ESR of Gd^{3+}: a surrogate for the study of lanthanide dispersion in zeolitic and amorphous catalysts

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Gd^{3+}-ESR spectroscopy can be used as a sensitive method for the study of lanthanide additives in catalysts. Here we present the results of a comparative study of $Gd/SiO_2–Al_2O_3$ and Gd/HZSM-5. ESR gives evidence of rigid bonding of isolated Gd^{3+} ions into both amorphous silica–alumina and into HZSM-5. In addition, the zeolitic matrix stabilizes very small Gd^{3+}-clusters (containing only a few ions) capable of interacting with water molecules. Excess Gd is present as non-dispersed, particulate oxide. Strong bonding of PO_4^{3-} anionic ligands irreversibly changes the local environment and reactivity towards H_2O of the Gd^{3+}-clusters in HZSM-5. The Gd^{3+} ions do not block the cationic positions of HZSM-5 from further interaction with paramagnetic Cu^{2+} or Rh^{2+} cations.

Keywords: Gd^{3+}-ESR, lanthanide dispersion, $SiO_2–Al_2O_3$ and HZSM-5, influence of PO_4^{3-}

1. Introduction

Zeolitic catalysts suffer from deactivation when operating in an environment containing water vapor at high temperatures. This has become a very serious obstacle in the application of such catalysts in the treatment of hydrocarbon combustion exhaust streams, which inevitably contain ample amounts of steam. Recently, several attempts have been made to attenuate the deactivation by the introduction of "stabilizing" lanthanide ions [1–6], mostly $Ce^{4+,3+}$ or La^{3+}. The understanding of the behavior of these catalytically inert ions and in particular their interaction with the active ions exchanged for the zeolite protons calls for new physico-chemical probes. The problem is difficult because of sensitivity limitations of common physical methods when low-loaded samples containing a highly dispersed promoter are studied. For the monitoring of the deactivation process and of the effect of modifiers direct in situ observations are very useful.

We have previously devised a method for high-temperature measurement of ESR-active ions under flow conditions and applied it to characterize specimens containing Cu^{2+} [7] or Cr^{5+} [8]. Here, we propose the use of Gd^{3+}-ESR spectroscopy as a surrogate for the study of dispersed lanthanide additives in low-loaded multi-component catalysts. The reason for this is that the more abundant rare earths, most widely used for catalyst stabilization, are not easily observable in situ while the Gd^{3+} ion is observable by ESR. The chemical reactivity properties of the trivalent lanthanides are very similar and one may infer from the information obtained from specimens containing Gd^{3+} about the stabilization of the zeolite by lanthanides under hydrothermal conditions, in general. Here we summarize the results of a comparative study of $Gd/SiO_2–Al_2O_3$ and Gd/HZSM-5, as a first step for further in situ ESR study of more complex systems. The effect of PO_4^{3-} addition on the interaction of Gd^{3+} with the zeolitic matrix is also investigated.

2. Experimental

2.1. Sample preparation

The Gd/ZSM-5 samples, with 1.0, 2.0 and 4.0 wt% Gd, were prepared by incipient wetness impregnation (0.8 cm^3 of solution per 1 g of dried support) of NH_4ZSM-5 (PQ Corporation; Si/Al = 25 or 40; residual Na_2O content < 0.05 wt%) by a water solution of $Gd(NO_3)_3{\cdot}5H_2O$ (Acros; 99.9%). The sample with 4% Gd was prepared by a two-fold impregnation to provide a more uniform distribution of the lanthanide. Samples were dried at 130°C for 2 h, and calcined in an air stream at 500–800°C.

A $Gd/(SiO_2–Al_2O_3)$ catalyst, with 2.5 wt% Gd, was prepared by incipient wetness impregnation of the amorphous silica–alumina (Si/Al = 14) precalcined at 550°C by a solution of the same salt. It had a surface area of 360 m^2/g. Zeolitic samples modified with PO_4^{3-} anions ($\sim$3–5-fold excess of anionic species as compared with the Gd cation content) were prepared by incipient wetness impregnation of precalcined samples by a 6% water solution of H_3PO_4 with subsequent drying and calcination in air. The samples were pressed without binder, crushed into 0.1–0.2 mm particles and placed in a quartz cell for ESR measurements. Dried samples were precalcined at

500–900°C in an [He + 10% O_2] stream for 2–5 h. Twice distilled water and dry, chromatographically pure CH_3OH, CH_3CN and benzene were used for the impregnation of the precalcined samples.

2.2. ESR measurements

The ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) either (1) at 120–293 K on a Bruker ESP300 spectrometer, equipped with a low-temperature cavity st8410.91 and a co-axial quartz gas flow cell [9] (Dearborn) or (2) at 77 and 293 K on a reflecting-type spectrometer, equipped with a quartz dewar (Moscow). Diphenylpicrylhydrazyl (DPPH) was used as the standard.

The sample, placed in an ampoule, was calcined at a given temperature, taken from the furnace, connected with the vacuum system, evacuated at 293 K to 10^{-2} Torr residual pressure, and sealed off. In studying the interaction of the samples with different compounds the ampoule was opened and the sample was immediately impregnated at 20°C with an excess of liquid (H_2O, CH_3CN, CH_3OH, C_6H_6), and spectra from frozen samples were registered at 120 or 77 K.

The Bruker ESP300E software and the special Bruker program WIN-EPR (version 901201) were used for data treatment. The Origin 3.5 program for Windows was used for the treatment (baseline correction, noise reduction, double integration, deconvolution) of the recorded spectra (resolution 4096 points). The ESR signals were registered in the field region of 0–4800 G. Resonances for various levels of microwave power were recorded to verify the lack of sample saturation.

3. Results and discussion

Most lanthanide ions are ESR-silent but there are some that exhibit paramagnetism. One of the most useful for ESR study is Gd^{3+}: (1) this ion does not differ substantially from La^{3+} in size and properties, (2) the strong signal from Gd^{3+} can be easily registered in a wide temperature range, and (3) the form of the Gd^{3+}-ESR signal depends on both ion aggregation and coordination. For these reasons we propose this ion as a probe in studying the distribution and properties of lanthanide stabilizers/modifiers/promoters.

Let us first discuss briefly the general magnetic properties of the Gd^{3+} ion. Cations of rare-earth elements possess paramagnetic properties associated with 4f-electrons shielded from external electric fields [10–12]. Therefore, exchange interactions between these cations are weak and they exhibit magnetic properties typical of isolated ions independent of the type of the compound. For example, for Gd_2O_3, $GdCl_3$ and $Gd_2(SO_4)_3{\cdot}8H_2O$ the Weiss constant, a measure of the exchange interaction for Gd^{3+}-containing systems, is equal to 18, 14 and ~2°C, respectively [10], confirming that the exchange interactions are weak. Some properties of the ESR spectra from Gd^{3+} (the S-state with an eight-fold spin degeneration) can be pointed out. To a first approximation, there must be no splitting of this state, having a spherical distribution of the electronic density, by an electric field [13]. However, in the higher approximations a weak zero-field splitting ($\delta = 0.176\ \text{cm}^{-1}$) takes place (as in the case of the Mn^{2+} ion), and the ESR spectrum of Gd^{3+} cations is easily seen at 300 K. Fine structure of the Gd^{3+}-spectrum was observed for the monocrystal sample (1 wt. part of Gd nitrate per 10 wt. parts of La nitrate) [14]. Powder samples of Gd_2I_3 and other Gd-salts, are characterized by a broad ESR line with $\Delta H = 2000$–2500 G and $g = 1.98$–2.00. The spin–lattice relaxation time is relatively long for Gd^{3+} (10^{-7}–10^{-8} s at 300 K) but depends quite sharply on the temperature (10^{-2}–10^{-4} s at temperature of liquid helium) [15]. Due to weak exchange interactions between Gd^{3+} ions, the width of the Gd^{3+}-ESR line is determined primarily by the dipole–dipole interaction. In other words, no spin coupling takes place in [Gd^{3+}–O–Gd^{3+}] bridged species but a strong line broadening is noted due to dipole–dipole interaction between neighbouring Gd^{3+} cations.

4. Gd/HZSM-5

4.1. Characteristics of Gd^{3+} location

It is necessary to note that the ESR traces obtained for the samples with 1, 2, and 4 wt% Gd are similar, with the signal intensities depending linearly on the Gd concentration in the samples. Henceforth the results are further illustrated mainly on the example of the 4% Gd/HZSM-5 sample. Figure 1 shows ESR spectra from several Gd-containing samples. Pure bulk Gd_2O_3 is characterized by a very broad line ($\Delta H > 2000$ G, $g \cong 1.98$) from paramagnetic ions with a strong dipole–dipole interaction (figure 1a). Dilution of Gd^{3+} ions in the ice matrix, a frozen 5% solution of $Gd(NO_3)_3$, weakens this interaction quite effectively and narrows the line down to ~500 G (figure 1b). An impregnated and dried $Gd(NO_3)_3$/HZSM-5 sample gives an intense, broad ESR signal typical of coupled Gd^{3+} ions (figure 1c; $\Delta H \approx 1300$ G, $g \cong 1.98$). Impregnationof this "as-made" sample with water results in formation of the symmetric ESR line with $\Delta H \approx 900$ G, $g \cong 1.98$. Such a narrowing of the line demonstrates that dissolution of Gd nitrate weakens, to some extent, the dipole–dipole interaction between Gd^{3+} ions. Calcination of the sample at $T \geqslant 500$°C in air is accompanied by sharp changes in the ESR spectrum: the signal 1c disappears irreversibly and a complex spectrum with narrow lines is formed pointing to the formation of Gd^{3+} ions in different types of environments (figure 1d; figure 2). The transforma-

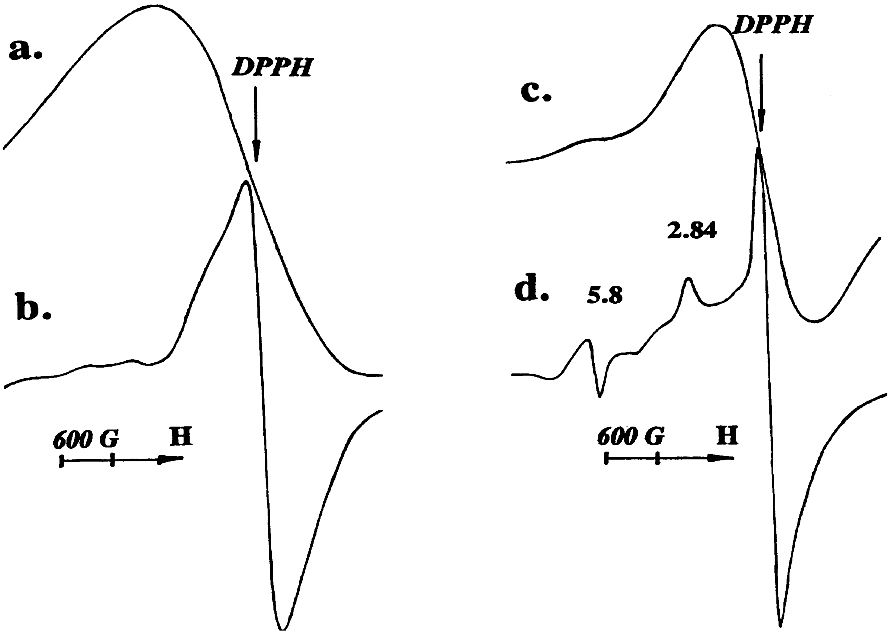

Figure 1. ESR spectra, at 77 K, of Gd-containing samples: (a) Gd_2O_3; (b) frozen 5% water solution of $Gd(NO_3)_3$; (c) "as-made" 4% Gd/HZSM-5, dried at 293 K; (d) sample (c) after calcination in air at 550°C for 2 h and impregnation with water.

tion of this spectrum upon different treatments of the Gd/HZSM-5 is illustrated by figure 3. A very broad signal can be first distinguished ($\Delta H > 2000$ G), seen as a broad deviation from the baseline (figure 2b, dotted line). No broad line of this type appears as a result of calcination of pure HZSM-5, hence it cannot be attributed to Fe-oxide impurities in the starting zeolite. This ESR line from strongly interacting Gd^{3+} ions (see figure 1a for comparison) confirms that some part of the Gd introduced into the starting sample is aggregated in bulk Gd_2O_3 particles upon calcination. Subsequent sample treatment under very different conditions is not accompanied by any change in this broad signal, and this part of aggregated ions in the sample can be considered an inert admixture.

Most interesting is the superimposed complex ESR signal with a set of quite narrow lines ($g = 1.98$; 2.84 and 5.8) typical of several types of isolated Gd^{3+} ions located in crystal fields of different symmetries (figsures 2 and 3). The signal with $g = 1.98$ is typical of ions in an environment close to octahedral, but the two low-field lines point to the location of the part of Gd^{3+} ions in a crystal field of low symmetry. Earlier, low-field ESR lines, with $g = 4.3$–6.5, were observed for Fe^{3+} cations stabilized by an HZSM-5 matrix in crystal fields of low symmetries [16]. For the Gd^{3+}-ESR spectrum the line with a g-factor of 5.8 is indicative of a distorted tetrahedral environment. The symmetry of the local crystal field cannot be attributed unambiguously to the line with $g = 2.84$ but further study of the interaction of Gd^{3+} cations with

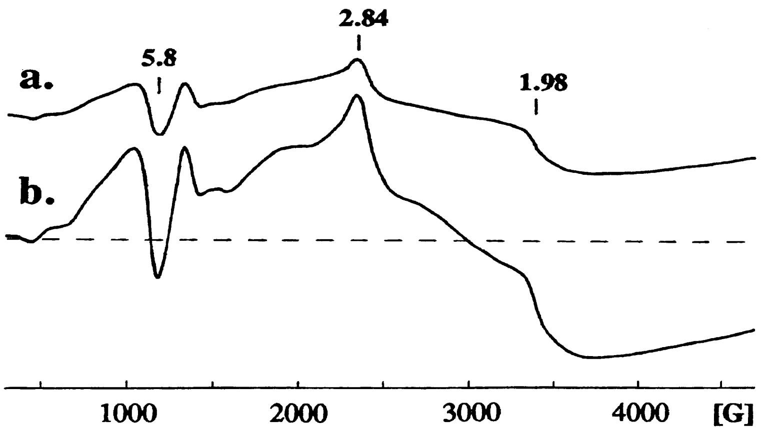

Figure 2. ESR spectra of 2% Gd/HZSM-5 precalcined at 700°C for 1 h and evacuated at 20°C: (a) taken at 293 K; (b) taken at 120 K (baseline for (b) is marked by the dotted line).

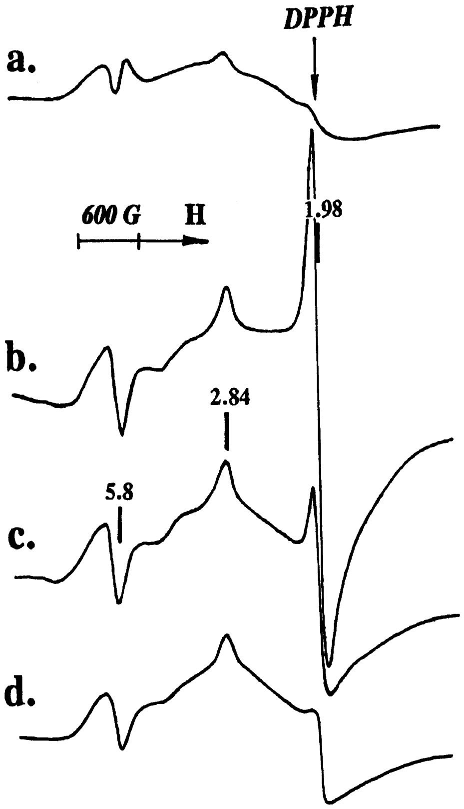

Figure 3. ESR spectra, taken at 77 K at same magnification, of 4% Gd/HZSM-5: (a) calcined in air at 600°C for 2 h; (b) impregnated with water at 20°C; (c) dried by evacuation at 20°C for 5 min; (d) dried by evacuation at 20°C for 50 min.

different molecules provides evidence that both low-field ESR lines are associated with isolated Gd^{3+} ions rigidly bonded *to* the support.

4.2. Rehydration of precalcined Gd/HZSM-5

Impregnation of precalcined Gd/HZSM-5 with water results in a drastic change of the complex Gd^{3+}-ESR spectrum (figure 3a→3b). The complex spectrum of Gd^{3+}-ESR (figures 2 and 3) can be subdivided in two groups of ESR lines differing in their response to adsorption of water molecules on calcined Gd/ZSM-5: for low-field lines, with $g = 5.8$ and 2.84, adsorption of water causes an about two-fold rise in signal amplitudes and subsequent sample drying by evacuation at 20°C results in a relatively small decrease of these lines (figure 3b→3d). The effect of intensity change due to the presence of H_2O molecules strongly bonded in ZSM-5 channels is not clear now. It is unlikely that some artifact takes place because the signal increases while, quite contrary, a decrease of the signal could be expected due to the introduction of polar molecules into the sample because this causes a degradation of the resonator quality factor (Q). In spite of the preservation of the g-factor value of 5.8 some change of the line shape occurs (figure 3). It is probable, that the effect is caused by a change in spin–lattice relaxation of Gd^{3+} ions chemically anchored to the zeolitic framework but this calls for a more detailed investigation. These ions are rigidly bound to the lattice of the support and are unable to bind additional ligands. It cannot be excluded that incorporation of some part of the Gd^{3+} ions into framework tetrahedral positions of HZSM-5 takes place upon calcination, judging from the appearance of the ESR lines at $g = 5.8$ and 2.84, but one needs to substantiate such assertion by other methods.

The behavior of the line at $g = 1.98$ upon sample impregnation with water differs: a very sharp narrow line (figure 3b) appears in a wet frozen sample. The integral intensity of this line increases by more than two orders of magnitude as a result of impregnation with water. Drying of this sample by evacuation at 293 K is accompanied by a gradual decrease in the line intensity, and a long-term vacuum treatment at room temperature lowers the intensity over ten-fold (figure 3d). The removal of adsorbed water by vacuum drying at 100°C completely restores the starting weak line with $g = 1.98$ (figure 2). Therefore, the strong effect is caused by weakly bonded water in the zeolitic channels. This type of isolated Gd^{3+} ions ($g = 1.98$) manifests the change in the symmetry of the local environment and/or in the extent of spin–lattice interaction upon hydration (figure 3). We surmise that this strong ESR line, being very sensitive to water, can be attributed to either (1) isolated Gd^{3+} ions located in distorted octahedral coordination exhibiting strong spin–lattice interaction or (2) small clusters (few ions) of interacting Gd^{3+} ions in the zeolitic channels. In both instances, the Gd^{3+} ions are not rigidly bound to the support and are readily accessible to H_2O molecules filling the inner zeolitic voids. Hydration shells effectively separate coupled paramagnetic ions or weaken the spin–lattice interaction of Gd^{3+} with the zeolitic framework. An effect of this type was noted earlier for Mn^{2+} cations in HZSM-5 [17]. Hydrated complexes, with octahedral Gd^{3+} location, are easily broken up by sample evacuation and a substantial dipole–dipole broadening of the ESR-line with $g = 1.98$ takes place.

4.3. Interaction of precalcined Gd/HZSM-5 with CH_3OH, CH_3CN and C_6H_6 molecules

Observation of the interaction of Gd/HZSM-5 with different molecules (H_2O, CH_3OH, CH_3CN and C_6H_6) demonstrates that the effect of these substances on different types of Gd^{3+} ions is quite specific. No measurable change in the ESR signal (figure 2) occurs upon Gd/HZSM-5 impregnation with benzene. Therefore, non-polar benzene does not affect either spin–lattice interactions of isolated, rigidly fixed Gd^{3+} ions or the dipole–dipole interactions in clustered Gd^{3+}-species.

Adsorption–desorption of polar CH_3OH and CH_3CN molecules is accompanied by transformations

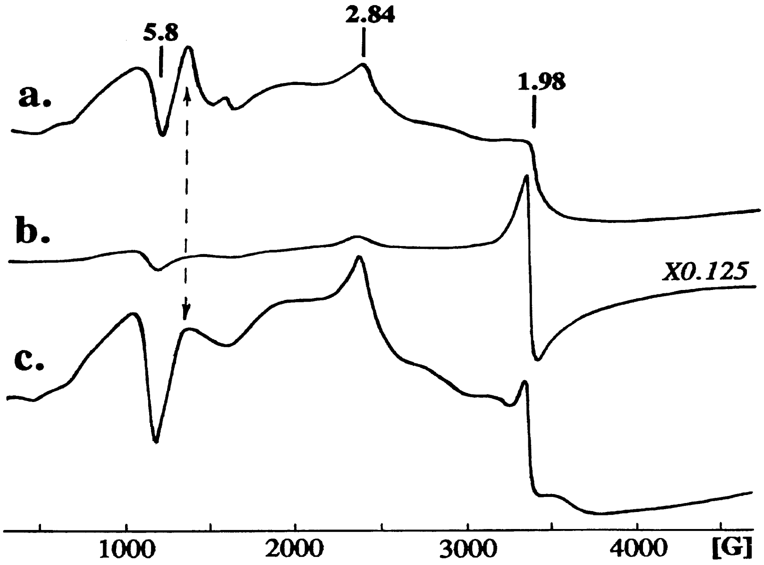

Figure 4. ESR spectra, at 120 K, of 4% Gd/HZSM-5: (a) calcined at 600°C for 1 h and evacuated; (b) impregnated with water at 293 K; (c) impregnated with CH_3CN at 293 K.

of the Gd^{3+}-ESR signals shown in figures 4 and 5. From the comparison of these spectra with those shown in figure 3, it is clearly seen that the action of these molecules on low-field ESR lines, with $g = 5.8$ and 2.84, is akin to that caused by water. The same 2–2.5-fold rise in the peak amplitudes takes place along with the change of the line shape (shoulders pointed by dotted arrows on figures 4 and 5). The cooperative effect caused by a change in the spin–lattice relaxation for rigidly fixed Gd^{3+} ions seems to be identical for different polar molecules with large dielectric constants. At the same time, adsorption–desorption of CH_3CN molecules is accompanied by much smaller changes in the integral intensity of the narrow $g = 1.98$ line, as compared with water sorption (figures 4b,c), and CH_3OH effect on this line is negligible (figure 5). Thus, the weak solvating ability of these solvents does not afford the separation of the interacting Gd^{3+} ions in small reactive clusters. Evacuation of the samples at 200°C restores completely the starting ESR spectrum (figure 2) and subsequent sample impregnation with water results in formation of the Gd^{3+}-ESR spectrum with the intense narrow line at $g = 1.98$ (figures 3b and 4b). Only the interaction with H_2O is strong enough to separate coupled Gd^{3+} ions in HZSM-5 and effectively weaken the dipole–dipole interaction between them.

From a practical point of view it is important to ascertain whether these small Gd^{3+}-clusters in HZSM-5 are localized in the cationic positions competing for the latter with the catalytically active ions. Based on our recent studies of interaction between Gd/HZSM-5 and Rh^{2+} or Cu^{2+} ions [18,19] it appears that Gd^{3+} clusters *do not block* these cationic positions of HZSM-5 from further interaction with paramagnetic Cu^{2+} or Rh^{2+} cations.

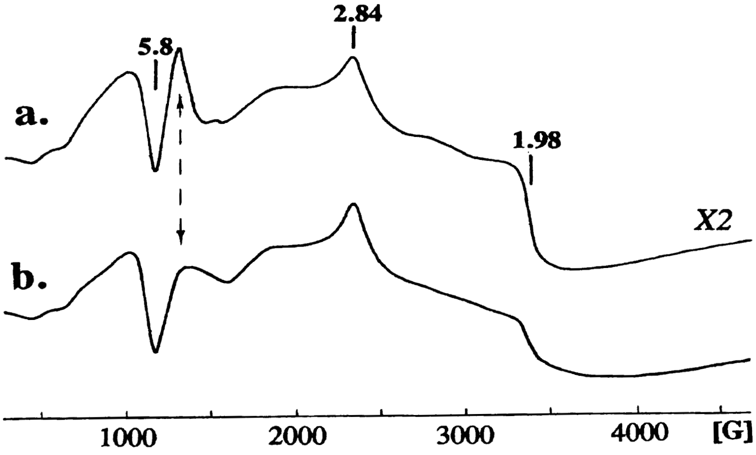

Figure 5. ESR spectra, at 120 K, of 4% Gd/HZSM-5: (a) calcined at 700°C for 1 h and evacuated; (b) impregnated with CH_3OH at 293 K.

The chemically anchored part of Gd^{3+} also does not influence migration/distribution of Cu^{2+} and Rh^{2+} ions to cationic positions and no new cationic positions are created as a result of rigid bonding of Gd^{3+} to HZSM-5.

4.4. Calcination of Gd/HZSM-5 at 500–900°C

The ESR signal of Gd^{3+} is altered by the oxidative calcination of Gd/ZSM-5. Stepwise treatment of the sample at 500–900°C for 2 h results in an irreversible transformation of the ESR lines in the complex ESR spectrum shown in figure 3b. Figure 6 shows the temperature dependence of the intensity for the two main types of Gd^{3+} ions. The line associated with the "octahedral" Gd^{3+} interacting with H_2O ($g = 1.98$) has a maximum intensity at $T_{calc.} = 500°C$ and decreases gradually with more severe treatments. The line associated with the rigidly bonded "tetrahedral" Gd^{3+} ions, $g = 5.8$, attains a broad maximum at $T_{calc.} = 600–800°C$, and even the most severe calcination at 900°C does not cause a sharp decrease of this line (figure 6). The heat treatments point again to *lattice-anchored* and *extra-lattice* types of fixation for the two fractions of dispersed Gd^{3+} ions in calcined Gd/ZSM-5: (1) the HZSM-5 framework is stable up to 900°C and lattice-anchored Gd^{3+} ions are quite stable at $T_{calc.} \leqslant 900°C$ as well; (2) severe calcination causes progressively large disappearance (aggregation) of small Gd^{3+} clusters, reactive toward H_2O, and a gradual loss of this type of Gd^{3+} is observed at $T_{calc.} > 500°C$ (figure 6). Presently, there is no information about which portion of the dispersed lanthanides imparts improved resistance to the deactivation of ZSM-5 by steam dealumination [5,6]. If the stabilization against dealumination is associated with the small lanthanide clusters the useful temperature range of its application may be limited to $< 500°C$.

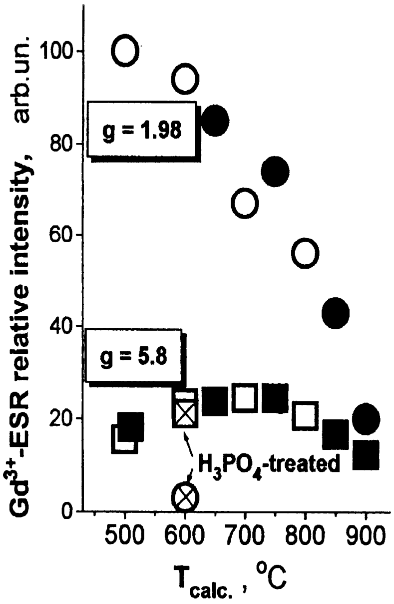

Figure 6. Relative intensity of the ESR signals from cluster ($g = 1.98$, circles) and "lattice" ($g = 5.8$, squares) Gd^{3+} ions (see figures 2 and 3) vs. $T_{calc.}$ of Gd/HZSM-5 in air. After calcination the samples were impregnated with water (open and closed points: two sets of measurements made at 120 K and 77 K, respectively). Points marked by X: the sample precalcined at 600°C, impregnated with 6% H_3PO_4 solution and calcined at 600°C for 1 h.

4.5. H_3PO_4 action on Gd/HZSM-5

The above-mentioned description of the dispersed lanthanide in HZSM-5 is further confirmed by the modifying action of PO_4^{3-} anions. Impregnation of 4% Gd/ZSM-5 (pre-calcined at 600°C) by H_3PO_4 solution followed by repeated calcination at 600°C for 1 h has only a minor effect on the signal from non-reactive, rigidly fixed "tetrahedral" Gd^{3+} ions. At the same time, a complete loss of the signal from reactive, "octahedral" Gd^{3+} ions capable of binding H_2O molecules is observed (figure 6, points marked by X). Irreversible strong fixation of reactive Gd^{3+} clusters by rigidly bonded multicharged PO_4^{3-} ligands can be assumed in this case.

4.6. Gd/(amorphous SiO_2–Al_2O_3)

To elucidate the specific role of the HZSM-5 crystal matrix a sample 2.5% Gd/(SiO_2–Al_2O_3) was studied for comparison. Amorphous silica–alumina with high surface area (~360 m^2/g) and comparable Al content was used as a support, and a somewhat lower absolute Gd concentration was chosen to provide the same surface concentration of Gd^{3+}, taking into account that the formal surface area of the zeolite is ~650 m^2/g. An impregnated and dried at 20°C $Gd(NO_3)_3$/(SiO_2–Al_2O_3) gives a broad symmetric ESR signal typical of coupled Gd^{3+} ions (figure 7a; $\Delta H \approx 800$ G, $g \cong 1.98$). This signal does not differ substantially from the spectrum of the Gd-impregnated zeolitic starting sample (figure 1c). Calcination of the sample at 500°C in air is accompanied by appearance of the ESR spectrum shown in figure 7b, and subsequent impregnation with water results in formation of the complex Gd^{3+}-ESR spectrum with narrow lines at $g = 1.98$, 2.84 and 5.8 (figure 7c). Drying of the sample by evacuation at 20°C for 30 min causes some change in the spectrum (figure 7c→d). The sample $Gd(NO_3)_3$/(SiO_2–Al_2O_3) calcined at 700°C for 2 h and impregnated by water gives the ESR signal figure 7e.

Comparison of the spectra presented of figures 3b and 7c demonstrates the similarities and differences between the two systems: (1) ESR signals resulting from Gd^{3+} ions rigidly anchored by the support ($g = 5.8$ and 2.84) are identical for crystalline HZSM-5 and amorphous SiO_2–Al_2O_3; (2) the ESR line from hydrated "octahedral" Gd^{3+} ions ($g = 1.98$) is weaker by two orders of magnitude in the amorphous silica–alumina than in the zeolitic sample. This indicates that the matrix

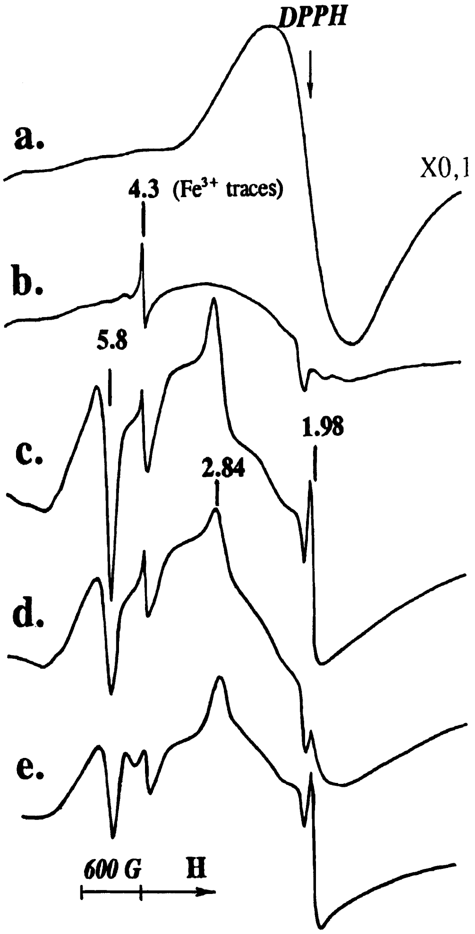

Figure 7. ESR spectra, taken at 77 K, at same magnification, of 2.5% Gd/(SiO_2–Al_2O_3): (a) fresh Gd(NO_3)$_3$/(SiO_2–Al_2O_3) dried at 293 K; (b) calcined in air at 500°C for 2 h; (c) impregnated with water at 20°C; (d) dried by evacuation at 20°C for 30 min; (e) calcined in air at 700°C for 2 h and impregnated with water at 20°C.

of high-silica HZSM-5 provides *specific* stabilization of very small Gd^{3+}-clusters reactive toward water molecules. Such highly dispersed lanthanide clusters are virtually absent in amorphous high-surface silica–alumina with a comparable Al content. The lanthanide dispersion on amorphous silica–alumina is also less thermally stable compared to Gd/HZSM-5.

5. Conclusion

The Gd^{3+}-ESR spectra provide a wealth of structural information useful for further in situ study of the effect of lanthanide additives on the catalytic properties of multi-cationic catalysts. This is relevant to the understanding of the activity stabilization by lanthanides of zeolitic catalysts under hydrothermal conditions as is the case in the selective catalytic reduction of NO_x.

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