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Mesostructured Iron Oxyhydroxides. 2. Soft Hydrothermal Restructuring Processes

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Received February 18, 2000. Revised Manuscript Received July 26, 2000

The properties of mesostructured iron oxyhydroxide–surfactant composites prepared from weakly acidic (pH between 2.3 and 2.6) Fe(III) solutions by the addition of dodecyl sulfate are studied. The mesocomposites exhibit superparamagnetic behavior with the magnetic ordering within the inorganic part being antiferromagnetic. Mössbauer spectra indicate the presence of significant interparticle interactions, as deduced from the closeness of the blocking temperature in these measurements and the peak temperature of zero-field-cooled magnetic susceptibility data. The blocking temperature in static magnetic measurements is dependent on the aging time of the mesostructured composites in the mother liquor and varies between 17 K and around 30 K. This shift is attributed to an internal restructuring process within the inorganic part of the mesostructured composites, namely, further cross-linking between not fully connected $[\text{Fe}(\text{O},\text{OH})_6]$ octahedra. This is supported by X-ray absorption spectroscopy: Shortly aged samples, that is, 1 or 2 days, have an inorganic part resembling that of bulk lepidocrocite ($\gamma\text{-FeOOH}$) with dominantly corner-linked $[\text{Fe}(\text{O},\text{OH})_6]$ units. With increasing aging time, further cross-linking within the inorganic part results in an increase of edge-sharing octahedra, making the local structures similar to those of goethite and akaganéite. The increase in the blocking temperature with aging time can be interpreted in terms of growth of the magnetically active domains.

Introduction

Recently, the preparation of mesostructured silica–surfactant composites^{1,2} was extended to include a variety of different compositions based on transition-metal oxide or sulfide inorganic parts.³ This has opened the way to materials with semiconducting⁴ and size-dependent optical⁵ properties. The first detailed work on the magnetic properties of lamellar iron oxide–

surfactant composites was recently reported.⁶ This study reported a correlation between peak temperatures in zero-field-cooled (ZFC) magnetic measurements and the average thickness of the inorganic iron oxide layer, which varied between 11 and 16 Å. By several modifications of the preparative methods, the thickness of the iron oxide layer can now be increased nearly continuously up to around 30 Å as demonstrated in the preceding paper. In this paper, we report a study on time-dependent structural changes induced in an iron oxyhydroxide–surfactant composite by aging of a precipitated solid in the surrounding solution at room temperature. We have found that a restructuring takes place, which is accompanied by a change of the magnetic properties of the composites.

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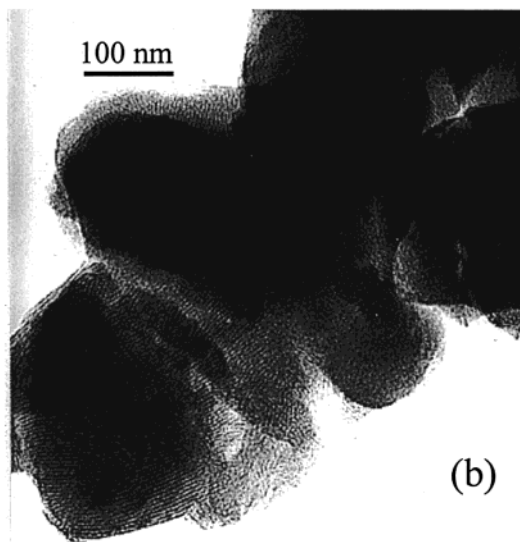
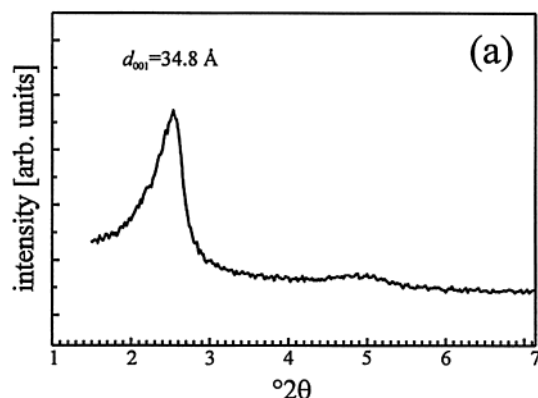


Figure 1. (a) Typical XRD pattern (sample aged for 1 day) and (b) TEM of an iron oxyhydroxide-surfactant composite prepared from diluted Fe(III) solutions.

Experimental Section

Iron oxyhydroxide-surfactant composites were prepared by adding 100 mL of a 0.007 M $C_{12}H_{25}OSO_3^-Na^+$ (Aldrich) solution to 500 mL of a 0.01 M $FeCl_3 \cdot 6H_2O$ solution with stirring. About 10 min after the addition of the surfactant solution, the solids began to sediment. These solids were aged in the mother solution for a specified time (between 1 and 21 days). Subsequently, they were separated from the solution and washed two times with 20 mL of deionized H_2O . Measurements and data evaluation were performed as described in the preceding paper.

Results and Discussion

Starting from strongly diluted Fe^{3+} solutions, iron oxyhydroxide-surfactant composites were precipitated by the addition of a $C_{12}H_{25}OSO_3^-Na^+$ solution at room temperature.⁷ The solids, which began to settle down after a time of around 10 min, were aged in the surrounding mother liquor for various times between 1 and 21 days. Under the conditions used, always lamellar mesostructured materials were obtained, as indicated by their corresponding X-ray diffraction (XRD) patterns (Figure 1a). These results are confirmed by transmission

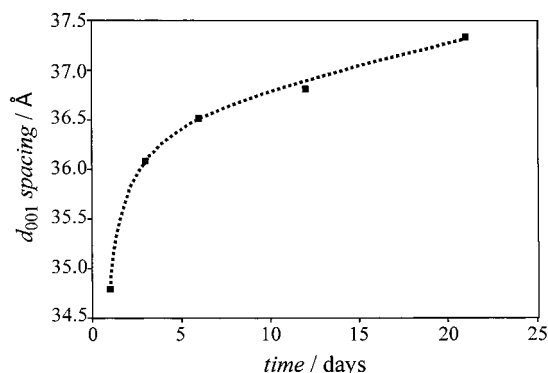


Figure 2. Increase of the interlayer spacing as a function of time. The dotted line is a guide to the eye.

electron microscopy (TEM, Figure 1b), which does not give any evidence for other symmetries, like hexagonal or cubic symmetries. XRD measurements reveal a slight increase in the d_{001} spacing with increasing contact time of the precipitated solid with the mother liquor (Figure 2). A lamellar-hexagonal structural transformation similar to that observed in silica-based⁸ or alumina-based⁹ systems can be excluded. However, whereas XRD measurements show the layer spacing to increase with aging time, elemental analysis gives constant Fe:surfactant ratios.¹⁰ The possibility that the increase in layer spacing is due to a time-controlled diffusion and incorporation of iron ions into the inorganic layer can therefore be excluded.

During aging of the mesocomposites in the mother solution, the morphologies remain unchanged, as revealed by secondary electron microscopy (SEM) observations. The typical morphological appearance of the samples is that of small-sized particles (diameter of around 100 nm) with rounded faces and edges. The average size of these particles remains constant during aging, evidencing that no further particle growth occurs when the solids are aged in the mother liquor. In addition, SEM pictures show that the small-sized composites are heavily aggregated (see Figure 3 for an example of a sample aged for 4 days). Hence, the boundaries between individual particles are often difficult to distinguish, and strong interactions or intergrowth between the primary particles may occur.

dc magnetic data recorded under both ZFC and FC conditions show behavior similar to that found for superparamagnetic systems. The ZFC susceptibility of a sample aged for 1 day (Figure 4) exhibits a peak at a temperature T_p of about 17 K related to a blocking of single-domain particles. The FC susceptibility continually increases up to the lowest measured temperature (around 4.5 K), thus demonstrating that some domains still exhibit relaxation at such low temperatures. The weak magnetic moment per iron ion ($\mu_{ion} = 3.2 \mu_B$)

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(10) Because of the lamellar structure of the composites, the composition is best expressed in terms of the molar ratio Fe/(2 surfactant); see ref 20. Elemental analysis gave the following values for samples aged for 2, 6, and 21 days, respectively: 5.08, 5.03, and 5.05. Assuming Fe-Fe distances of around 3 Å, the inorganic wall thickness can be roughly estimated to be around 15 Å.

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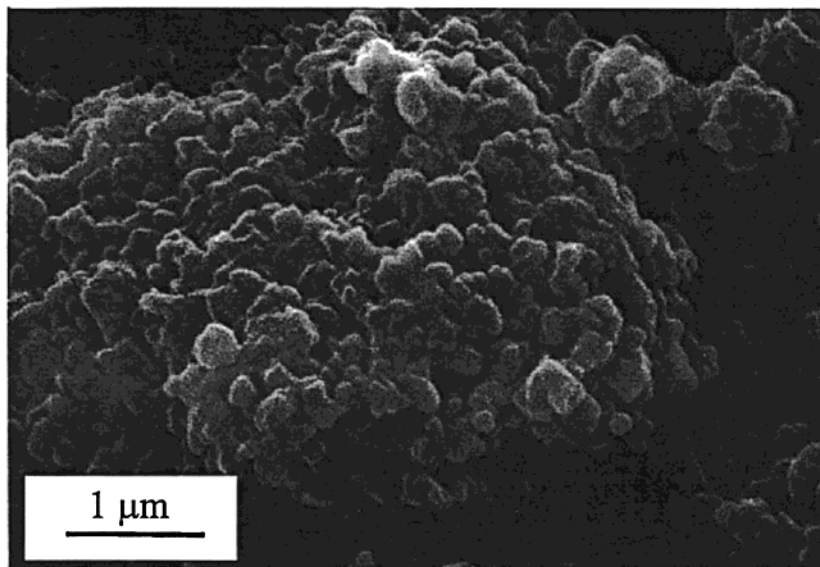


Figure 3. SEM of a sample aged for 4 days showing particles of around 100 nm, which are heavily aggregated.

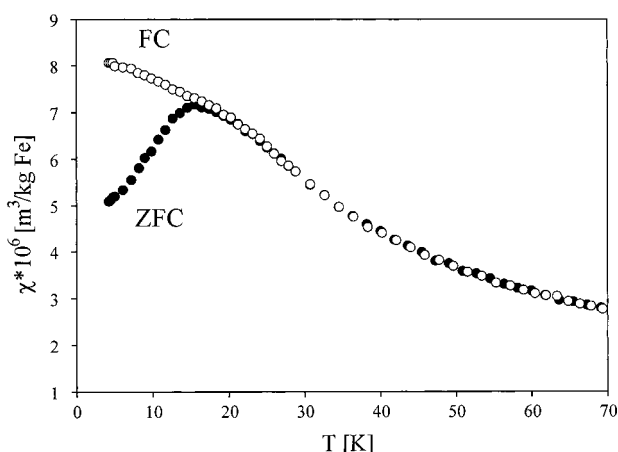


Figure 4. dc magnetic susceptibility (200 kA m^{-1}) of a composite aged for 1 day (FC, field-cooled; ZFC, zero-field-cooled).

clearly reveals that the magnetic ordering within the inorganic part is antiferromagnetic or antiferromagnetic-like¹¹ as found for most iron oxides/oxyhydroxides. The net moment, which gives rise to hysteresis at temperatures below T_p , can be attributed to a nonperfect spin compensation. Two possibilities must be taken into account: Both vacancies and surface ions can be considered as defect centers preventing a perfect compensation of antiparallel spins.

Mössbauer data obtained in an applied field of 0.8 T at 80 K do not show any changes when compared to zero-field measurements at 80 K. This shows that the particles have a low or zero magnetic moment at this temperature. Provided that 80 K is below the magnetic ordering temperature of the material, this supports the above interpretation from static susceptibility measurements. A series of zero-field Mössbauer spectra obtained as a function of temperature on a sample aged for 1 day are depicted in Figure 5. The average Mössbauer parameters at 295 K ($\delta = 0.49 \text{ mm s}^{-1}$, $\Delta E_Q = 0.71 \text{ mm}$

s^{-1}) unambiguously show that all iron ions are present in the form of high-spin Fe(III). The 17 K spectrum consists of magnetically ordered components only with an average hyperfine field of about 44 T. The quadrupole shift is larger than that for most iron oxides, indicating a relatively large local distortion. The spectrum is clearly different at 25 K, where a significant broadening of the components is found, indicating a wide distribution of hyperfine fields. These dynamic phenomena are also present in the 17 K spectrum and at both temperatures it is seen that the inner lines (2, 3, 4, 5) are narrower than the outer ones (1, 6). This implies that the broad feature is not due to conventional para- or superparamagnetic relaxation in which the inner lines broaden before the outer lines.¹² Rather, the behavior seen here is characteristic of a distribution of hyperfine fields. It has been observed in similar form for natural ferrihydrite.¹³ Another characteristic feature of the spectra is asymmetry of the room temperature spectrum with a slightly larger dip in the first line. Such asymmetry could be due to texture effects of the composite. However, measurements with the absorber holder at the magic angle (which eliminates these effects) show the spectra to remain unchanged (see Figure 5, bottom), so that this effect can be excluded. Asymmetry like this is also observed when the principal axis of the electric field gradient is along the hyperfine field whereas the opposite asymmetry is characteristic for a perpendicular alignment of the principal axis of the electric field gradient to the hyperfine field.¹⁴ However, taking the temperature dependence of lines 1 and 2 into account, it is most probable that the asymmetry is due to the presence of more than one iron site and the change with temperature is due to different variations of δ and ΔE_Q with temperature. This interpretation is consistent with the finding that in the 17 K spectra lines 1 and 5 are sharper than lines 2 and 6, indicating more than one site. Furthermore, the asymmetry at 17 K and the change from one asymmetry at 40 K (where line 1 is sharper than line 2) to another type of asymmetry at

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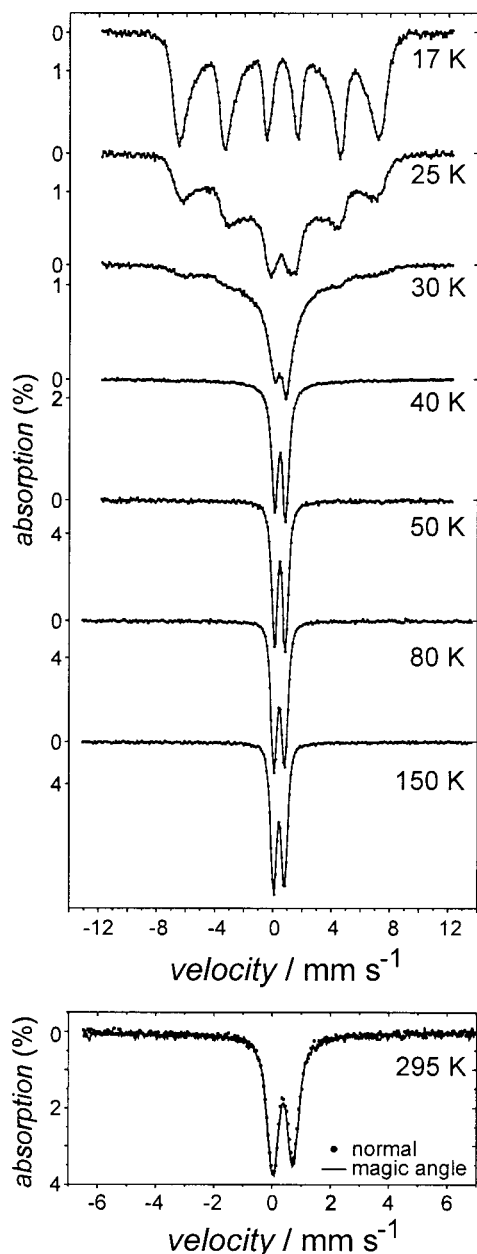


Figure 5. Temperature-dependent Mössbauer spectra of a sample aged for 1 day. The room-temperature spectrum was recorded under magic angle conditions, too (bottom; note different scale).

room temperature (where line 2 is sharper than line 1) are in agreement with this interpretation.

At first glance, the occurrence of a magnetically split sextet that collapses into a doublet at higher temperatures points to the existence of superparamagnetic relaxation as frequently observed for nanostructured iron oxides/oxyhydroxides.¹⁵ As a rule, the magnetically split component and the doublet resulting from superparamagnetic relaxation coexist over a rather wide temperature range. In the spectra of this sample the sextet has disappeared at 40 K and the blocking temperature deduced from the Mössbauer spectra is close to 30 K. This is only slightly higher than the peak

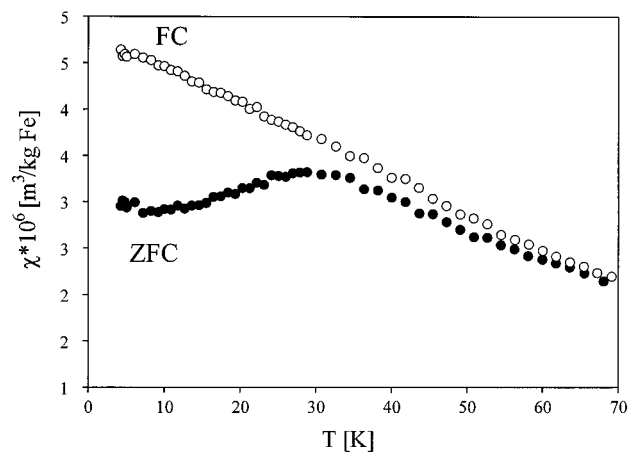


Figure 6. dc magnetic susceptibility (200 kA m^{-1}) of a composite aged for 21 days (FC, field-cooled; ZFC, zero-field-cooled).

maximum of about 17 K in the ZFC magnetic measurements. This behavior is similar to that found for very closely stacked microcrystals (dimensions of around 100 nm) of goethite.¹⁶ Collective magnetic excitations cannot explain the large reduction of the magnetic hyperfine field because they can only cause a hyperfine field reduction of 5–15%. Therefore, the only remaining explanation is interparticle interactions possibly combined with a low Néel temperature of the material. Such interactions lead to an effective magnetic field, which slows down the relaxation of the individual particles.^{16,17} For sufficient interaction, the individual particles must be in close contact as is the case for the samples obtained by the preparation method reported here (see Figure 3). For this case, the exchange coupling between the different crystallites may become significant and result in both a large reduction of the magnetic hyperfine field and a very narrow temperature range for the transition from a frozen “superferromagnetic” state (sextet) to a superparamagnetic doublet.

With increasing aging time, the magnetic susceptibility changes significantly (Figure 6). The data obtained for a sample aged for 21 days (the longest aging time investigated) show the largest shift of T_p to 29 K (compared to 17 K of the sample aged for 1 day). Moreover, the peak in the ZFC measurement becomes significantly broader, thus indicating a broad distribution of domains contributing to the signal. A possible explanation for this would be a restructuring within the inorganic part of the composites.

With increasing aging time, the low-temperature (≈ 20 K) characteristics of the Mössbauer spectra (Figure 7) remain essentially identical with two (or more) sites with closely overlapping spectra and average hyperfine fields of about 44 K. However, the temperature dependence of the spectra is markedly modified. Magnetically ordered components are seen at higher temperatures (compare the spectra measured at 50 K), and the collapse of the major part of the magnetically ordered components occurs at higher temperatures. In the transition region, where magnetically split and col-

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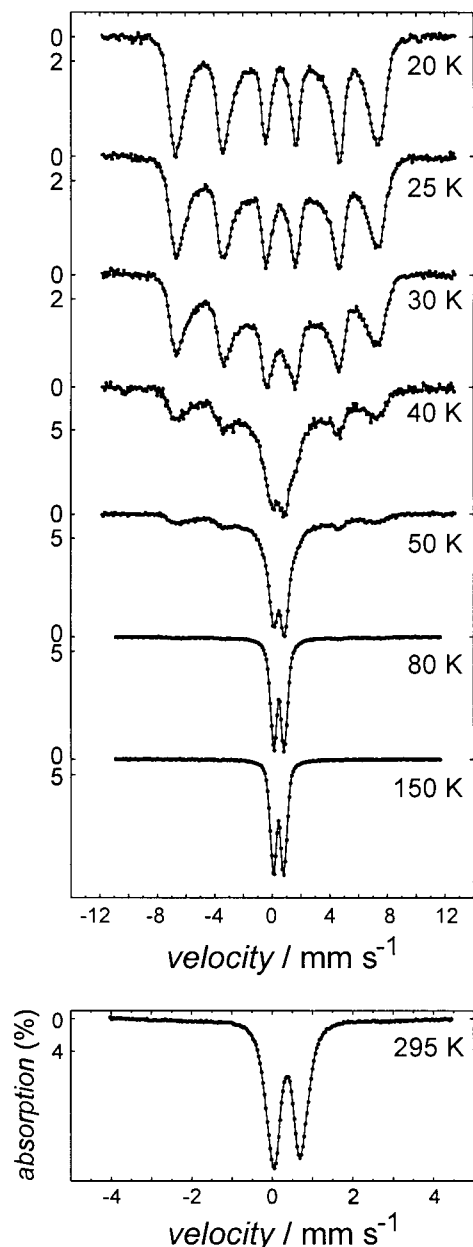


Figure 7. Temperature-dependent Mössbauer spectra of a sample aged for 21 days. The room-temperature spectrum was recorded under magic angle conditions, too.

lapsed components are seen simultaneously, the broadening of the magnetically split components decreases, indicating a transition from a thermally blocked state to a superparamagnetic state. This transition may be somewhat influenced by interparticle interactions and possibly a distribution of Néel temperatures near the transition region. The latter is likely for a poorly defined noncrystalline structure.

In summary, Mössbauer spectroscopy indicates an increase of the effective volume of the magnetic domains with aging time. For all aging times, the local structure appears to be more strongly distorted than those in the majority of the bulk reference materials. The observed value of the quadrupole shift indicates goethite as the most likely candidate model structure among the commonly known bulk oxyhydroxides.

To probe the structural changes further, we have employed EXAFS, which helps to elucidate the local

Table 1. Fit Results Obtained from EXAFS Analysis of the First Coordination Shell of Fe K Edge Data^a

aging time (days)	R (Å)	CN	ΔE (eV)	$\sigma \times 10^2$ (Å ²)	$C_3 \times 10^3$ (Å ³)	$C_4 \times 10^4$ (Å ⁴)
1	2.06	6.9	1.2	1.64	1.62	3.28
21	2.04	5.0	0.0	0.42	1.22	1.71

^a σ denotes the Debye–Waller factor, C_3 and C_4 the higher order cumulants, and CN the coordination number. S_0^2 was fixed to 0.7. Fe–O distances R are accurate to ± 0.02 Å.

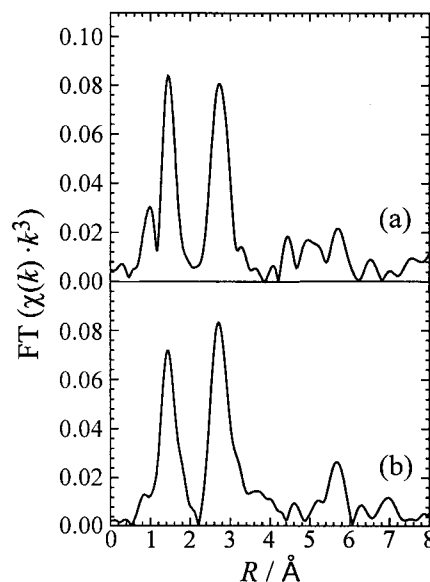


Figure 8. FTs of the Fe K edge EXAFS data (77 K) for samples aged for (a) 1 day and (b) 21 days. Note that the R values are not corrected for phase shifts.

structure around the Fe ions. Measurements on the Fe K edge reveal information of Fe–O and next-nearest Fe–Fe distances and coordination numbers (Table 1). Typical Fourier transforms (FTs) of EXAFS data recorded at 77 K are depicted in Figure 8. Here, the first peak (around 1.5 Å) corresponds to backscattering from the oxygen atoms around the iron ions, whereas the second and third peak (between 2.2 and 4.2 Å) are due to backscattering from the iron ions constituting the next-nearest coordination shells. For shortly aged composites (i.e., 1 or 2 days), no third peak in the FTs attributable to corner-sharing octahedra can be detected. This also holds when the starting Fe(III) solution is more diluted, that is, at higher pH values. Compared to the shortly aged composites, the peaks corresponding to contributions stemming from higher coordination shells (i.e., Fe–Fe distances) become broader and gain in intensity for the materials with increasing aging time. Quantitatively, EXAFS analysis (Figure 9) clearly reveals both an increase in the average coordination number for the second shell and an additional contribution of a third shell arising newly for samples with longer aging times. With prolonged aging treatment, the coordination number of the second shell increases from 1.6 to 2.0 and, for the third shell, from 0 to 2.3 (Table 2).

Possible structural models for the layers in these mesostructured composites are the bulk iron oxyhydroxides, more specifically, goethite (α -FeOOH), akaganeite (β -FeOOH), and lepidocrocite (γ -FeOOH). In the structure of lepidocrocite, octahedra are interconnected

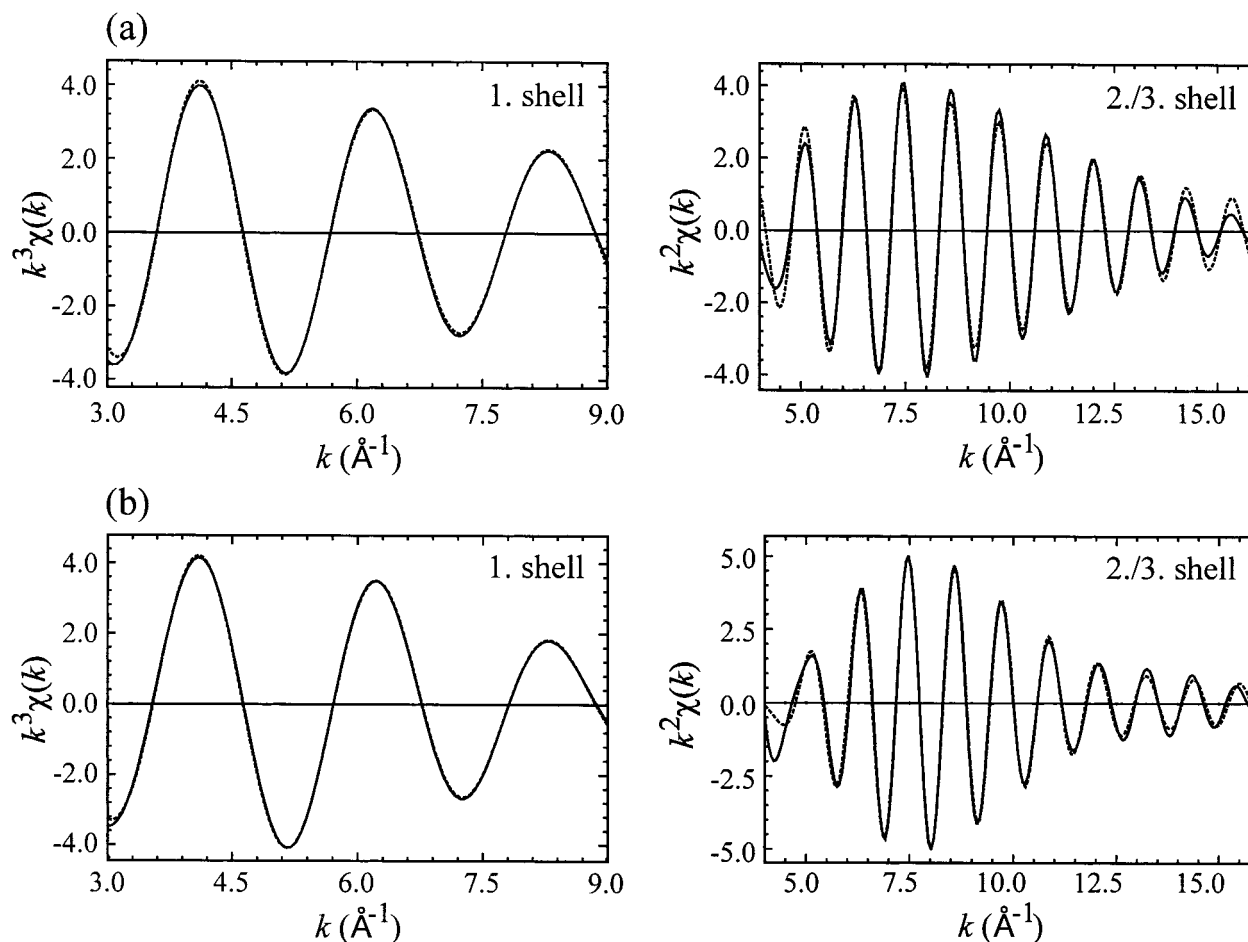


Figure 9. Fit of the Fe K edge data (77 K) for the first and second/third coordination shell around the iron ions in the samples aged for (a) 1 and (b) 21 days.

Table 2. Fit Results Obtained from EXAFS Analysis of the Second and Third Coordination Shell of Fe K Edge Data^a

aging time (days)	second shell				third shell			
	R (\AA)	CN	ΔE (eV)	$\sigma \times 10^3$ (\AA^2)	R (\AA)	CN	ΔE (eV)	$\sigma \times 10^3$ (\AA^2)
1	1.6	3.05	0.6	1.6				
21	2.0	3.02	-4.1	3.05	3.4	2.3	-4.1	7.0

^a σ denotes the Debye–Waller factor and CN the coordination number. S_0^2 was fixed to 0.7. Fe–Fe distances R are accurate to $\pm 0.02 \text{ \AA}$.

mainly via common edges whereas there are fewer corner-links between the octahedra (the exact ratio is 6:2). Lepidocrocite can thus be considered as a good structural model for samples aged for a short time, which do not show the third coordination shell typical of corner-linking. Longer aging times lead to increased linking of octahedra via corners, thus explaining the growth of single magnetic domains in the inorganic part indicated by an increase in the T_p value in the magnetic measurements. This local structure resembles that of bulk goethite/akaganéite with a lower ratio of edge-versus corner-linking. The slight increase in the inter-layer spacing with time occurs on the same time scale as the internal cross-linking within the inorganic part and may reflect the response of the surfactant packing to the restructuring of the iron oxyhydroxide layers.

Conclusion

It has been shown that very mild time-dependent restructuring processes of iron oxyhydroxide–surfactant composites precipitated from diluted Fe(III) solution by the addition of a solution of $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$ can be used to alter and fine-tune both the local structure of the inorganic part of the composites and their magnetic properties. Although the inorganic part of the composites is not crystalline, EXAFS analysis and Mössbauer spectra show that local structures within this part are similar in structure to that of known iron oxyhydroxides. The results show that mild preparative methods can be used to change the physicochemical properties of mesostructured materials such as local ordering and magnetic blocking temperatures.

Acknowledgment. This work was supported by the Jubiläumsfonds der Österreichischen Nationalbank (Grant 7110) and the Fonds der Chemischen Industrie. One of us (B.P.) acknowledges the Freistaat Bayern for a Ph.D. scholarship. Further, we would like to thank the HASYLAB at DESY in Hamburg (Germany) for the possibility to perform X-ray absorption measurements and H. Schultz (Ludwig-Maximilians-Universität Munich) for carrying out elemental analysis.

CM9912122