would undergo oligomerization similarly to the case of a zeolite sample subjected to thorough thermal activation[26]. Figure 5 illustrates EPR spectra of the Fe-ZSM-5-phenol sample (before and after drying as well

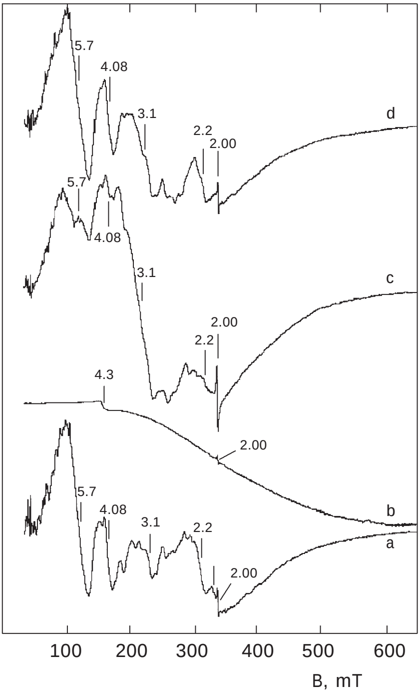

FIG. 5
EPR spectra of Fe-ZSM-phenol: a before drying at room temperature; b before drying at –196 °C; c after drying at 100 °C (1 h); d after rehydration by water vapour at room temperature. Spectra a, c and d were measured at room temperature

as after rehydration). By comparing Figs 4 and 5, it was possible to ascertain that the diffusion of phenol into zeolite channels caused a complex change in the EPR spectrum of the sample. In this spectrum a new, very narrow signal ($g = 2.00$) was observed. In the region with $g = 2.1–4$, more lines with $g = 2.2$, 3.1, 4.08 and 5.7 appeared and were superimposed on the very wide line ($\Delta H_{pp} \approx 250$ mT with $g \approx 2$). At –196 °C, all lines merged into a very wide line with $\Delta H_{pp} \approx 500$ mT and $g \approx 2$, the signals at $g = 4.3$ and $g = 2.0$ being preserved. The dehydration led to a growth of the intensity of signals in the region of $g = 2.2$ up to 4 and the rehydration resulted in its repeated decrease. This observation points to the fact that phenol molecules in zeolite channels, and similarly also water, enter into the co-ordination sphere of Fe^{3+} ions where new organometallic complex compounds develop. The very narrow signal at $g = 2.0$ can be attributed with all probability to the phenol cation-radical. The retained character of EPR spectra after repeated rehydration suggests that phenol is efficiently bound in the co-ordination sphere of Fe^{3+} ions incorporated in the zeolite, and neither water nor OH^- displace it.

Figure 6 shows EPR spectra of the Fe-ZSM-5-thiophene sample (before and after drying and also after rehydration). The characteristic phenomenon of these spectra is a narrow line of the relatively strong intensity at $g = 2.00$. This narrow signal can be assigned to polarons (cation-radicals) localized in thiophene oligomers, which are produced by oxidative oligomerization in Fe-ZSM-5, zeolite channels. The EPR lines belonging to Fe^{3+} ions consist at least of three lines with $g = 2.1$, 2.8 and 4.3 and with the total width of *ca* $\Delta H_{pp} \approx 150$ mT. The character of the EPR spectra of Fe-ZSM-5 together with thiophene changes only little by drying and by repeated rehydration. At the temperature of liquid nitrogen (–196 °C), the EPR spectrum has a large width ($\Delta H_{pp} \approx 500$ mT), similarly to the previous case, and of the initial lines only those at $g = 2.00$ and $g = 4.3$ are preserved. From Fig. 6 it follows that in the EPR spectrum taken after oxidative oligomerization of thiophene, the intensity of signals ($g = 2.1$, 2.8) assigned to Fe^{3+} ions and Fe_2O_3 was considerably lower, but after dehydration and subsequent rehydration the signals did not distinctly change. The narrow signal with $g = 2.00$ belonging to polarons (cation-radicals) of thiophene oligomers did not change, either after drying or after rehydration. In accordance with these results, the Fe^{3+} ions oxidize thiophene effectively also in the presence of water occurring in its co-ordination sphere. It can be assumed that both forms of iron (Fe_2O_3 and Fe–O–Fe) participate in the oxidative reaction.

The question whether the assumed complexes of $[HO–Fe^{3+}–O–Fe^{3+}–OH]^{2+}$ [31] exist in zeolite can be answered using the EPR spectra at –196 °C. A comparison of these spectra with those at room temperature (spectra in Figs 3–6) suggests that all lines merge and constitute a very wide line with $\Delta H_{pp} \approx$ 500 mT and $g \approx 2$. Only the lines of low intensity having $g = 4.3$ and $g = 2.01$ remain unchanged. This means that the ions, which interact, are present in the samples. Therefore, an assumption exists that iron ions are in antiferromagnetic interactions through the oxygen bridge[22]. This fact can be associated with the presence of the above-mentioned complex $[HO–Fe^{3+}–O–Fe^{3+}–OH]^{2+}$ participating not only in the Fe_2O_3 clusters but also in the oxidation reactions of thiophene.

Figures 7 and 8 illustrate diffusion reflectance spectra of the Fe-ZSM-5-phenol and Fe-ZSM-5-thiophene samples (after subtracting the Fe-ZSM-5 spectrum). Figure 7 reveals that the co-ordinatively unsaturated iron ion interacts with the present phenol and that the stable "product" formed in zeolite channels can be observed in the absorption spectrum at λ_{max} =

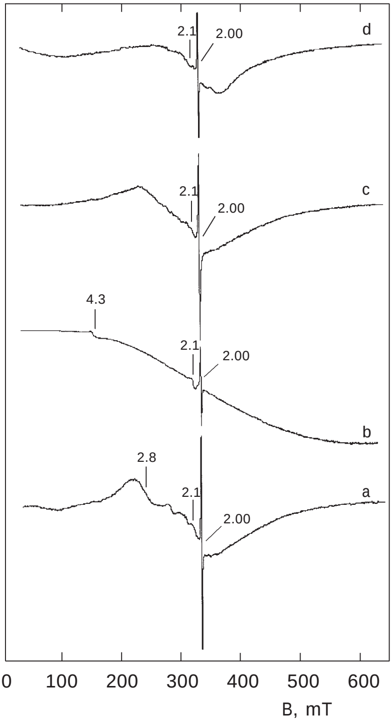

FIG. 6

EPR spectra of Fe-ZSM-thiophene: a before drying at room temperature; b before drying at –196 °C; c after drying at 100 °C (1 h); d after rehydration with water vapour at room temperature. Spectra a, c and d were measured at room temperature

478 nm. According to refs[38–41] dealing with UV-VIS spectra of the cation-radical derivatives of phenols and hydroxy derivatives of fused aromatic hydrocarbons, the absorption band can be assigned to the phenol cation-radical absorbing in the 420–480 nm region in accordance with the above references. Inasmuch as the keto-form of the phenol cation-radical absorbs at *ca* 550 nm [38], the absorption maximum at 478 nm can be assigned to the stabilized cation-radical $PhOH^{\bullet+}$ which is co-ordinated to Fe^{2+} or Fe^{3+} ions.

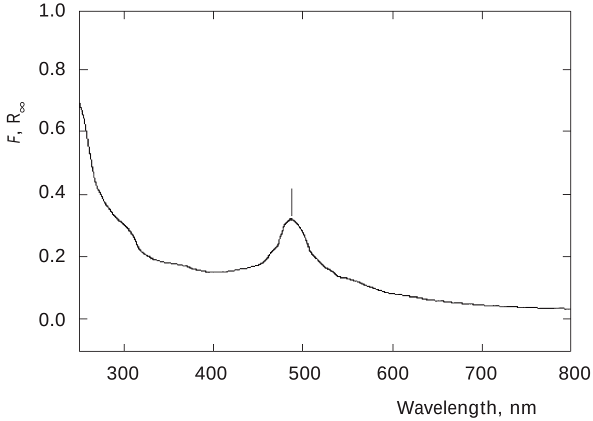

FIG. 7
Diffusion reflectance spectrum of Fe-ZSM-5-phenol after subtracting the Fe-ZSM-5 spectrum

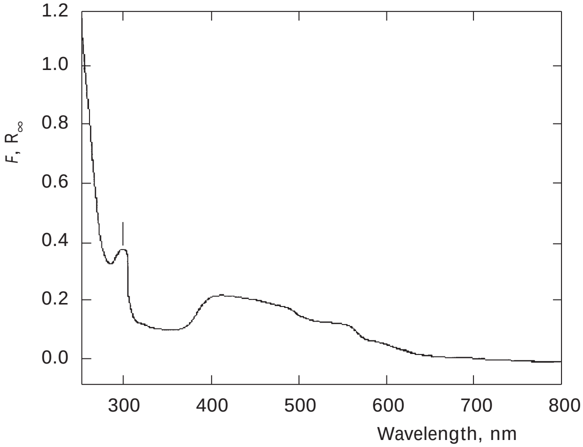

FIG. 8
Diffusion reflectance spectrum of Fe-ZSM-5-thiophene after subtracting the Fe-ZSM-5 spectrum

The UV-VIS spectra of thiophene oligomers and their cation-radicals (λ_{max} = 302, 402, 486 and 555 nm; Fig. 8) correspond approximately to the spectra which were obtained by us when the oligomerization was carried out after thermal activation of the Fe-ZSM-5 sample in the way described in our previous work[26] (λ_{max} = 300, 398, 478 and 575 nm). A comparison of these spectra suggests that oligomers and their oxidized forms (polarons) show a flatter spectrum in the 400–500 nm region, in which no absorption maxima above 600 nm assigned to bipolaron states (dications)[42] are observable. This fact can be accounted for by the presence of a bigger quantity of water in zeolite channels entering into interaction with the cation-radicals of oligothiophenes. This statement is supported by the fact that the intensity of EPR signals of the polarons of oligomers was substantially lower after rehydration (Fig. 6d).

CONCLUSION

1. The ion exchange of Fe^{3+} for Na^+ in ZSM-5 zeolite channels is accompanied by the formation of Fe_2O_3 and complex Fe–O–Fe particles (most probably $[HO–Fe^{3+}–O–Fe^{3+}–OH]^{2+}$) already at low concentration of the extra-framework Fe. The iron sites are co-ordinatively unsaturated with water and can therefore enter into the interactions with organic molecules (phenol, thiophene) at room temperature, also in the presence of moisture.

2. The interaction of Fe-ZSM-5 with phenol gives rise to the stabilized phenol cation-radical. Phenol enters very efficiently into the co-ordination sphere of iron in the presence of complexes insensitive to water. By the interaction of Fe-ZSM-5 with thiophene its oxidative oligomerization proceeds also during the generation of neutral forms of the oxidized paramagnetic polarons localized on thiophene oligomers. It is probable that the thiophene oligomers having the number of monomeric units n = 2–6 enter into the iron co-ordination sphere, which is documented by relatively small changes of the EPR spectra caused by moisture.

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