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Quantitative Determination of Isolated Fe^{3+} Cations in FeHZSM-5 Catalysts by ESR

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A method for the quantitative determination of isolated Fe^{3+} ions in FeHZSM-5 by EPR was devised. The method is based on the comparison of signals, taken at -196°C, from pyridine-impregnated catalysts with signals from solutions of Fe(III)-phthalocyanine in pyridine. $FeCl_3$ was introduced into HZSM-5 having Si/Al ratios of 15 and 25. The amount of Fe was between 0.5 and 5.5 wt%. The samples were prepared either by sublimation of $FeCl_3$ into the zeolite in an N_2 flow or by impregnation with $FeCl_3$ water solutions, and subsequently calcined at 400–800°C. The measurement of "ESR-visible Fe^{3+}" in $FeCl_3$/HZSM-5 calcined at 400°C in vacuum demonstrates that virtually all ferric ions, present as isolated $FeCl_2^+$-species, contribute to the ESR signal in samples with Fe/Al ratios <0.6. Introduction of iron in HZSM-5 by $FeCl_3$ sublimation in an N_2 flow results in the stabilization of the same amount of isolated $FeCl_2^+$ species with the excess forming aggregates. The number of isolated Fe^{3+} ions decreases sharply after treatment in an air flow at $T \geq 500$°C. Irrespective of the starting concentration of iron, after oxidative calcinations at 500–520°C, the amount of isolated low-coordinated Fe^{3+} cations in FeHZSM-5 does not exceed Fe/Al $\sim$0.15; the rest aggregates into ESR-invisible species or forms bulk α-Fe_2O_3. Calcination of FeHZSM-5 with the lower Si/Al ratio of 15 at 800°C causes further loss of ESR-visible isolated Fe^{3+} ions, whereas the higher silica samples, with Si/Al $=25$, are tolerant to this treatment. Formation of aggregated iron species is minor in the most diluted, low-loaded sample, 0.5% Fe/HZSM-5(Si/Al $=25$), where the majority of Fe^{3+} ($\sim 2/3$) remains well isolated and contributes to the ESR signal even after oxidative treatment at 800°C. Redox treatment of this sample even under mild conditions significantly redistributes the iron, with irreversible loss of of isolated Fe^{3+} ions and formation of ferromagnetic aggregates of Fe_3O_4. © 2000 Academic Press

Key Words: **electron spin resonance; quantitation of Fe^{3+} ions; HZSM-5.**

INTRODUCTION

Iron-containing alumosilicate and zeolite catalysts prepared by sublimation of a volatile iron compound have been claimed to have high activity and resistance to deactivation for selective catalytic reduction (SCR) of nitrogen oxides (1–7). There also have been conflicting reports on these catalysts whose activity and poison resistance appear to be dependent on preparation and pretreatment. The state of the iron in different zeolites is not entirely well defined, being discussed mostly in qualitative terms (8–13). In iron-containing zeolite catalysts there may be present at least four different states of trivalent Fe cations: isolated cations; small clusters; Fe_2O_3 microcrystals; Fe_3O_4 microcrystals. To relate the catalytic activity in selective catalytic reduction of NO_x to the active isolated ferric ions it is necessary to measure the latter quantitatively.

Earlier we examined the ESR spectra of ferric ions, introduced by sublimation into ZSM-5 and SAPO matrices, in the 20–500°C temperature range. The interaction of isolated low-coordinated Fe^{3+} ions with O_2, H_2O, C_3H_6, NO, and their mixtures, as registered by the changes in the ESR spectra was studied (14). In the study of FeZSM-5 by ESR spectroscopy complex signals with different g-factor values are observed and the intensity of the ESR signal is expressed in arbitrary units. Moreover, a part of the Fe^{3+} ions is usually present as nonparamagnetic species. The question of what fraction of the Fe^{3+} ions in the sample is associated with the specific low-field ESR signal ($g \geq 4.3$) is not addressed. To answer this question it is necessary to compare double integrals of the ESR spectra from FeHZSM-5 with an absolute Fe^{3+} standard exhibiting the ESR signal at $g \sim 4.3$ and measured under identical conditions.

In earlier quantitative studies of Cu^{2+} in H-ZSM-5 we have used frozen water solutions of copper salts to prepare a solid specimen with isolated Cu^{2+} ions well resembling the CuH-ZSM-5 zeolite saturated with H_2O (15, 16). This approach cannot be used for FeH-ZSM-5. Indeed, water adsorption on FeH-ZSM-5 replaces the complex ESR spectrum from ferric ions in different distorted tetrahedral sites by one narrow ESR line at $g = 4.27$ due to H_2O bonding to Fe(III) sites (14) which could simplify Fe^{3+} quantitation. But even very diluted frozen water solutions of inorganic Fe salts ($FeCl_3$, for example) cannot serve as a good reference, since they generate a complex, very broad ESR signal. As

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an alternative absolute standard, a Fe(III)-phtalocyanine chloride solution in pyridine, was tried. Freezing of the solution yields a solid specimen with isolated Fe^{3+} ions resembling quite well the FeHZSM-5 zeolite impregnated with pyridine.

EXPERIMENTAL

Sample Preparation

The H-forms of ZSM-5 were obtained by thermal decomposition of NH_4-zeolites, having a Si/Al ratio of 15 and 25 and crystallinity of >90% (PQ Corp), in an air flow at 520–540°C. The zeolite with Si/Al = 25 was treated with 0.1 M solution of HNO_3 at 80°C for 2 h to remove extralattice Al and amorphous impurities. The treated zeolite was washed thoroughly with distilled water and dried at 120°C overnight. The samples were pressed without binder and crushed into 0.5- to 2-mm particles.

(a) $FeCl_3$ sublimation. A layer of quartz wool (∼2 cm) was placed in a quartz tube, and charges of HZSM-5 (∼2 g) and $FeCl_3$ (∼0.5 g) were placed in the tube on both sides of this layer. Nitrogen flow (∼30 cc/min) was switched on at room temperature, and the tube was heated gradually (100°C, 30 min; 200°C, 30 min, 250°C, 30 min; 300°C, 30 min, 400°C, 15 min). After thermal treatment the sample was cooled to room temperature in an N_2 flow, and a part of the treated zeolite (∼0.5 g, yellow-brown) was taken out as *sample 1[subl]* (∼2.8% wt Fe by analysis). Then, the treatment at 400°C in N_2 flow was repeated for 30 min, and the rest of the zeolite (dark brown-red) was taken as *sample 2[subl]* (∼5.5% wt Fe by analysis).

(b) $FeCl_3$ impregnation. The samples were made by consecutive incipient wetness impregnation (0.8–0.9 cc/1 g) of H-forms of zeolites by water solution of $FeCl_3$ (6.25 mg Fe/1 cc H_2O) containing a small amount of HCl to prevent hydroxide precipitation (1 cc of concentrated HCl per 100 cc of H_2O). A weighed amount of zeolite (∼4 g) was dried at 50°C, impregnated with $FeCl_3$ solution, and dried at room temperature overnight. Then a part of the zeolite (∼1 g) was designated as *sample 1[impr]*, and the treatment of the rest of zeolite was repeated several times. Prepared samples were placed in a glass tube connected with a vacuum system and heated gradually (100°C, 30 min; 200°C, 30 min, 250°C, 30 min; 300°C, 30 min, 400°C, 60 min) under a vaccum (0.01 Torr). No sublimation of $FeCl_3$ from heated samples to the cold part of the tube was noted. Since the introduced amount of iron ions was retained by the samples no further analysis was done. Samples $FeCl_3$/HZSM-5 (Si/Al = 25) with 0.5, 1.0, 1.5, and 2.1% wt Fe, and $FeCl_3$/HZSM-5 (Si/Al = 15) with 1.2, 2.35, and 3.5% wt Fe were prepared by this method.

ESR Measurements

The ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) at 20 and −196°C on a Bruker ESP300 spectrometer, equipped with a 4104OR cavity and a coaxial quartz Dewar. The ESR signals were registered at microwave power 6.41 mW and modulation amplitude 3.8 G in the field range of 100–4900 G (two scans with a sweep time of 168 s). The Bruker ESP300E software and the special Bruker program WIN-EPR (version 901201) were used for data treatment (baseline correction, noise reduction, double integration).

The samples were crushed into 0.1- to 0.2-mm particles, and sample charges (38–42 mg) were placed in identical quartz ampoules (3.5 mm diameter), calcined in a furnace at a given temperature, taken out, immediately connected to the vacuum system, evacuated for 2–3 min to 0.01 Torr, and sealed off. Then the spectra were registered at 20 and −196°C and normalized for the differences in sample weight.

Frozen pyridine solutions of Fe(III)-phthalocyanine chloride (Aldrich, 95% purity) with 0.019 and 0.010% wt Fe were used as standards for the measurement of the absolute number of low-coordinated Fe^{3+} ions by ESR. The spectra were taken at −196°C for weighted solutions of approximately equal volume placed in the same quartz ampoules. Freezing the solutions produces solid specimens with isolated low-coordinated Fe(III) ions approximating quite well the FeZSM-5 samples saturated with pyridine. Therefore, for direct quantitative comparison, our iron-containing zeolites were impregnated with pyridine (99.9% purity), kept for 4 h at room temperature, and then the ESR spectra were taken at −196°C. For highest accuracy, sets of samples were measured consecutively, with ampoules in the same position inside the ESR resonator.

RESULTS AND DISCUSSION

$FeCl_3$/HZSM-5 Calcined in the Absence of Air

Figure 1 shows ESR spectra, taken at 20°C, of $FeCl_3$/HZSM-5 (Si/Al = 25) samples calcined in vacuum at 400°C. As one can see, an increase in the iron content from 0.5 to 2.1% wt Fe is accompanied by a gradual increase in intensity of ESR lines in two different regions of the magnetic field: at $g \sim 2.0$ and in the complex set of lines from $g \sim 3.2$ to $g \sim 8.9$. A broad line at $g \cong 2.0$ originating from octahedral mutually interacting Fe^{3+} ions is weak even for the most concentrated sample (Fig. 1d) indicating that this step of sample preparation resulted in very little agglomeration of the iron species. The main part of Fe^{3+} contributes to a complex superposition of ESR signals in a low-field region (g = 3.65, 4.27, 5.6; 6.5, and 8.9) from isolated Fe^{3+} ions (or rather isolated $(FeCl_2)^+$ species) in tetrahedral and distorted tetrahedral coordinations (14, 17, 18). The samples

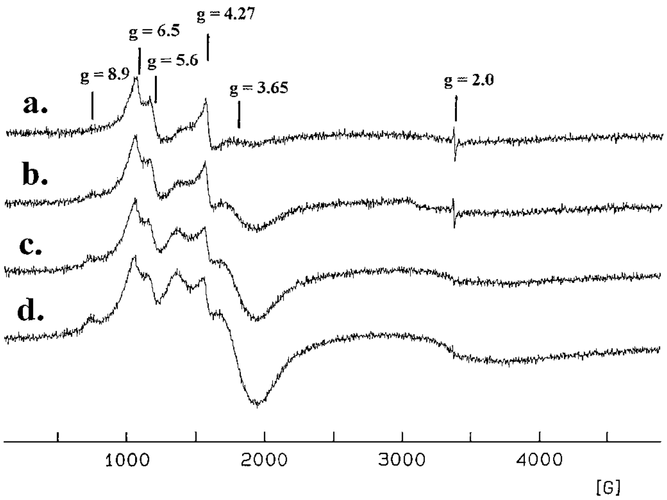

FIG. 1. ESR spectra, taken at 20°C, of $FeCl_3$/HZSM-5 (Si/Al = 25) samples calcined at 400°C in vacuum: (a) 0.5% wt Fe; (b) 1.0% wt Fe; (c) 1.5% wt Fe; (d) 2.1% wt Fe.

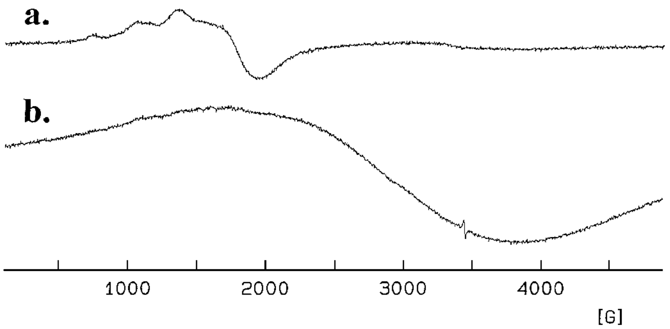

FIG. 3. ESR spectra, taken at 20°C, of $FeCl_3$/HZSM-5 (Si/Al = 25) samples prepared by sublimation of $FeCl_3$ in N_2 flow at 400°C: (a) 2.8% wt Fe; (b) 5.5% wt Fe.

$FeCl_3$/HZSM-5 (Si/Al = 15) demonstrate Fe^{3+}-ESR spectra of the same shape (Fig. 2). If we assume stabilization of one $FeCl_2^+$ on one Al^{3+} Brønsted site, the calculated atomic ratio Fe/Al reaches ≅0.6 for the most concentrated samples prepared on the two zeolites, and the negligible formation of agglomerated species is not surprising.

Figure 3 shows ESR spectra, taken at 20°C, of the two $FeCl_3$/HZSM-5 (Si/Al = 25) samples prepared by $FeCl_3$ sublimation in nitrogen flow at 400°C. The ESR signal from *sample 1[subl]* (~2.8% wt Fe) (Fig. 3a) is practically identical to the spectrum shown in Fig. 1d for the impregnated sample with 2.1% wt. Continuation of $FeCl_3$ sublimation changes the ESR signal: the complex low-field spectrum disappears, and the broad line at $g \cong 2.0$ from interacting Fe^{3+} ions becomes strong for the *sample 2[subl]*, with ~5.5% wt Fe. Therefore, an increase in the iron content in zeolite up to Fe/Al ≅ 1.6 results in disappearance of isolated Fe^{3+} ions and formation of agglomerated iron species.

Complex signals from $FeCl_3$/HZSM-5 are not altered at −196°C save for an intensity increase due to the Curie-Weiss law (Fig. 4). However, impregnation of the samples with pyridine sharply simplifies the Fe^{3+}-ESR signals. Ligand bonding to Fe(III) sites results in substitution of the superimposed signals from isolated ferric ions in different distorted tetrahedral sites (Fig. 4) by a single, narrow ESR line at $g = 4.27$ (Fig. 5). The residual signal at $g \sim 8.9$ is very weak and was ignored in the integration. Figure 6, with the two spectra of the sample 0.5% $FeCl_3$/HZSM-5 (Si/Al = 25) taken with the same magnification, illustrates these changes. The integral intensity of the line at $g = 4.27$ for pyridine-impregnated sample (Fig. 6b) exceeds the intensity measured for the dry sample (Fig. 6a) by a factor of ~1.5. Therefore, the local crystal field symmetry changes from distorted tetrahedral to tetrahedral due to bonding

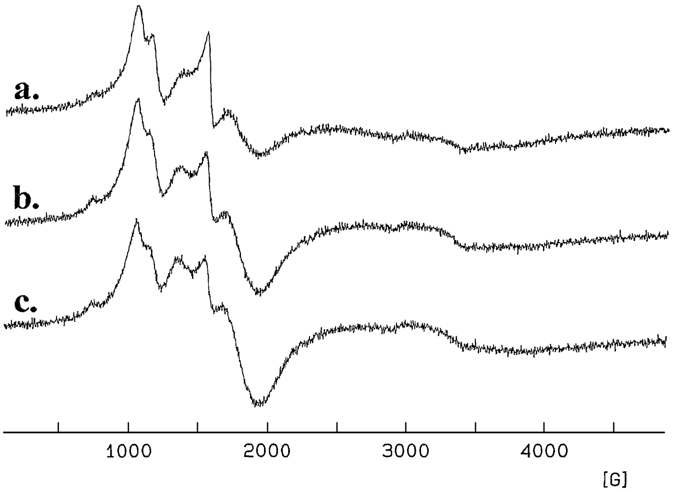

FIG. 2. ESR spectra, taken at 20°C, of $FeCl_3$/HZSM-5 (Si/Al = 15) samples calcined at 400°C in vacuum: (a) 1.2% wt Fe; (b) 2.35% wt Fe; (c) 3.5% wt Fe.

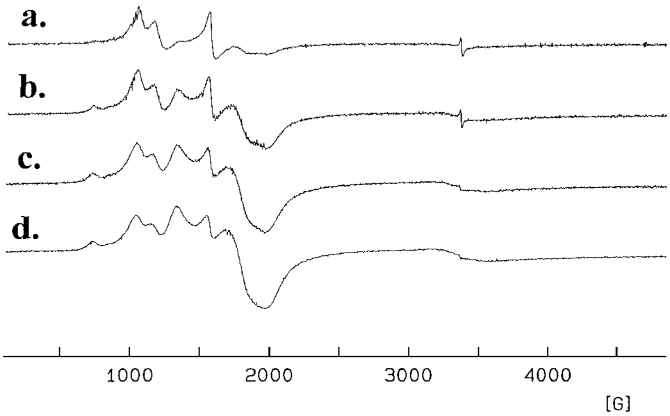

FIG. 4. ESR spectra, taken at −196°C, of $FeCl_3$/HZSM-5 (Si/Al = 25) samples calcined at 400°C in vacuum: (a) 0.5% wt Fe; (b) 1.0% wt Fe; (c) 1.5% wt Fe; (d) 2.1% wt Fe.

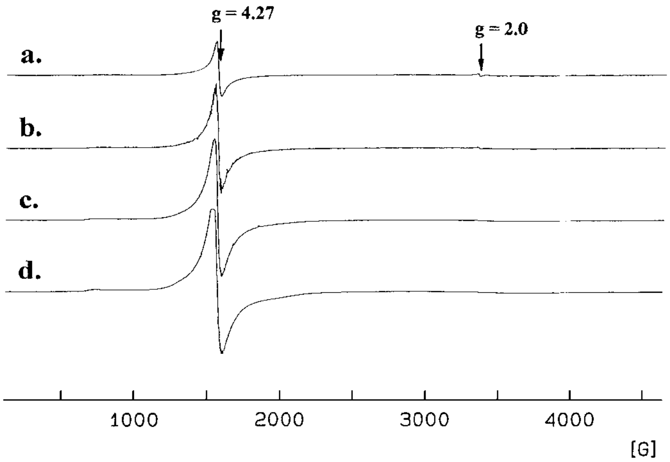

FIG. 5. ESR spectra, taken at −196°C, of $FeCl_3$/HZSM-5 (Si/Al = 25) samples calcined at 400°C in vacuum and impregnated with pyridine: (a) 0.5% wt Fe; (b) 1.0% wt Fe; (c) 1.5% wt Fe; (d) 2.1% wt Fe.

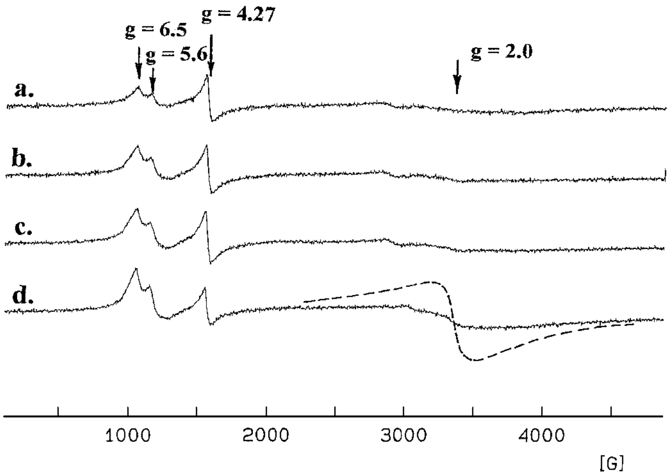

FIG. 7. ESR spectra, taken at 20°C, of FeHZSM-5 (Si/Al = 25) samples calcined at 500°C for 4 h in air flow: (a) 0.5% wt Fe; (b) 1.0% wt Fe; (c) 1.5% wt Fe; (d) 2.1% wt Fe.

of Py and simultaneously the relaxation conditions of the paramagnetic Fe^{3+} sites are affected by pyridine bonding. No measurable decrease in the intensity of the broad ESR line at $g = 2.0$ is observed and no narrow line at $g \cong 2.0$, being typical of isolated Fe^{3+} complexes with octahedral symmetry, appears upon impregnation of the sample with pyridine. The effect caused by pyridine is essentially the same as that caused by water adsorption on FeHZSM-5 samples (14).

FeHZSM-5 Prepared by Oxidative Calcination

Oxidative calcination of $FeCl_3$/HZSM-5 (Si/Al = 25) samples at 500–520°C for 4 h transforms the Fe^{3+}-ESR spectra, as shown in Fig. 7. Change in the shape of the low-field part of the signal could be indicative of change in the symmetry of the local crystal field of cations due to the transformation of $(FeCl_2)^+$ to $(FeO)^+$ isolated species (17). A noticeable decrease in the integral intensity of the low-field ESR lines indicates, on a qualitative level, the loss of low-coordinated, isolated Fe^{3+} sites. At the same time, a rise of the broad line from octahedral interacting Fe^{3+} ions ($g \cong 2.0$) is seen, especially for the most concentrated sample (Fig. 7d). Thus, even a mild oxidative treatment of $FeCl_3$/HZSM-5 causes agglomeration of the iron species.

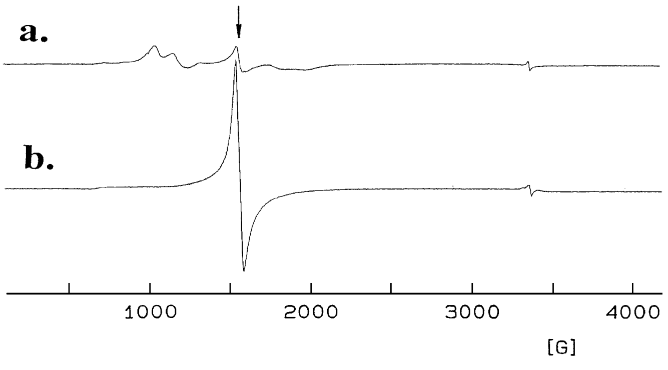

FIG. 6. ESR spectra, taken at −196°C with identical magnification, of the $FeCl_3$/HZSM-5 (Si/Al = 25) sample with 0.5% wt Fe calcined at 400°C: (a) in vacuum; (b) after impregnation with pyridine.

The distribution of Fe^{3+} ions contributing in the low-field ESR signal from FeHZSM (Si/Al = 25) is stable after the high temperature treatment: calcination in dry air at 700 and 800°C for 1.5 h does not alter noticeably the ESR lines at $g = 4.27$ and $g = 5.6$ and 6.5 shown in Fig. 7. A substantial further rise of the broad line at $g \cong 2.0$ takes place during high temperature calcination, as illustrated by the dotted line on Fig. 7d. It appears that small nonparamagnetic clusters of iron oxide form bigger magnetic aggregates (α-Fe_2O_3, for example). The distribution of Fe^{3+} ions contributing in the low-field ESR signal from FeHZSM-5 (Si/Al = 15) is less stable at high temperature: calcination at 700°C does not alter noticeably the ESR lines at $g \geq 4.27$ but thermal treatment at 800°C causes substantial loss of these low-field lines.

Sample 1[subl] (2.8% Fe) responds to oxidative treatment identically to the impregnated sample with 2.1% wt Fe. Conversely, in the highly loaded *sample 2[subl]* (5.5% Fe), the broad ESR line from aggregated species is substantial after all the steps of thermal treatment.

When FeHZSM-5 samples are impregnated with pyridine a similar simplification of the spectrum is observed, as mentioned above for $FeCl_3$/HZSM-5: the ESR signal associated with the coordinatively unsaturated ferric ions ($g = 5.6$ and 6.5) disappears completely and the sharp line at $g = 4.27$ appears.

Quantitation of Low-Coordinated Isolated Fe^{3+} ions

(a) Choice of the standard. As demonstrated above, $FeCl_3$/HZSM-5 and FeHZSM-5 samples show quite complex ESR signals from paramagnetic Fe^{3+} species, differing substantially in g-factor values. In addition, some part of Fe^{3+} ions can form nonparamagnetic species, and another one can be agglomerated in microcrystals of paramagnetic and ferromagnetic phases. Quantitation of isolated low-coordinated ions contributing in the specific low-field ESR signal ($g \geq 4.3$) is of prime importance because just this fraction of Fe^{3+} can be associated with *specific* bonding of isolated $(FeCl_2)^+$ and $(FeO)^+$ species in cationic positions of high-silica HZSM-5 zeolite, as distinct from other forms being typical for all supported catalysts. To evaluate the fraction of isolated cationic species it is necessary to compare double integrals of the ESR spectra from FeHZSM-5 with an absolute Fe^{3+} standard giving the ESR signal at $g \sim 4.3$ and measured under identical conditions.

In earlier quantitative studies of Cu^{2+} in H-ZSM-5 we used frozen water solutions of copper salts to prepare a solid specimen with isolated Cu^{2+} ions resembling quite well the CuH-ZSM-5 zeolite saturated with H_2O (15, 16). This approach does not work for FeH-ZSM-5. Water bonding to Fe^{3+} sites simplifies the ESR signal, with substitution of the complex ESR spectrum from ferric ions in different distorted tetrahedral sites by one narrow ESR line at $g = 4.27$ (14). Therefore, the bonding of H_2O ligands takes place with formation of coordinatively unsaturated structures. No line at $g \cong 2.0$, being typical of Fe^{3+} complexes with octahedral symmetry, appears upon saturation of FeHZSM-5 with water (14). However, diluted water solutions of inorganic Fe salts give complex, very broad ESR signal, as shown in Fig. 8a for $FeCl_3$ solution. Here the major part of Fe^{3+} ions contributes to the signal with $g \sim 2.0$ (octahedral coordination), and the mutual interaction between ions is quite strong (Fig. 8a). Therefore, even a very diluted frozen water solution of the $FeCl_3$ employed in the preparation of $FeCl_3$/HZSM-5 and FeHZSM-5 cannot be used as a reliable reference for Fe^{3+} quantitation in our samples.

As an alternative absolute standard, we need some compound providing low symmetry of Fe^{3+} ions in solid state and in solution. Fe(III)-phthalocyanine chloride is one of possible compounds of this type but only few solvents can be used in this case. Pyridine is a reasonably good solvent for Fe(III)-phthalocyanine chloride, and the pyridine molecule is small enough to penetrate HZSM-5 channels and form complexes with Fe^{3+} sites. Therefore, freezing of the solution produces a solid specimen with isolated Fe^{3+} ions resembling quite well the FeHZSM-5 zeolite impregnated with pyridine. Figure 8b shows the ESR spectrum of frozen solution of Fe(III)-phthalocyanine chloride in pyridine, in comparison with that of Fe(III)-Cl_3 in water (Fig. 8a). The spectrum of frozen solution of Fe(III)-phthalocyanine chloride (Fig. 8b) demonstrates the presence of the two main states of isolated Fe^{3+} ions (narrow line at $g = 4.27$ and the signal at $g \sim 2.2$), with negligible contribution from interacting ions. Hence, this diluted solution contains Fe^{3+} ions in both tetrahedral and distorted octahedral coordinations, and comparison of the double integrals of the two signals gives the ratio of the two states $Fe^{3+}{}_{\text{tetrahedral}}/Fe^{3+}{}_{\text{octahedral}} = 1/3$ for the solution with 0.019 wt% Fe. For a more diluted solution, with 0.010 wt% Fe, this ratio increases to ~1/2. The presence of the two different states of iron ions in our reference sample complicates somewhat the use of this standard for quantitation of tetrahedral Fe^{3+} but the accuracy of evaluation of the amount of these ions is still reasonable. Thus, for the assessment of the amount of ESR-visible low-coordinated isolated Fe^{3+} ions we use as the reference the solution with 0.010% wt Fe assuming that it contains only ~0.0033 wt% Fe^{3+} in the low-coordinated state.

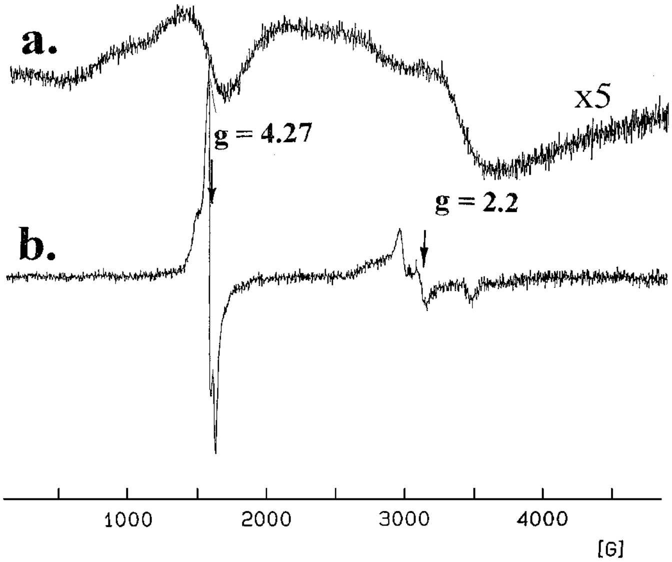

FIG. 8. ESR spectra, taken at −196°C, of (a) frozen water solution of $FeCl_3$, (0.0625 wt% Fe) and (b) frozen pyridine solution Fe(III)-phtalocyanine chloride, with 0.019 wt% Fe.

(b) Quantitation of low-coordinated Fe^{3+} ions in FeHZSM-5. Changes in the absolute concentration of Fe^{3+}, ESR-visible as low-coordinated isolated Fe^{3+} ions in pyridine-impregnated samples, are presented on Figs. 9 and 10 as a function of treatment steps of $FeCl_3$/HZSM-5 (Si/Al = 25) and $FeCl_3$/HZSM-5 (Si/Al = 15). All the quantitative data are also summarized on Fig. 11. The dashed line (Fig. 11) shows the theoretical limit when *all* the iron ions introduced into zeolite contribute to the Fe^{3+}-ESR signal at $g = 4.3$. As one can see, quantitation of "ESR-visible Fe^{3+}" in $FeCl_3$/HZSM-5 samples calcined at 400°C in vacuum (Fig. 11, ◇, ◆) demonstrates that virtually all ferric ions form isolated $FeCl_2^+$ species and contribute to the ESR signal up to a Fe/Al ratio ~0.6. It was

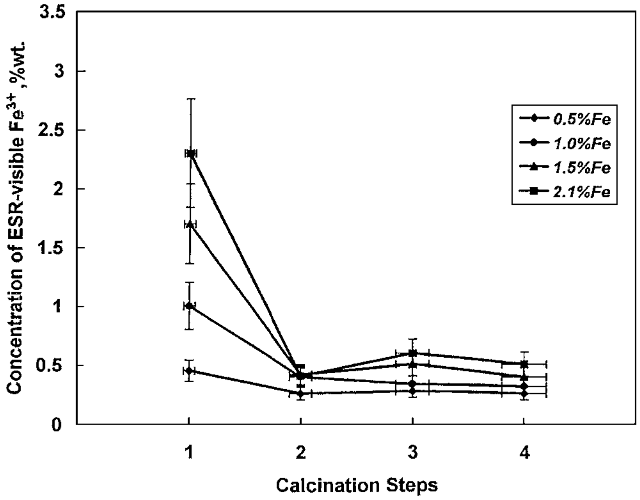

FIG. 9. Change in absolute concentration of Fe^{3+}, ESR visible as low-coordinated, isolated ions, after stepwise calcination of $FeCl_3$/HZSM-5 (Si/Al = 25) samples: (1) 400°C, vacuum; (2) 500°C, 4 h, air; (3) 700°C, 1.5 h, air; (4) 800°C, 1.5 h, air.

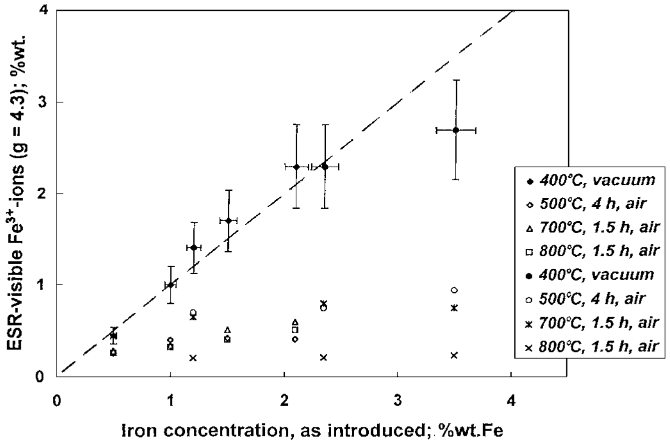

FIG. 11. Absolute concentration of Fe^{3+}, ESR visible as low-coordinated isolated ions, in $FeCl_3$/HZSM-5 (Si/Al = 25) (◇, ◆, △, □) and $FeCl_3$/HZSM-5 (Si/Al = 15) (●, ○, ∗, ×) samples calcined under different conditions and impregnated with pyridine. Dotted line corresponds to the theoretical limit (all the Fe^{3+} ions introduced into zeolite contribute to the ESR signal at $g = 4.3$).

shown earlier, with the use of different methods, that the majority of Fe^{3+} species are isolated after interaction of $FeCl_3$ with HZSM-5 in the absence of air (5, 9). The good agreement of the data confirms once more the accuracy of this approach for quantitative ESR study of iron-containing HZM-5. The question whether the pyridine treatment enhances the ESR signal by converting some nonisolated Fe^{3+} ions into isolated ones cannot be answered unambiguously. If some of these ions were oxygen-bridged in the original sample by strong bonds this is unlikely. On the other hand, if the oxygen bonds are weak (i.e., having long distances) then such an effect may be conceivable but probably small.

The number of isolated ESR-visible Fe^{3+} ions decreases drastically after sample treatment in an air flow at $T \geq 500$°C, except for the most diluted sample with 0.5% Fe (Fig. 9). In general, whatever the starting concentration of iron, the amount of isolated low-coordinated Fe^{3+} cations in FeH-ZSM-5 reduces to Fe/Al ~ 0.15 as a result of the transformation of $(FeCl_2)^+$ to $(FeO)^+$ isolated species upon oxidative calcination at 500–520°C (Figs. 9–11). The rest of the iron aggregates in either ESR-invisible species or in bulk α-Fe_2O_3 during oxidation of $FeCl_3$/HZSM-5 in an air This newly formed distribution of iron is quite stable in high-silica zeolite, with Si/Al = 25. The samples are surprisingly tolerant to further oxidative calcination at 700 and 800°C (Fig. 9). For the most diluted, low-loaded sample, 0.5% Fe/HZSM-5 (Si/Al = 25), the majority of Fe^{3+} ($\sim$2/3) remains well isolated and contributes to the ESR signal at $g = 4.3$ even after oxidative treatment at 800°C. However, reductive treatment of this sample even under mild conditions (1% $H_2 + He$, 300°C) redistributes the iron, with irreversible loss of a large part of isolated Fe^{3+} ions and formation of ferromagnetic aggregates of Fe_3O_4. Subsequent oxidation at 500–800°C does not completely restore the parent distribution of isolated Fe^{3+} species; the sample retains a part of iron aggregates once formed.

As to the zeolitic matrix with higher density of the lattice Al, FeHZSM-5 (Si/Al = 15), these samples are less tolerant to oxidative calcination. Substantial loss of ESR-visible isolated Fe^{3+} ions and formation of aggregated iron species takes place upon oxidative calcination of FeHZSM-5 (Si/Al = 15) at 800°C (Fig. 10).

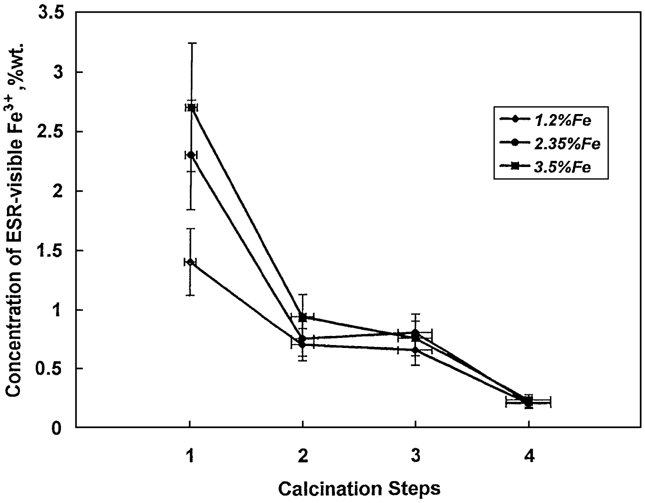

FIG. 10. Change in absolute concentration of Fe^{3+}, ESR visible as low-coordinated isolated ions, after stepwise calcination of $FeCl_3$/HZSM-5 (Si/Al = 15) samples: (1) 400°C, vacuum; (2) 500°C, 4 h, air; (3) 700°C, 1.5 h, air; (4) 800°C, 1.5 h, air.

Recent work by Lobree *et al.* (19) reaches very similar results using similar samples but completely different methods, namely infrared spectroscopy of adsorbed NO, temperature programmed desorption of NO and NH_3, and temperature-programmed reduction by hydrogen. In fresh samples the 1 : 1 exchange of protons for isolated Fe^{3+} was limited to a Fe/Al ratio <0.56. In heat-treated samples this was reduced to a an Fe/Al ratio <0.19.

(c) Comparison of FeHZSM-5 samples prepared by different methods. Our quantitative ESR measurements show that, irrespective to the method of iron introduction and starting concentration, the amount of isolated low-coordinated Fe^{3+} cations in FeH-ZSM-5 prepared by sublimation or ion-exchange corresponds to the ratio Fe/Al <0.15 after oxidative calcination at 500–520°C. The rest of the introduced iron forms both ESR-invisible aggregates and species of bulk α-Fe_2O_3. When sublimation is used to prepare the sample with Fe/Al >1, formation of species with magnetically interacting Fe^{3+} ions becomes dominant and the amount of isolated Fe^{3+} ions is lowered to Fe/Al <0.1. These samples are also less tolerant to oxidative calcination at 700°C and especially at 800°C, as compared with impregnated samples with lower loading.

CONCLUSIONS

1. Impregnation of FeHZSM-5 samples with pyridine simplifies the low-field Fe^{3+}-ESR spectra: superimposed signals from isolated ferric ions in different distorted tetrahedral sites are substituted by a single, narrow ESR line at $g = 4.27$ due to ligand bonding to Fe(III) sites. Frozen diluted solutions of Fe(III)-phthalocyanine chloride in pyridine could be used as an absolute standard for quantitative comparison with low-field ESR signals of pyridine-impregnated FeHZSM-5 taken at −196°C.

2. Quantitation of ESR-visible Fe^{3+} in $FeCl_3$/HZSM-5 prepared by impregnation and calcined at 400°C in vacuum demonstrates that virtually all ferric ions are isolated (as $FeCl_2^+$ species) and contribute to the ESR signal in samples with Fe/Al ratio up to ∼0.6. Introduction of iron in HZSM-5 by $FeCl_3$ sublimation in N_2 flow results in stabilization of the same amount of isolated $FeCl_2^+$ species, with the excess forming aggregates.

3. The number of isolated Fe^{3+} ions decreases sharply after sample treatment in an air flow at $T \geq 500$°C. Whatever the starting concentration of iron, the amount of isolated low-coordinated Fe^{3+} cations in FeH-ZSM-5 does not exceed the ratio Fe/Al ∼0.15 after oxidative calcination at 500°C, with the rest aggregating in either ESR-invisible species or in bulk α-Fe_2O_3. It seems that the ratio Fe/Al ≤ 0.15 is quite general for isolated Fe^{3+} cations in FeHZSM-5 calcined in air, irrespective of preparation method (impregnation, sublimation, ion-exchange) and the Si/Al ratio of the starting zeolite.

4. Further loss of ESR-visible isolated Fe^{3+} ions and formation of aggregated iron species takes place upon oxidative calcination of FeHZSM-5 with Si/Al = 15 at 800°C, whereas more high-silica samples, with Si/Al = 25, are tolerant to this treatment. Formation of aggregated iron species is of minor importance for the most diluted, low-loaded sample only, 0.5% Fe/HZSM-5 (Si/Al = 25) where the majority of Fe^{3+} (∼2/3) remains well isolated and contributes to the ESR signal even after oxidative treatment at 800°C.

5. Redox treatment of the sample 0.5% Fe/HZSM-5 (Si/Al = 25) even under mild conditions results in significant redistribution of iron, with irreversible loss of a part of isolated Fe^{3+} ions and formation of Fe_3O_4 ferromagnetic aggregates.

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