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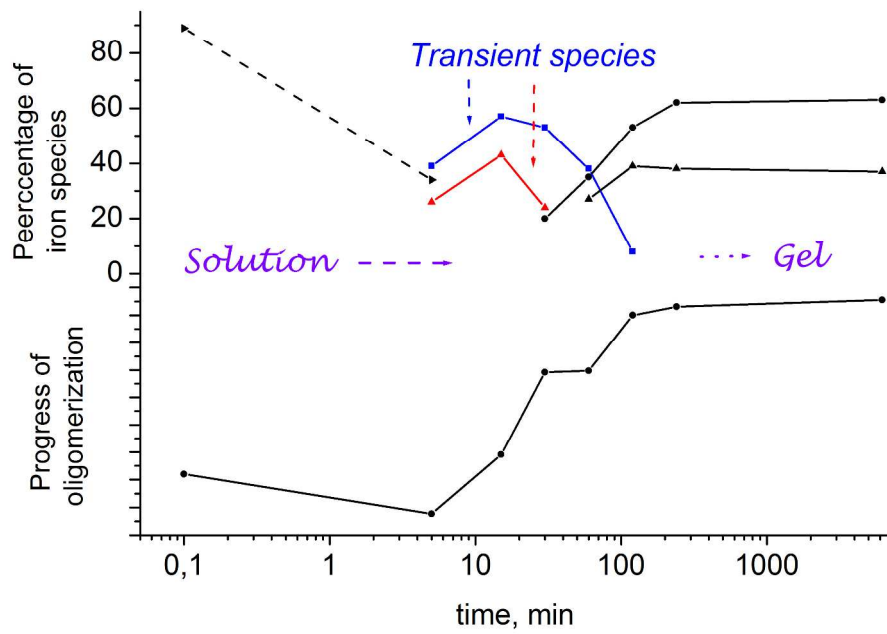


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ARTICLE

Iron oxyhydroxide aerogels and xerogels by controlled hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in organic solvents: stages of formation

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Iron oxyhydroxide aerogels and xerogels were prepared by controlled hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in organic solvents by using limited amount of water or consuming solely water molecules available from the crystals. Ethanol, ethylene glycol, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMFA) solvents were used, the hydrolysis was promoted with epichlorohydrin proton scavenger. High surface area aerogels were prepared by supercritical CO_2 extraction of solvents, surface area and pore distribution measurements were performed on them. Aerogel and xerogel samples were characterized by XRD, Mössbauer spectroscopy and HRTEM methods. The process of hydrolysis was followed by recording Mössbauer spectra of frozen reaction mixtures. Stepwise progress and appearance of transient components were detected in DMSO and DMFA solvents. Aerogel samples exhibit asymmetric spectra with low probability of Mössbauer effect in their as synthesized state. In contrast, frozen reaction mixtures, gels, dry xerogels and compressed aerogels display symmetric spectra with high probability of the Mössbauer resonance. XRD proves the dominant presence of 2-line ferrihydrite. HRTEM studies reveal 4 – 8 nm typical particle sizes with 0.21 – 1.0 nm characteristic lattice distances. Different types of coordination environments are distinguished for iron in the formed ferrihydrite nanoparticles due to structural features and imperfections.

Introduction

Syntheses and application of mesoporous transition metal oxides have attracted enhanced interest recently¹. Among these, preparation of mesoporous iron oxide is also subject of various studies. It can be synthesized e.g. by hydrolysis of ethoxy-iron^{2,3} or by sol-gel technique in inverse micelles¹. Aerogels attract particular interest since they exhibit specific properties, e.g. their moderate stiffness is combined with very high specific surface area and low density^{4,5}. They can be used as substances with special magnetic properties⁶⁻⁸, as catalysts⁹⁻¹⁰ or as precursors of specific reagents ($\text{Al}/\text{Fe}_2\text{O}_3$)¹¹ or as heat insulators⁵. Furthermore, oxyhydroxide gels can also be used for water remediation¹². Iron oxide and –oxyhydroxide xero- and aerogels have already been successfully synthesized in various laboratories by controlled hydrolysis. In a version of these processes only a limited amount of water is used. For instance, even the stoichiometric amount of crystalline water in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ might be sufficient. Ethanol (ET), ethylene glycol (EGLY), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMFA) are

often used. They have different solvation characteristics. Namely, glycol is chelating, both DMSO and DMFA are donor aprotic solvents, the latter has more basic character. Each of them may form stable complexes with iron or iron chloride as well¹³⁻¹⁸. Mixtures of water with organic solvents have also been tested for preparation of xero- and aerogels.

In this procedure, an important condition is the control of hydrolysis by addition of 1,2-epoxide, e.g. propylene oxide, which may eliminate the proton formed in the first step of hydrolysis of the hexaqua iron complex¹⁹. Propylene oxide can be replaced with epichlorohydrin for more convenient handling^{6,7,11,20}. Successful application of 1,3 epoxides (e.g. trimethylene oxide) has also been reported²¹. The syntheses of xero- and aerogels are similar, except the very final step, the removal of solvents after gelation. For obtaining aerogels, supercritical CO_2 extraction should be applied^{8,22} otherwise dense xerogels form.

Early stages of hydrolysis in aqueous media are well-known in detail²³. First dimers are formed with hydroxo bridges in aqueous media (olation). A detailed study reports on existence of six types of dimeric species²⁴. In non-aqueous media oxo bridges may form (oxolation), then network of condensed oxyhydroxide develops. Formation of complexes with solvent molecules may retard hydrolysis and enhance condensation^{20,25}.

Products of hydrolysis can be identified from HRTEM studies by determining the values of lattice constants in the formed small particles. Formation of different oxyhydroxides (ferrihydrite²⁶,

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goethite, α -FeO(OH), akageneite, β -FeO(OH), lepidocrocite, γ -FeO(OH)²⁷ can be observed depending on the conditions.

Another frequently applied method is the X-ray diffractometry (XRD). Even the most poorly ordered structure, ferrihydrite can be also analysed^{8,20,22}. Depending on the extent of the ordering, “2-line” and “6-line” ferrihydrites are distinguished²⁷. More recent high energy X-ray scattering studies reveal that the observed signal depends on the size of the scattering domains²⁶.

Mössbauer spectroscopy is also a convenient tool for studying iron compounds. This technique is used primarily to characterize solid substances. Various oxides, oxyhydroxides have been investigated in detail with the method²⁸. Structure of crystalline molecules e.g. FeCl₃.6H₂O is well-known from XRD studies²⁹, it can be compared with corresponding Mössbauer spectra³⁰. Stable solid molecular complexes of iron formed with DMSO, DMFA have already been prepared and characterized with this technique, as well^{14,15}. Very early stages of hydrolysis of iron were also followed by careful separation of products with dialysis and measurements after freeze-drying in solid state. Monomeric, dimeric and polymeric species were identified in characteristic spectra³¹. The process of hydrolysis can also be studied directly in frozen solutions, as described in detail in aqueous media³². Solvation in different aprotic solvents was also followed^{12,33}. Xero- and aerogel end products were also characterized in several instances by the technique^{7,10,20}, in particular details in³⁴. Further on, the probability of the Mössbauer effect (f-factor) can also be extracted from the spectra and its value may supply additional information on the bonding conditions of various species^{29,35}. Namely, the logarithm of the f-factor is inversely proportional to the product of the effective mass and the vibration frequency of the γ -emitting species³⁶. Significant differences have been observed in the probability of the Mössbauer effect for xero- and aerogels, and a parameter, the Mössbauer effective thickness has also been introduced to describe the efficiency of the absorption/emission process in the lattice³⁴. Although usually one type of iron site exists in the oxyhydroxides (exception β -FeOOH)²⁴ superposition of three components was necessary for the acceptable description of spectra of xero- and aerogels³⁴.

It can be noticed however that the first stages of hydrolysis of iron in non-aqueous, organic media have not been studied in detail yet. Therefore the aim of the present communication is laid primarily on this aspect. First stages of hydrolysis are supposed to proceed in the same way for both the aerogels and xerogels prior to completion of gel formation. Thus, studies both on aerogels and on xerogels are described in our present report.

First, preparation and characterization of aerogels and xerogels are described. Hydrolysis of FeCl₃.6H₂O in DMSO/water and ET/water solutions, and in anhydrous DMSO, DMFA and EGLY solvents was performed by using epichlorohydrin as proton scavenger. Products are characterized with adsorption measurements, XRD, HRTEM and Mössbauer methods. Main emphasis is laid on the study of the first stages of gel formation by Mössbauer spectroscopy of frozen reaction mixtures.

Experimental

Processes and samples

Hydrolysis of FeCl₃.6H₂O was performed in two types of experiments, either in DMSO-water and in ethanol-water mixtures or without additional water, in pure DMSO, DMFA, and EGLY solvents. Epichlorohydrin was used as a proton scavenger. The used chemicals were obtained from SigmaAldrich. First, iron chloride was completely dissolved, then epichlorohydrin (C₃H₅OCl) was added to the clear solution in portions.

The molar ratio of components in the DMSO-water experiments was Fe : DMSO : H₂O : C₃H₅OCl = 1 : 30 : 36 : 8.3 . Aerogels were also prepared from these samples by supercritical extraction of solvents. First the DMSO and water media was exchanged for methanol solvent, then methanol was exchanged gradually to dry acetone. The sample was placed to an autoclave, then liquid CO₂ was introduced at ca. 50 bar pressure. The acetone solvent was removed as a separate phase. Then the temperature was increased to 80 °C, where CO₂ transforms to supercritical state. After 3 h the CO₂ was slowly decompressed and cooled, thereby dry monolithic aerogel was obtained.

In the second type of experiments (under anhydrous conditions) 2.9 mmol of FeCl₃.6H₂O was dissolved in 6 ml of solvent (DMSO or DMFA or EGLY) and after dissolution of the salt 1.6 ml of epichlorohydrin was dropwise added with stirring. To follow the progress of hydrolysis ca. 1 ml samples were taken after different elapsed time intervals, even before gelation has been completed. These samples were immediately frozen by immersion to liquid nitrogen. Gelation has taken place in the remaining portions of the mixtures after 4 – 6 hours. These gels were stored for several days at room temperature. Primary solvents were removed by repeated extraction with ethanol, then xerogels formed upon evaporation of the ethanol at room temperature. The drying process resulted in ca. 50-fold decrease in the volume of the original gel.

In specification of samples A and X prefixes are used for aerogels and xerogels, respectively. The next label identifies the solvent media. For example A-(DMSO+H₂O) denotes an aerogel sample prepared in DMSO+water mixture, or X-DMFA stands for a xerogel prepared in non-aqueous DMFA media.

Characterization of samples

Specific surface area/BET and pore size distribution measurements were performed on aerogel samples with a Quantachrome Nova 2200e surface area and porosity analyzer using nitrogen gas adsorbate (Quantachrome Instruments, Boynton Beach, FL, USA) at 77 K temperature. Prior the measurement samples were outgassed at 50 °C in vacuum for 3 hours. In addition, sample A-(DMSO+H₂O) was outgassed at higher temperatures (150 and 250 °C) as well.

X-ray powder diffraction patterns were recorded by a Philips PW 1810/3710 diffractometer with Bragg-Brentano parafocusing geometry applying monochromatized CuK α (λ = 0.15418 nm)

radiation (40 kV, 35 mA) and proportional counter. Counts were collected at 0.02 degree two theta steps for 1 sec.

Combustion analysis was applied to determine the elemental composition of some aerogel samples with a Vario MICRO Cube CHNS analyser (Elementar Analysensysteme GmbH, Hanau, Germany). The samples are incinerated at temperatures exceeding 1000 °C, the products of oxidation are analysed.

Scanning electron microscopic (SEM) images were recorded on a Hitachi S-4300 instrument (Hitachi Ltd., Tokyo, Japan) equipped with a Bruker energy dispersive X-ray spectroscope (Bruker Corporation, Billerica, MA, USA). The monolithic aerogel samples of approximately 2 – 4 mm sizes were embedded in a low melting point alloy (Wood's metal) to decrease the possibility of accumulation of electric charge in the highly insulating aerogel samples. All fresh fracture surfaces were covered by a sputtered gold conductive layer. Typically, a 10 – 15 kV accelerating voltage was used for taking high resolution pictures.

TEM and HRTEM measurements for aero- and xerogel samples were performed by using either a Philips CM20, 200 kV conventional Transmission Electron Microscope (TEM, point resolution: 0.24 nm) or a JEOL 3010 300kV High Resolution TEM (HRTEM – point resolution: 0.17 nm) equipped with an Electron Energy Loss Spectrometer (EELS) and a GATAN Tridiem Image Filter (GIF). Selected Area Electron Diffraction (SAED) patterns could be obtained with the former instrument, whereas characteristic lattice distance values were determined from certain good quality images by Fast Fourier Transformation (FFT) process in the latter apparatus. Qualitative analysis for chlorine was also performed with EELS elemental mapping.

Mössbauer spectra were obtained both on the frozen solutions and on the final products as well. Frozen solutions were measured in ca. 1 ml volumes (ca. 2.5 mm thick disks with 2 cm diameter) at 77 K. In order to prove that primarily iron oxyhydroxides are formed one aerogel sample was evacuated at 260 °C in the in situ Mössbauer cell. Both the 77 K measurements of the frozen samples and the mentioned evacuation were performed in the in situ cell described in Ref³⁷. As prepared dry aerogel samples were also measured. In some instances they were compressed to obtain better quality spectra (30 MPa cm²). The used spectrometer is a KFKI equipment, the drive was operating in constant acceleration mode. For recording these spectra 0.5 GBq ⁵⁷Co/Rh source was used. Spectra were decomposed to Lorentzian lines, no constraints were used, the accuracy of the positional data is c.a. ± 0.03 mm/s. The isomer shift values are related to alpha-iron. Temperature dependence of the shape of Mössbauer spectra was also investigated on a partly dried sample (ca. 50 wt % glycol solvent remained). This series was recorded in another apparatus, in a vertical cryostat with a WISSEL drive operating in sinusoidal mode³⁸. There is no temperature shift in the observed isomer shift value in the latter case since both the sample and the Mössbauer source are at the same temperature (in contrast to the previous KFKI assembly).

Results

Aerogel samples

Aerogel samples were prepared first. Their density was c.a. 0.1 g cm⁻³ after extraction with the supercritical CO₂. A typical photograph of the A-(ET+H₂O) sample is shown in Fig. 1.



Fig. 1 Photograph of a typical aerogel sample A-(ET+H₂O) compared to a cm scale

Adsorption measurements

Sorption isotherms were measured on the A-(DMSO+H₂O) and A-DMSO samples. The former sample was outgassed at different temperatures in order to study the stability and the extent of possible textural changes upon moderate heat treatments. For illustration, adsorption and desorption isotherms of the sample outgassed at 50 and 250 °C are shown in Fig. 2.

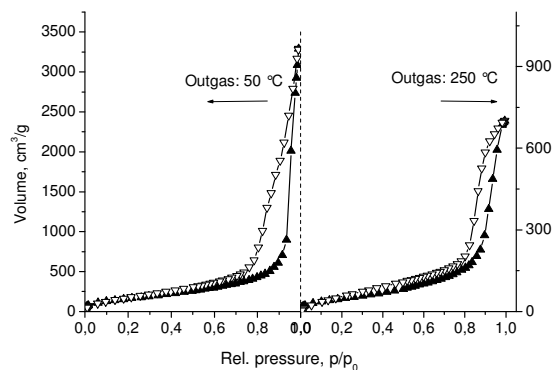


Fig. 2 Adsorption-desorption isotherms for the A-(DMSO+H₂O) sample outgassed at 50 °C (left) and 250 °C (right). Adsorption: ▲, desorption: ▽.

The obtained isotherms are of type II (IUPAC classification) with H3 type hysteresis loop, typical for oxides with aggregated particles. BET surface area, principal constants of BET equation³⁹, pore volume values, and pore size distributions were also determined (Table 1).

Table 1 Basic sorption data obtained on aerogel samples (T_{out} : temperature of outgassing, Sp. area: specific surface area, B Eq slope and B Eq C const: Slope and C constant of BET equation, respectively, Por. vol.: pore volume, Max. diam, location of maximum in the pore size diameter distribution, calculated from the desorption branch)

Sample	T_{out} °C	Sp. area. m^2g^{-1}	B Eq Slope	B Eq C	Por. vol. cm^3g^{-1}	Max. diam. nm
DMSO+H ₂ O	50	615	5.52	39.0	5.33	12.8
DMSO+H ₂ O	150	471	7.20	39.3	3.9	16.8
DMSO+H ₂ O-1	250	179	18.6	25.8	1.12	14.5
DMSO+H ₂ O-2	250	191	17.45	24.2	1.17	14.6
DMSO	50	671	5.05	38.1	3.7	17.0

The obtained specific surface area and pore volume values are close to those reported in Ref⁸, whereas the pore size distributions in our samples are more narrow.

Comparison of data obtained on sample A-(DMSO+H₂O) outgassed at different temperatures reveal that significant textural changes take place in the aerogel above 150 °C. In spite of the textural changes the high surface area and the maximum at ca. 15 nm pore diameter is preserved after 250 °C treatment, i.e. basic characteristics of aerogels are sustained.

X-ray diffraction patterns were recorded on A-(DMSO+H₂O) sample after drying and after a further evacuation performed at 260 °C (Figs. 3a and 3b). The diffractograms exhibit broadened lines characteristic to small particles with sizes of domains of coherent reflection with 3 - 5 nm. The two broad peaks are characteristic of the 2-line ferrihydrite (Fhyd2).

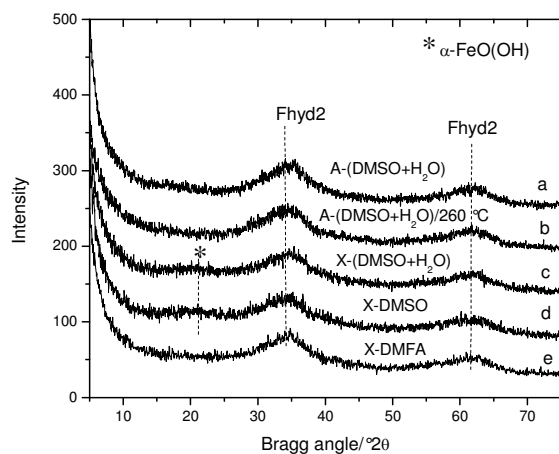


Fig. 3 X-ray diffractograms of various aerogel and xerogel samples. For comparison locations of the peaks of 2-line ferrihydrite and α -FeOOH (goethite) are also marked.

SEM, TEM and HRTEM measurements revealed also the porous structure of the assembled iron oxyhydroxide nanoparticles. For illustration TEM micrograph of the A-(DMSO+H₂O) sample and SEM and HRTEM images of A-DMSO sample are shown in Figs. 4 and 5 respectively.

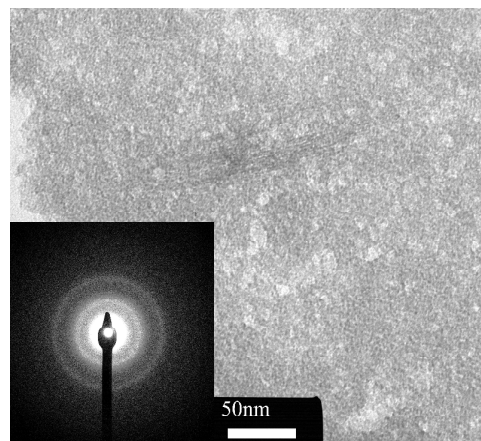


Fig. 4 TEM micrograph of the A-(DMSO+H₂O) sample with SAED insert of the corresponding region

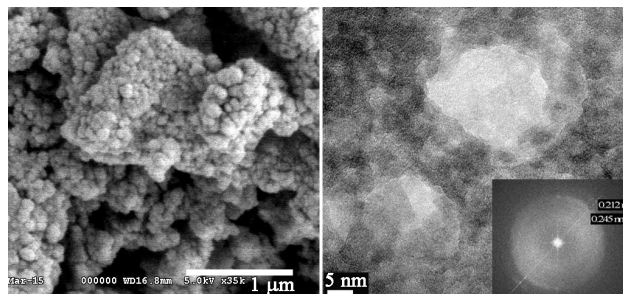


Fig. 5 SEM (left) and HRTEM (right) images of A-DMSO sample, the latter with FFT insert, displaying 0.212 and 0.245 nm characteristic lattice distance values.

The HRTEM image reveals that the aerogel is assembled from nanocrystallites of ca. 5 nm diameter, with 0.212 and 0.245 nm characteristic lattice distance values.

Further, the A-(ET+water) sample was also characterized by SEM and HRTEM, similar lattice constant values can be extracted by FFT analysis (0.206, 0.251 and 0.297 nm) from these images as well.

Mössbauer spectroscopy can be applied to follow the whole process of dissolution, gelation, drying and even effects of further heat treatments can be studied. Spectra corresponding to stages of preparation of A-(DMSO+H₂O) sample are presented in Fig. 6.

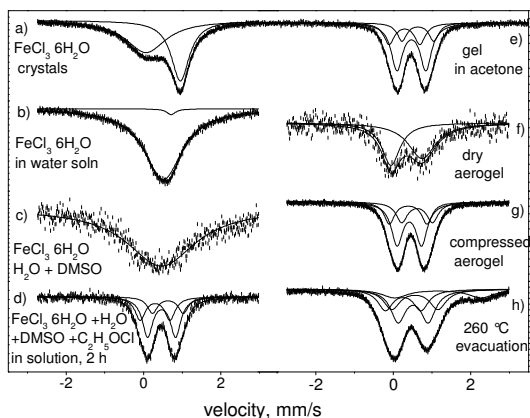


Fig. 6 Stages of aerogel formation in DMSO-water media shown in 77 K Mössbauer spectra. Crystalline solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (top left, a), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution (b), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{water} + \text{DMSO}$ (c), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{water} + \text{DMSO} + \text{epichlorohydrin}$, 2 h after mixing, still in liquid state (d), after gelation, washed in acetone (top right, e), dry aerogel after supercritical CO_2 extraction (f), after compressing the aerogel (g), and after evacuation at 260°C (h).

Spectra, shown in the left side of Fig. 6 were obtained on frozen samples containing similar amounts of iron. Surprisingly, despite of the solid (frozen) state the probability of Mössbauer effect decreased significantly in the DMSO + water mixture. It is also worth noticing that in the very early stage, even prior to the gel formation almost the same parameters can be obtained from the Mössbauer spectrum (Fig. 6d) than after gelation (Fig. 6e), or after extraction with supercritical CO_2 (Fig. 6g). After gelation the probability of Mössbauer effect increased again.

Good quality fits can be obtained by spectral decomposition to three doublets. (Table 2). It should be noted that the parameters are rather similar either gels or solid (dried and compressed) aerogels are considered. (Data extracted from spectra of further samples are also shown in Table 2 for comparison.)

The combination of high porosity with loose structure in aerogels can also be demonstrated by comparing the Mössbauer spectra of the original light aerogels with those obtained after compression of samples. Corresponding 300 and 77 K spectra for A-DMSO sample are shown in Fig. 7. It is clearly seen that the response factor dramatically increases by the compression (100 MPa). More surprisingly not only the probability of the effect but the shape of spectra are also influenced. The phenomenon is general, it can be observed on all the studied aerogel samples (Table 3).

Table 2 Data extracted from 77 K Mössbauer spectra (δ : isomer shift, Δ : quadrupole splitting, RI: relative spectral contribution)

Sample media/condition	Component	δ mm/s	Δ mm/s	RI %
A-(DMSO+H ₂ O)	Fe^{3+} (1)	0.30	0.79	30
gel in acetone	Fe^{3+} (2)	0.47	0.74	47
frozen	Fe^{3+} (3)	0.63	0.81	24
A-(DMSO+H ₂ O)	Fe^{3+} (1)	0.28	0.80	22
dry aerogel	Fe^{3+} (2)	0.46	0.74	54
compressed	Fe^{3+} (3)	0.64	0.80	24
A-(ET+H ₂ O)	Fe^{3+} (1)	0.21	0.96	3
dry aerogel	Fe^{3+} (2-1)	0.47	0.61	55
compressed	Fe^{3+} (2-2)	0.47	0.96	42
X-(DMSO+H ₂ O)	Fe^{3+} (1)	0.30	0.77	32
reaction mixture	Fe^{3+} (2)	0.47	0.72	45
frozen gel	Fe^{3+} (3)	0.63	0.79	22
X-(DMSO+H ₂ O)	Fe^{3+} (1)	0.26	0.77	36
dried gel	Fe^{3+} (2)	0.46	0.75	29
	Fe^{3+} (3)	0.65	0.80	35
X-DMSO	Fe^{3+} (1)	0.29	0.82	30
dried gel	Fe^{3+} (2)	0.52	0.73	58
	Fe^{3+} (3)	0.56	1.11	12
X-EGLY	Fe^{3+} (1)	0.31	0.83	23
reaction mixture	Fe^{3+} (2)	0.47	0.77	49
frozen gel	Fe^{3+} (3)	0.64	0.81	28
X-EGLY	Fe^{3+} (1)	0.28	0.85	5
dried gel	Fe^{3+} (2-1)	0.49	0.58	43
	Fe^{3+} (2-2)	0.50	0.94	52
X-DMFA	Fe^{3+} (2-1)	0.46	0.60	71
reaction mixture	Fe^{3+} (2-2)	0.46	0.96	26
frozen gel	Fe^{3+} (2-3)	0.47	1.32	12
X-DMFA	Fe^{3+} (1)	0.26	0.79	24
dried gel	Fe^{3+} (2)	0.50	0.67	55
	Fe^{3+} (3)	0.53	1.03	20

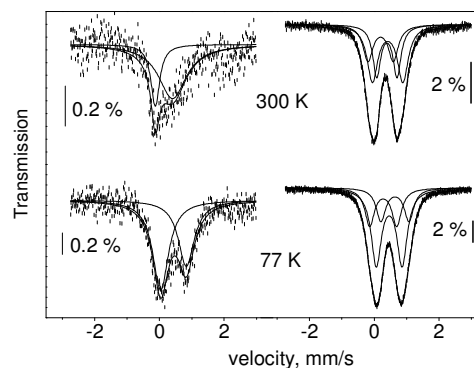


Fig. 7. Comparison of 300 and 77 K Mössbauer spectra of the aerogel sample prepared in anhydrous DMSO media in as received aerogel form (left) and after compression (right)

Table 3. Comparison of the relative spectral area values of pristine aerogel samples and after compression extracted from 77 and 300 K spectra. ($R_{77/300}$ is the ratio of the 77 and 300 K values)

Sample	Temp.	aerogel	$R_{77/300}$	compr.	$R_{77/300}$
A-(ET+H ₂ O)	77 K	0.149		2.478	
	300 K	0.120	1.243	0.728	3.404
A-(DMSO+H ₂ O)	77 K	0.187		2.391	
	300 K	0.068	2.764	1.131	2.113
A-DMSO	77 K	0.183		1.722	
	300 K	0.078	2.347	0.650	2.650

Thermal treatments were also carried out on the aerogel samples in order to study the stability and eventual transformations of oxyhydroxides.

Mild thermal treatment, namely evacuation at 260 °C was performed to distinguish whether oxide or oxyhydroxides are formed during gelation and drying. Sorption measurements on A-(DMSO+H₂O) sample reveal a significant decrease in the specific surface area and pore volume values (Table 1). However, the structure has not been modified significantly, X-ray diffractograms for the same non-heated and heated samples are similar (Figs. 3a and 3b). Evacuation or moderate heating of oxyhydroxides in inert atmospheres may result in formation of mixed Fe²⁺/Fe³⁺ oxides (e.g. magnetite). Indeed, Fe²⁺ appears in the corresponding Mössbauer spectrum in accordance with the expectation (Fig. 6h). Furthermore, this sample can be magnetized with a permanent magnet, too.

More severe combustion treatment was also applied to access information on the approximate composition of samples, high chlorine contents were obtained (Fe : Cl ≈ 1 : 0.3, Table 4).

Table 4. Approximate nominal molar compositions of aerogels determined from combustion measurements

Sample/solvent	Fe ₂ O ₃	H ₂ O	DMSO	C ₃ H ₅ OCl
A-(DMSO+H ₂ O) (1)	1	1.24	0.006	0.53
A-(DMSO+H ₂ O) (2)	1	1.0	0.017	0.72
A-DMSO	1	1.0	0.031	0.61
A-(ET+H ₂ O)	1	1.5	0.0	0.63

Xerogel samples

Adsorption measurements have not been performed on xerogel samples since they are ca. 50-fold denser than their aerogel counterparts.

X-ray diffractograms were recorded on certain xerogel samples (Fig. 3c-3e). Patterns are similar to those obtained on aerogels. The broad peaks are primarily originated from 3-5 nm 2-line ferrihydrite particles. Presence of goethite in minor amounts can also be detected in samples prepared in DMSO media (Figs. 3c, 3d).

SEM and HRTEM studies provided similar images to those found on aerogel samples. Namely, xerogel samples are composed from small nanoparticles of iron oxyhydroxides of c.a. 5 nm size in average. This indicates that first stages of formation of aerogels and xerogels are similar.

As an illustration, HRTEM images recorded on the X-EGLY sample are presented in Fig. 8. EELS elemental mapping was performed at 200 eV energy loss, characteristic to chlorine. The bright contrast image in bottom right indicates the presence of chlorine in significant amount (in correspondence with data presented in Table 4 for aerogel samples).

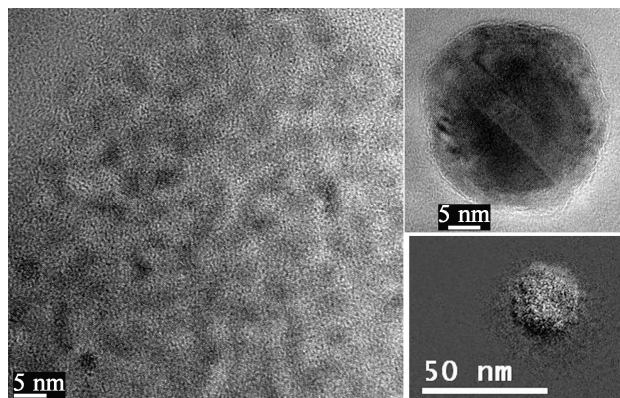


Fig. 8 HRTEM images of the X-EGLY sample. Part of an extended region (left), separate particle (right top), bright contrast chlorine EELS Elemental Map on the same particle (right bottom - note the different magnification on the right side)

Other xerogels were also studied by HRTEM, and corresponding characteristic lattice constant values were obtained. For X-DMFA 0.208, 0.253 and 0.305 nm values were extracted by FFT analysis.

Mössbauer studies on xerogels provided similar δ and Δ values to those obtained on frozen reaction mixtures and on aerogels (see Table 2). The dense structure of the products is reflected in the characteristic high response factors of the dried samples.

Further on, a particular feature, stepwise development of the final structure can be illustrated in the xerogels. Namely, deviation from the expected regular temperature dependence of the probability of the Mössbauer effect can be observed on samples from which the original solvent has not been removed completely. Extraction of glycol with ethanol was incomplete in preparation of a X-GLY sample, c.a. 2-3 glycol molecules per iron atoms were still present after removal of ethanol with drying. On this sample only a weak signal could be detected at room temperature. To clarify further details a series of spectra was collected on this sample in dependence of temperature in the 80 – 300 K region (Fig. 9). Spectra were collected at 80, 120 and 160 K as well (not shown), they exhibit the same shape as the 200 K one. The relative spectral contribution (proportional to the f-factor) can also be calculated and plotted against temperature (Fig. 10).

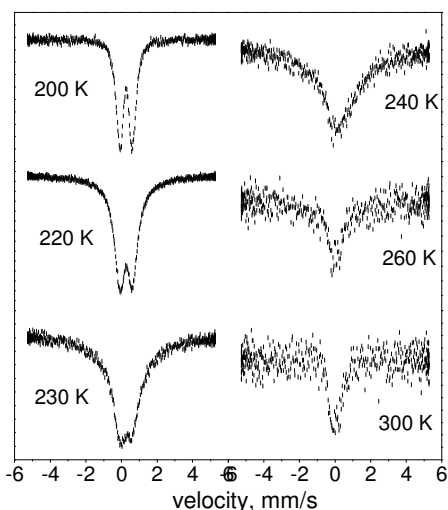


Fig. 9 Temperature dependence of Mössbauer spectra on an X-GLY sample recorded after incomplete extraction with ethanol (containing still ca. 50 wt % glycol)

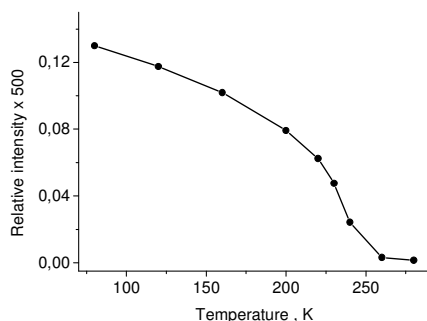


Fig. 10 Temperature dependence of the relative spectral area values of a X-GLY sample after incomplete extraction with ethanol (based on spectra shown in Fig. 9).

The curve exhibits the expected shape of temperature dependence in the 80 – 200 K region which can be described with a single Debye temperature value. In contrast, there is an expressed breakdown at higher temperatures, starting from 220 K.

Kinetics of gel formation

Depending on the solvent media (EGLY, DMSO and DMFA) significant differences are revealed in the early stages of gel formation.

In ethylene glycol formation of the primary oxyhydroxide particles is fast – within 10 minutes their final structure develops. The same data can be extracted from the Mössbauer spectrum of the sample frozen after 10 minutes of mixing of the components and from the spectrum of the final state after washing and drying (see Table 2).

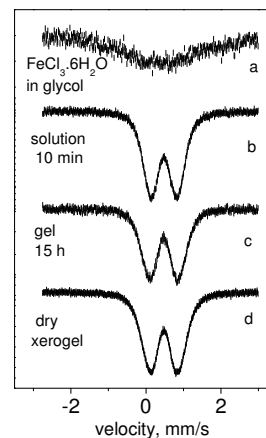


Fig. 11 77 K Mössbauer spectra recorded during the stages of formation of X-GLY sample. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ethylene glycol, frozen (a), reaction mixture, 10 minutes after addition of epichlorohydrin (b), in gel form (c) and after drying, as X-GLY (d)

The hydrolysis is slower in DMSO, Mössbauer spectra of intermediate stages can be intercepted. The main component in the spectrum of the reaction mixture recorded after 5 minutes of mixing exhibits high quadrupole splitting ($\Delta \sim 1.7$ mm/s). This value exceeds significantly the $0.6 < \Delta < 0.8$ mm/s values, characteristic for the stabilized products. These components became dominant only after ca. 30 minutes of mixing the components in DMSO (Fig. 12 and Table 5).

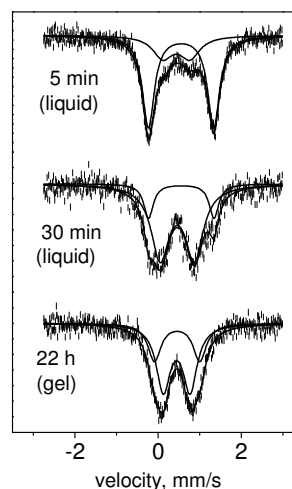


Fig. 12 77 K Mössbauer spectra obtained at different intervals after addition of Fig. epichlorohydrin to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + DMSO solution.

Table 5 Mössbauer parameters extracted from the fits of 77 K spectra in stages of formation of X-DMSO gel (δ : isomer shift, Δ : quadrupole splitting, RI: relative spectral contribution)

Time	Comp	δ mm/s	Δ mm/s	RI %
5 min	Fe ³⁺ (2)	0.44	0.65	28
	Fe ³⁺ (tr)*	0.55	1.57	72
30 min	Fe ³⁺ (2)	0.46	0.82	80
	Fe ³⁺ (tr)*	0.56	1.57	20
22 h	Fe ³⁺ (2-1)	0.45	0.64	65
	Fe ³⁺ (2-2)	0.46	1.09	35

* Fe³⁺(tr) stands for transient species

In DMFA media the process of hydrolysis proceeds apparently more slowly as compared to DMSO. The stages are more distinct, as could be deduced from corresponding 77 K Mössbauer spectra shown in Fig. 13 (with corresponding data in Table 6).

The first spectrum was recorded prior to the addition of epichlorohydrin (top left). The process of gelation commences ca. within 4 h. In correspondence, all the spectra are obtained on frozen liquid samples, except the very last spectrum, which was recorded on frozen gel (Fig. 13, right bottom).

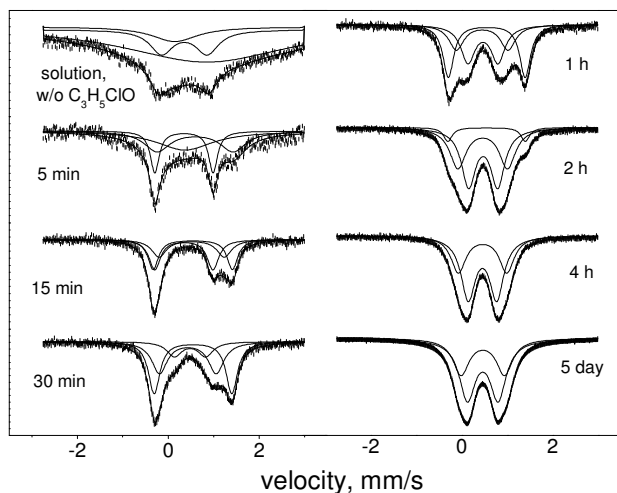


Fig. 13 Mössbauer spectra displaying stages of formation of X-DMFA gel, after different intervals of addition of epichlorohydrin

Appearance and relative contributions of various components can also be plotted in dependence of time (Fig. 14). It is seen that Fe³⁺(singlet), Fe³⁺(t-1) and Fe³⁺(t-2) are transient species, they are transformed to the stable Fe³⁺(2-1) and Fe³⁺(2-2).

Table 6 Data obtained from decomposition of 77 K Mössbauer spectra of frozen FeCl₃.6H₂O + DMFA + C₃H₅OCl, solutions recorded after different intervals after addition of epichlorohydrin (δ , isomer shift, Δ quadrupole splitting, FWHM, line width, RI, relative spectral contribution)

	δ mm/s	Δ mm/s	FWHM mm/s	RI %
DMFA solution				
Fe ³⁺ (singlet)	0.31	-	2.71	89
Fe ³⁺ (soln1)	0.36	0.64	0.22	3
Fe ³⁺ (soln2)	0.36	1.18	0.30	8
5 min				
Fe ³⁺ (singl)	0.35	-	1.51	34
Fe ³⁺ (t-1)*	0.35	1.28	0.24	26
Fe ³⁺ (t-2)*	0.60	1.66	0.77	39
15 min				
Fe ³⁺ (t-1)	0.34	1.31	0.32	43
Fe ³⁺ (t-2)	0.55	1.65	0.36	57
30 min				
Fe ³⁺ (t-1)	0.36	1.39	0.31	23
Fe ³⁺ (t-2)	0.57	1.64	0.34	53
Fe ³⁺ (3)	0.46	0.76	0.44	24
1 h				
Fe ³⁺ (t-2)	0.55	1.69	0.29	38
Fe ³⁺ (2-1)	0.46	0.66	0.38	35
Fe ³⁺ (2-2)	0.45	1.14	0.42	27
2 h				
Fe ³⁺ (t-2)	0.54	1.70	0.23	8
Fe ³⁺ (2-1)	0.47	0.64	0.38	53
Fe ³⁺ (2-2)	0.46	1.10	0.42	39
4 h				
Fe ³⁺ (2-1)	0.45	0.63	0.38	62
Fe ³⁺ (2-2)	0.46	1.07	0.40	38
5 day				
Fe ³⁺ (2-1)	0.46	0.63	0.42	63
Fe ³⁺ (2-2)	0.47	1.07	0.42	37

* Fe³⁺(t-1) and Fe³⁺(t-2) stand for the transient components

Further important information can also be extracted from the Mössbauer spectra. Namely, the response factors, i.e. the probabilities of Mössbauer effect are distinctly different in dependence of time (Fig. 15). An expressed (almost five-fold) increase can be revealed in the values of the average relative spectral area. In other words, the sums of response factors for components Fe³⁺(singl), Fe³⁺(t-1) and Fe³⁺(t-2) are significantly smaller than response factors of components Fe³⁺(2-1) and Fe³⁺(2-2) in Table 6 and Fig. 14.

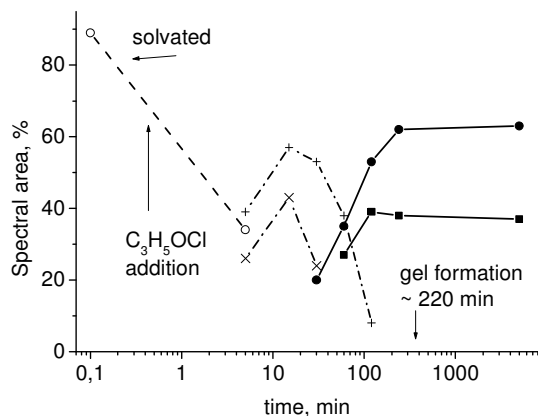


Fig. 14 Kinetics of oligomerisation: proportions of components appearing in the spectra of Fig. 13. - o - $\text{Fe}^{3+}(\text{singl})$, - x - $\text{Fe}^{3+}(\text{t-1})$, - + - $\text{Fe}^{3+}(\text{t-2})$, - • - $\text{Fe}^{3+}(\text{2-1})$, - ■ - $\text{Fe}^{3+}(\text{2-2})$

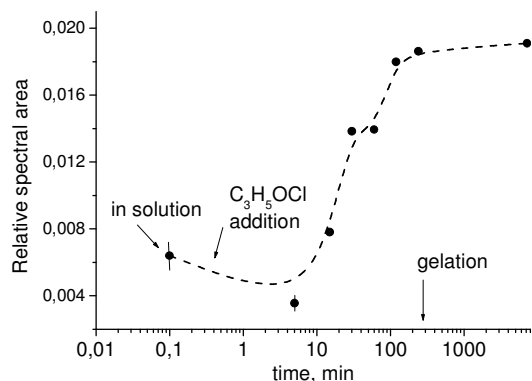


Fig. 15 Time dependence of the average relative spectral area (spectral area related to the “full area”, i.e. intensity of base line multiplied by channel number). Note the logarithmic time scale.

Discussion

Stages of hydrolysis – early products and kinetics

New insights were achieved in the study of the early steps of formation of iron oxyhydroxide gels by using Mössbauer spectroscopy of frozen solutions in organic media. Stages of hydrolysis, replacement of ligands around iron from the initial $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+$ could be followed. In particular, the spectrum of the starting crystalline $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is a characteristic asymmetric doublet, originated both from relaxation and Karyagin-Goldanskii effects³⁰. Dissolution in water results in the destruction of the crystal lattice, the mentioned effects vanish, a single broad line is seen in the spectrum of the frozen aqueous solution. This spectrum is similar to those found in freeze-dried samples and is attributed to monomeric species³¹. A rather good response factor is observed – the structure of frozen water is rigid – hydrogen bridges are stabilizing it (Figs. 6. a and b). In contrast, the probability of the

effect is decreased significantly in the frozen solution at the $\text{FeCl}_3 : \text{DMSO} : \text{H}_2\text{O} = 1 : 30 : 36$ molar ratio, showing that the structure of frozen DMSO + water solution is less rigid than in ice. (Fig 6. c). At the actual molar ratios of components certain exchange of H_2O ligands to DMSO around iron can be expected. The $[\text{FeCl}_2(\text{H}_2\text{O})_{4-x}(\text{DMSO})_x]^+$ \rightarrow $[\text{FeCl}_2(\text{OH})(\text{H}_2\text{O})_{3-x}(\text{DMSO})_x]$ hydrolysis proceeds by addition of epichlorohydrin, since the formed protons are consumed for protonation of epoxy groups. Chloride ions can also be consumed for opening the epoxy bridges in the protonated epichlorohydrin as described in¹⁹. In the further stage olation takes place, di- and oligomers may form, and at the end of the process a network of oxyhydroxide particles is assembled. Hydrolysis and agglomeration are probably fast in water containing media, iron oxyhydroxide agglomerates form but they probably cannot grow to large size as a result of hindered particle motion due to presence of DMSO. The oxyhydroxide particles in the gel are stacked and fixed as is shown in the TEM image of Fig 4.

Kinetics of hydrolysis is significantly slower in non-aqueous media when only six water molecules per iron are available from the starting $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ crystals. Condensation is preferred when complexes can be formed with the solvent molecules compared to fast hydrolysis²⁵. It was even possible to follow the different subsequent stages of hydrolysis in DMFA which is the strongest complexing molecule among the used aprotic solvents. Various stages of the process can be followed in Figs. 13-15. The $[\text{2FeCl}_3(\text{DMFA})_3(\text{H}_2\text{O})_2]$ complex is rather stable^{16,17}. In the solution probably this complex molecule is prevailing. Upon addition of epichlorohydrin the hydrolysis commences. The axial symmetry around iron can be distorted, oligomerization may start. In accordance, transient (5, 15, 30 and 60 min) spectra are dominated with large quadrupole splitting components. It is worth to compare the number and parameters of species shown in Figs. 13 and 14 and listed in Table 6 with those found and identified in a pure aqueous phase. In aqueous phase three early products (with molecular weights less than 500) were identified: monomeric (broad singlet), dimeric (with a characteristic doublet, $\Delta \sim 1.2$ mm/s) and polymeric (doublet, $\Delta \sim 0.6 - 0.8$ mm/s, observed at 300 K)³¹. In our case at hydrolysis in DMFA five components are clearly present, one of them exhibits a rather large quadrupole splitting ($\Delta \sim 1.7$ mm/s – Table 6). The larger number of participating transient components and the appearance of a particular component with large quadrupole splitting value clearly attests that not only aqua/hydroxo but mixed aqua/hydroxo/DMFA (/chloro) complexes are involved in the hydrolysis.

All these transient spectra are obtained on liquid samples frozen before gelation could commence. A further proof for the propagation of chain growth and network formation is also reflected in the progressive increase of the response factor of the Mössbauer effect during the ageing (Fig. 15). The significant, c.a. five-fold increase in the f-factor is probably related both to the increase of the size of the involved species, and also to a simultaneous hardening, reflected in the increase of frequency of lattice vibrations³⁶. Meanwhile, at the end of the process stable and symmetric octahedral environment composed of oxygen atoms around iron is constructed, the

quadrupole splitting drops to $\Delta_{\text{Fe}^{3+(3)}} \sim 0.6$ mm/s and $\Delta_{\text{Fe}^{3+(4)}} \sim 1.07$ mm/s values, which are characteristic already for the formed polymeric species and oxyhydroxides^{31,34}.

Aggregation of particles – variations of the f factors and change in the shape of spectra

The structure of obtained aerogels is rigid when supercritical extraction is used to remove the solvent media (Fig. 1). However, the microscopic structure is rather loose (Fig. 2). This is clearly demonstrated by comparing the spectra of pristine aerogels with those after compression (Fig. 7, Table 3). Similar observation is reported by comparing iron oxide aero- and xerogels, namely, 10 – 20-fold increase is reported in the Mössbauer effective thickness parameter (i.e. the same amount of iron in the sample gives 10 - 20 times larger response in xerogels than in aerogels³⁴). In our case, a moderate compression of aerogels results in a ca. six-fold increase of the Mössbauer effect. Similarly to the previous instance this observation can probably be related to the change of the mass involved in the emission/absorption of γ -quanta, and to the change of vibration conditions of the lattice³⁶. The effect of compression on the intensity of components in case of ¹¹⁹Sn Mössbauer spectra of small particles is discussed in more detail in Ref⁴⁰.

It is important to note that not only the probability of the Mössbauer effect but the shape of spectra has also changed upon compression. Aerogels in their loose as received state display asymmetric spectra (see e.g. Fig. 7, left), and the asymmetry is more prevailing at higher temperatures. Similar change in the shape of spectra was reported in case of ferric hemin, the phenomenon was attributed to temperature dependent spin-spin relaxation times⁴¹. The effect of compression is also in accordance with this interpretation: particles get to close contact with each other, the spin-spin relaxation becomes much faster, the conventional symmetric shape of the doublet is restored.

Formation of xerogels probably has not been completed fully while a small portion of the original solvents is present in the structure after incomplete removal with ethanol. This is clearly illustrated in the case of one of the samples prepared in glycol media, when the final product contained ca. 50 wt% glycol. By physical appearance this sample is a rigid solid substance. Fig. 9 displays the change of the shape of spectra in dependence of the temperature, and Fig. 10 shows the temperature dependence of the response factor. In Fig. 9 the characteristic doublet starts to broaden at 220 K, and is smeared at 250 K. In correspondence, the temperature dependence of the response factor, which is proportional to the relative spectra area (shown in Fig. 10), exhibits a similar transition. In the 80 – 200 K region the regular Debye-Waller temperature dependence is followed, which can be described with a ca. $\Theta_D \approx 180$ K³⁵. At higher temperatures (225 – 250 K) a significant drop appears, distinctly deviating from the expected shape. Thus, upon raising the temperature in this range a significant part of the bonds was released, only short oligomers participate in the resonance effect, instead of an extended network of tightly bound species. It can be mentioned that a similar behaviour is reported for

$[\text{Fe}(\text{DMSO})_5\text{Cl}]^{2+}$ cation, a significant drop in the response factor is described in the 300 – 320 K region. The irregular behaviour of the DMSO complex is attributed to a structural phase transition¹⁴. The explanation of the irregular behaviour in our case can be different and more simple. Namely, the phenomenon can probably be connected to the gradual softening of the bonds with the interparticle glycol molecules (~melting) starting at 220 K. For comparison, it should be added that the sample after complete removal of glycol with ethanol and drying afterwards does not show this feature, it displays the expected doublet with high response factor at 300 K.

Further on it should also be mentioned that the formed particles are isolated from the point of view of magnetic coupling as well in our xero- and aerogel samples. For instance ferrihydrite samples composed of particles with 2 – 5 nm diameter exhibit resolved magnetic sextet at 80 K^{7,42}. In contrast, in spite of the same particle size region this feature does not appear in our samples.

Final products of hydrolysis and their conversions at modest temperatures

Final products of hydrolysis carried out at ambient temperatures usually are oxyhydroxides (not oxides). It has been proven in our case as well.

At the first approach formation of all of the possible four types can be considered (ferrihydrite, and α -, β -, γ -oxyhydroxides). Depending on the rate of hydrolysis various structures may be stabilized. Rapid hydrolysis under ambient conditions favours formation of ferrihydrite³¹, slower hydrolysis and elevated temperatures (80 – 100 °C) may result in the formation of more ordered structures^{24,25,43}. Several publications describe Mössbauer spectra of ferrihydrite, in most of cases spectra are interpreted as superpositions of signals originated from two octahedral sites^{41,44,45}, however, contribution from tetrahedral site has not been excluded either⁴⁶.

In previous studies on formation of xero- and aerogels formation of ferrihydrite¹⁹, goethite²⁰, akagenite²¹ were likewise reported. In all the mentioned regular structures (except β -FeOOH, akagenite) mostly one type of coordination is available for iron, i.e. one pair of δ , Δ values should describe the obtained Mössbauer spectra. (In akagenite two types of sites exist²⁷.) In contrast to these expectations, three doublets are necessary to obtain acceptable fits for our samples (Table 2). As for the number of necessary doublets the same conclusion is reported in Ref³⁴. Additionally, size effect of particles should also be taken into account. In the case of a regular iron oxide, hematite, it has been known since long time that the value of quadrupole splitting explicitly depends on the size of particles⁴⁷. Similar behaviour of oxyhydroxide particles of different size may result in spectra composed of components displaying various quadrupole splittings.

Evaluating the data of Table 2 in more detail three groups of Fe^{3+} sites can be separated by considering the δ values ($0.2 < \text{Fe}^{3+(1)} < \sim 0.33 < \text{Fe}^{3+(2)} < \sim 0.52 < \text{Fe}^{3+(3)} < 0.66$ mm/s,

respectively). The gap between these intervals is significant, thus probably different chemical environments should be assigned to the different δ values. The first region (0.2 – 0.33 mm/s) may characterize tetrahedral sites, the second interval (0.33 – 0.52 mm/s) can be assigned probably to the octahedral sites. The δ value for the third interval (0.52 – 0.66) is rather high – this component may probably indicate some incomplete structure, e.g. inclusion either of chloride or solvent molecules. In particular chloride may promote stabilisation of oxyhydroxides^{27,48}. In correspondence, presence of chlorine in significant amounts is revealed in correspondence with combustion measurements of samples prepared in DMSO media (Table 4) and EEL spectroscopy of X-GLY sample (Fig. 8). Chlorine can be present either in form of chloride ions, or retained epichlorohydrin, 3-chloro-propane-1,2-diol or even 1,2-dichloropropanol can be formed by the addition of chloride to protonated epichlorohydrin as described in Ref²¹.

Primary formation of ferrihydrite can also be proven from our XRD measurements, too. XRD patterns reveal dominant presence of 2-line ferrihydrite in each of characterized samples (Fig. 3). Additionally, small contribution from goethite could also be detected in xerogel samples formed in DMSO media (Figs. 3 c and d). Data are in good correspondence with results of recent X-ray scattering studies²⁶.

Additional structural supporting information can be extracted from HRTEM data as well. SAED rings and HRTEM images of DMSO-water aerogel sample display rather large lattice constant (≈ 1 nm). This value is in good correspondence with the 0.9 nm value reported for ferrihydrite in c direction of the hexagonal unit cell⁴⁹. FFT patterns of aerogel samples exhibit diffraction rings at 0.21, 0.25 and 0.30 nm (Fig. 5). The very same values are reported for ferrihydrite in a recent report, too²⁶. However, the rings in our samples are less sharp, and diffraction spots can hardly be distinguished even at the best resolution. Thus, considering the results obtained with various methods, dominating presence of imperfect ferrihydrite particles can be suggested in our samples.

As for transformations of aerogels due to modest temperature treatments one of our samples (A-(DMSO+H₂O)) was characterized after evacuation carried out at 260 °C. Adsorption measurements revealed significant textural changes. However, characteristic properties of aerogels were retained (high specific surface area, large pore volume etc., Fig. 2 and Table 1). XRD measurements attest also for preservation of the original structure, the diffraction patterns of the original and evacuated samples are similar (Figs. 3a and 3b). Mössbauer spectra reveal also certain changes, early stages of magnetite formation can be traced from appearance of a minor Fe²⁺ component in the corresponding spectrum (Fig. 6h), however it is clearly different from spectra of regular magnetite. Furthermore the product can be magnetized with a permanent magnet. Similar behaviour upon a moderate heat treatment has also been reported in several communications^{6-8,43,50}

Conclusions

Aerogels and xerogels were prepared by hydrolysis of FeCl₃·6H₂O in organic solvents by using water molecules accessible solely from crystals of the starting iron salt. The process was promoted with addition of a proton scavenger, epichlorohydrin. High surface area and low density aerogel products were obtained by supercritical CO₂ extraction of solvents. Xerogel samples are tight, compact and transparent substances.

Appearance of transient components in the early stages of formation of oxyhydroxo complexes can be revealed by Mössbauer spectroscopy in frozen solutions. In particular, stepwise exchange of ligands was clearly demonstrated in DMFA solvent. Simultaneously, dramatic increase of the probability of Mössbauer effect was also observed with the progress of hydrolysis. The process was slightly faster in DMSO, and even faster in ethylene glycol.

The loose structure of aerogels is reflected in their Mössbauer spectra: low response factor and asymmetric spectra are observed. The response factor dramatically increases upon compression, and the spectra display symmetric shape. On the other side high response factor and symmetric spectra are characteristic for frozen gel or dried xerogel samples. The formed nanoparticles are separated in both the aero- and xerogels, since magnetic ordering has not been detected in any of the Mössbauer spectra.

The xero- and aerogels are probably composed of imperfect ferrihydrite particles due to the low (ambient) temperature of synthesis. Their typical sizes are in the 4 – 8 nm region. SAED and FFT images are in good correspondence with results of other structural studies. In accordance, three characteristic coordination environments could be distinguished in the Mössbauer spectra, two of them reflect the structure of ferrihydrite, the third may correspond to certain imperfect iron siting, most probably in relation with presence of chloride.

Acknowledgements

The work was supported by the TÁMOP-4.2.2.A-11/1/KONV-2012-0036 project. The project is co-financed by the European Union and the European Social Fund. The authors are thankful to Lajos Daróczy (Dept. of Solid State Physics, University of Debrecen) for preparing the SEM micrographs.

References

- 1 A. S. Poyraz, C.-H. Kuo, S. Biswas, C. K. King'onde and S. L. Suib, *Nature Communications*, 2013, **4**, 2952.
- 2 F. Jiao, A. Harrison, J.-C. Jumas, A. V. Chadwick, W. Kockelmann and P. G. Bruce, *Angew. Chem. Int. Ed.*, 2004, **43**, 5958.
- 3 D. N. Srivastava, N. Perkas, A. Gedanken and I. Felner, *J. Phys Chem B*, 2002, **106**, 1878-1883.
- 4 Ai Du, Bin Zhou, Zhihua Zhang and Jun Shen, *Materials*, 2013, **6**, 941-968.
- 5 I. Lázár and I. Fábrián, Patent WO 2013/061104.

- 6 Jing Xu, Haibin Yang, Wuyou Fu, Kai Du, Yongming Sui, Jiuju Chen, Yi Zeng, Minghui Li and Guangtian Zou, *J. Magn. Mater.* 2007, **309**, 307-311.
- 7 E. E. Carpenter, J. W. Long, D. R. Rolison, M. S. Logan, K. Pettigrew, R. M. Stroud, L. Theil Kuhn, B. Rosendahl Hansen and S. Mørup, *J. Appl Phys*, 2006, **99**, 08N7117.
- 8 J. W. Long, M. S. Logan, C. P. Rhodes, E. E. Carpenter, R. M. Stroud and D. R. Rolison, *J. Am. Chem. Soc.*, 2004, **126**, 16879-16889.
- 9 P. Fabrizioli, T. Bürgi, M. Burgener, S. van Doorslaer and A. Baiker, *J. Mater Chem.*, 2002, **12**, 619-630.
- 10 S. Bali, F. E. Huggins, G. P. Huffman, R. D. Ernst, R. J. Pugmire and E. M. Eyring, *Energy & Fuel*, 2009, **23**, 14-18.
- 11 M.-S. Shin, J.-K. Kim, J.-W. Kim, C. A. Mendes Moraes, H.-S. Kim and K.-K. Koo, *J. Industrial and Engineering Chemistry*, 2012, **18**, 1768 – 1773.
- 12 S.-O. Kim, W. C. Lee, H. G. Choo, B.-T. Lee, P.-K. Lee, and S. H. Choi, *Environmental Technology*, 2014, **35**, 251-261.
- 13 F. Gschwind and M. Jansen, *Z. Kristallogr.*, 2014, **229**, 5-6.
- 14 I. G. Gusakovskaya, T. I. Larkina, V. I. Ponomarev and L. O. Atovmyan, *Journal of Structural Chemistry*, 1982, **23**, 864-869.
- 15 I. P. Lavrentiev, L. G. Korableva, E. A. Lavrentieva, G. A. Nifontova, M. L. Khidekel, I. G. Gusakovskaya, T. I. Larkina, L. D. Arutyunian, O. S. Filipenko, V. I. Ponomarev and L. O. Atovmyan, *Transition Metal Chemistry*, 1980, **5**, 193-200.
- 16 V. T. Yilmaz and Y. Topcu, *Termochim. Acta*, 1997, **307**, 143-147.
- 17 A. Asan, M. Andac and I. Isildak, *Analytical Sciences*, 2003, **19**, 1033-1036.
- 18 U. N. Tripathi, Afshan Siddiqui, Mohd. Safi Ahmad and Kajal Singh, *J. Coord. Chem.*, 2010, **63**, 894-905.
- 19 A. E. Gash, T. M. Tillotson, J. H. Satcher, Jr., J. F. Poco, L. W. Hrubesh and R. L. Simpson, *Chem. Mater.*, 2001, **13**, 999-1007.
- 20 L. Durães, B. F. O. Costa, J. Vasques, J. Campos and A. Portugal, *Materials Letters*, 2005, **59**, 859 – 863.
- 21 A. E. Gash, J. H. Satcher, Jr. and R. L. Simpson, *Chem. Mater.*, 2003, **15**, 3265-3278.
- 22 S. Bali, G. C. Turpin, R. D. Ernst, R. J. Pugmire, Vivek Singh, M. S. Seehra and E. M. Eyring, *Energy and Fuels*, 2008, **22**, 1439-1443.
- 23 M. V. Twigg and J. Burgess, in: *Comprehensive Coordination Chemistry II, Vol. 5*. Elsevier, 2003, 403-553
- 24 G. Lente and I. Fábián, *Inorganic Chemistry*, 1999, **38**, 603-605.
- 25 J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, 1988, **18**, 259-341.
- 26 F. M. Michel, L. Ehm, G. Liu, W. Q. Han, S. M. Antao, P. J. Chupas, P. L. Lee, K. Knorr, H. Eulert, J. Kim, C. P. Grey, A. J. Celestian, O. J. Gillow, M. A. A. Schoonen, D. R. Strongin and J. B. Parise, *Chem. Mater.*, 2007, **19**, 1489-1496.
- 27 R. M. Cornell and U. Schwertmann, *The Iron Oxides*, Weinheim, 1996.
- 28 E. Murad and J. H. Johnston, in: *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Ed. G. J. Long, Vol. 2., Plenum Press, 1987, pp. 507-582.
- 29 M. D. Lind, *J. Chem. Phys.*, 1967, **47**, 990-993.
- 30 N. Thrane and G. Trumpy, *Phys. Rev. B*, 1970, **1**, 153-155.
- 31 J. H. Johnston and D. G. Lewis, in: *Industrial Applications of Mössbauer Effect*, Eds: G. J. Long and J.G. Stevens, Plenum, 1986, 565-583.
- 32 A. Vértes: The chemical structure of liquid solutions studied by Mössbauer spectroscopy, in: *Mössbauer Spectroscopy of Frozen Solutions* (eds: A. Vértes and D. L. Nagy), Akadémiai, Budapest, 1990.
- 33 K. Burger, Solvation, ionic and complex formation reaction in non-aqueous solvents. *Studies in Analytical Chemistry, Vol. 6*, Elsevier – Akadémiai, Budapest, 1983.
- 34 F. E. Huggins, S. Bali, G. P. Huffman and E. M. Eyring, *Spectrochimica Acta, Part A*, 2010, **76**, 74-83.
- 35 A. Vértes, L. Korecz and K. Burger, *Mössbauer spectroscopy*, Akadémiai Kiadó, Budapest, 1979.
- 36 R. V. Parish, in: *Mössbauer Spectroscopy Applied to Inorganic Chemistry, Vol. 1.*, Plenum, 1984, 527-575.
- 37 K. Lázár, K. Matusek, J. Mink, S. Dobos, L. Gucci, A. Vizi-Orosz, L. Markó and W. M. Reiff, *J. Catal.*, 1984, **87**, 163-178.
- 38 T. Belgya and K. Lázár, *Hyperfine Interactions*, 2006, **167**, 875-879.
- 39 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309-319.
- 40 P. Bussière and P. Vergnon, *Journal de Physique, Coll. C1*, 1980, **41**, C1-147-148.
- 41 M. Blume, *Phys. Rev. Lett.*, 1967, **18**, 305-308.
- 42 Y. Guyodo, S. K. Banerjee, R. L. Penn, D. Burleson, T. S. Berquo, T. Seda and P. Solheid, *Physics of the Earth and Planetary Interiors*, 2006, **154**, 222-233.
- 43 V. Klimas, K. Mažeika, V. Jasulaitiene and A. Jagminas, *J. Fluorine Chem.*, 2015, **170**, 1-9.
- 44 Q. A. Pankhurst and R. J. Pollard, *Clays and Clay Minerals*, 1992, **40**, 268-272.
- 45 E. Murad, *J. Magnetism and Magnetic Materials*, 1988, **74**, 153-157.
- 46 C. M. Cardile, *Clays and Clay Minerals*, 1988, **36**, 537-539.
- 47 W. Kündig, H. Bömmel, G. Constabaris and R.H. Lindquist, *Phys. Rev.*, 1966, **142**, 327-333.
- 48 A. S. Campbell, U. Schwertmann and P.A. Campbell, *Clay Minerals*, 1997, **32**, 615-622.
- 49 F. M. Michel, L. Ehm, S. M. Antao, P. L. Lee, P. J. Chupas, Gang Liu, D. R. Strongin, M. A. A. Schoonen, B. L. Phillips and J. B. Parise, *Science*, 2007, **316**, 1726-1729.
- 50 Ö. Özdemir and D. J. Dunlop, *Earth and Planetary Science Letters*, 2000, **177**, 59-67.