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Effect of urea on the hydrolysis of Fe^{3+} ions in aqueous solutions at elevated temperature

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Abstract

The hydrolysis of 0.1 M $FeCl_3$ or 0.1 M $Fe(NO_3)_3$ solutions containing urea was investigated at elevated temperature. β-FeOOH was the principal hydrolytical product of 0.1 M $FeCl_3$ hydrolysis at 90°C. Its structural stability was preserved up to pH 7.55 for initial concentration of 2 M urea. After the formation of α-FeOOH, the phase transformation β-FeOOH → α-Fe_2O_3, via dissolution, was accelerated. For the initial concentration of ≥ 3 M urea, the formation of α-Fe_2O_3 and a small amount of α-FeOOH was observed. In the presence of nitrate anions, the mixtures of α-Fe_2O_3 and α-FeOOH were produced with tendency for the formation of α-Fe_2O_3 as the end product. In some samples, the presence of a small amount of γ-FeOOH could be detected on the basis of IR bands at 1024 and 745 cm^{-1}. The ^{57}Fe Mössbauer spectra indicated that α-FeOOH and α-Fe_2O_3 particles were very small and probably not well-crystallized. The samples were also characterized with transmission electron microscopy.

Keywords: Fe^{3+} hydrolysis; Urea; α-FeOOH; β-FeOOH; γ-FeOOH; α-Fe_2O_3; Mössbauer spectroscopy; Infrared

1. Introduction

An aqueous solution of urea, $(NH_2)_2CO$, can be utilized as a generator of OH^- ions at elevated temperature in accordance with the reaction:

$$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2.$$
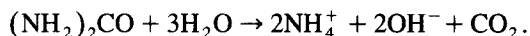
This chemical reaction was used by Willard [1] and Willard and Tang [2] to precipitate and separate metal cations as a function of pH. Krleža and Težak [3] investigated the precipitation of AgOH, $Zn(OH)_2$ and $Al(OH)_3$ from solutions of the corresponding nitrate salts and urea at 90°C. Their experiments

showed that the critical nitrate concentration for metal hydroxide formation in these precipitation systems was near to 0.001 N.

After these early works on the precipitation of metal hydroxides in the presence of decomposing urea, for many years, researchers did not pay significant attention to this chemical reaction. Then, in the eighties, researchers rediscovered the precipitation of metal hydroxides in decomposing urea. The reason for this was very simple; a search for various methods of chemical synthesis which can modify the chemical and physical properties of oxide materials was undertaken. For example, the hydrolysis of $AlCl_3$, $Al(NO_3)_3$ or $Al_2(SO_4)_3$ salt in the presence of urea was performed at 95°C [4]. X-ray diffraction

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analysis of the products of hydrolysis indicated that the fresh precipitates were amorphous and with prolonged time of aging the amorphous precipitates transformed to poorly crystallized boehmite. This phase transformation was inhibited in the presence of the sulphate anion. The effect of ultrasound on the precipitation of aluminium basic sulphate from homogeneous solution of urea was also investigated [5].

Ookubo et al. [6] investigated the hydrolysis of $TiCl_3$ + urea at 98°C with different urea to titanium mole ratios. Rod-like particles, 0.2 μm wide and 1.0 μm long, were obtained for the urea to titanium mole ratio of 2. Actually, these particles were aggregates of nanosized acicular crystals. The crystallite size of 13.6 nm was calculated using Scherrer's equation and the half-width of the rutile (110) peak. A small amount of brookite was also detected. With further increase of of the urea-to-titanium mole ratio only rutile was obtained.

The hydrolysis of $ZrOCl_2$ in an aqueous solution containing urea was performed under boiling conditions [7]. X-ray diffraction indicated the presence of m-ZrO_2 particles with dimensions of 15 to 100 nm.

The formation of Fe(III)-oxyhydioxides and oxides from Fe(III)-salt solutions [8,9] and $FeSO_4$ solution [10] in the presence of decomposing urea was also investigated. However, the phase composition and microstructure of the Fe-oxides (group name) formed by this reaction is still a matter of controversy.

In the present work we investigated the hydrolysis of 0.1 M $FeCl_3$ or 0.1 M $Fe(NO_3)_3$ solutions in the presence of urea. The aim of this work was (a) to elucidate exactly the nature of the products of hydrolysis of Fe^{3+} ions and the dependence on urea concentration and type of anion, and (b) to recognize if some of the reactions are of technological interest.

2. Experimental

Analytical grade reagents, $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and urea by Kemika were used. Twice distilled water was also used. Experimental conditions for the preparation of the samples are given in Table 1. The precipitation systems were not

Table 1
Experimental conditions for the preparation of the samples by hydrolysis of Fe(III) salts in urea solutions

Sample	$FeCl_3$ (mol dm^{-3})	$Fe(NO_3)_3$ (mol dm^{-3})	Urea (mol dm^{-3})	Temperature of precipitation (°C)	Time of precipitation (h)	Final pH
S1	0.1		0.1	90	8	1.61
S2	0.1		0.4	90	8	1.70
S3	0.1		0.6	90	81.81	
S4	0.1		0.9	90	8	2.41
S5	0.1		1.2	90	8	7.22
S6	0.1		2.0	90	8	7.55
S7	0.1		3.0	90	8	7.64
S8	0.1		4.0	90	8	8.64
S9	0.1		8.0	90	8	9.18
S10	0.1		5.5	60	8	2.41
S11	0.1		5.5	90	8	9.06
S12	0.1		5.5	100	8	9.41
S13	0.1		5.5	100	24	9.69
S14	0.1		5.5	100	40	9.65
S15		0.1	0.1	90	8	1.33
S16		0.1	0.4	90	8	1.63
S17		0.1	0.6	90	8	1.73
S18		0.1	0.9	90	8	2.93
S19		0.1	1.2	90	8	7.72
S20		0.1	2.0	90	8	8.91
S21		0.1	4.0	90	8	9.05

mechanically stirred during the hydrolysis of Fe^{3+} ions. After subsequent washing of the precipitates using an ultra-speed centrifuge (up to 20000 rpm), the isolated precipitates were dried. All samples were characterized by Fourier transform infrared (FTIR) spectroscopy, ^{57}Fe Mössbauer spectroscopy and transmission electron microscopy (TEM). Mössbauer spectra were fitted using the SIRIUS program [11].

3. Results and discussion

The characteristic results, obtained by FTIR spectroscopy, aresummarized in Figs. 1–3. Fig. 1 shows FTIR spectra of selected samples, produced with initial content of urea varying from 0.1 to 8 M. The spectrum of sample S1 is characterized by a band at 839 cm^{-1} and shoulder at 814 cm^{-1}, a band at 698 cm^{-1} with shoulder at 641 cm^{-1} and a band at 421 cm^{-1} with shoulder at 473 cm^{-1}. These bands are typical of β-FeOOH [12]. The main spectral characteristics of β-FeOOH were preserved up to 2 M urea, i.e. β-FeOOH as a single phase was isolated at pH 7.55. With increase of the initial content of urea to 3 M, significant changes in the phase composition of the produced sample (S7) were observed by FTIR spectroscopy. The spectrum of sample S7 indicated the presence of β-FeOOH and α-Fe$_2$O$_3$, as well as a

small amount of α-FeOOH on the basis of the shoulder at 891 cm^{-1} and the band at 794 cm^{-1}. The spectrum of sample S9 indicated the presence of α-Fe$_2$O$_3$ (bands at 552 and 473 cm^{-1}) and small amount of α-FeOOH (bands at 891 and 794 cm^{-1}).

Fig. 2. FTIR spectra of samples S10, S11 and S12, recorded in KBr matrix at room temperature.

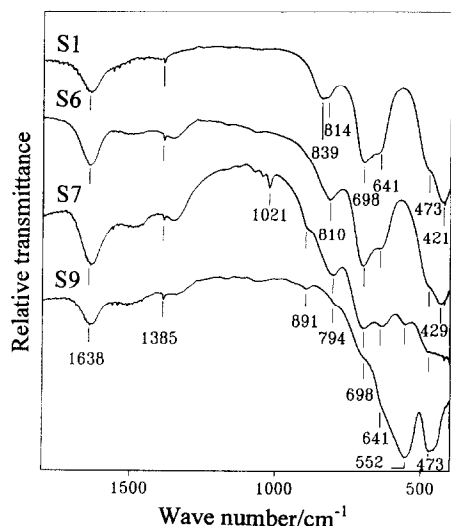
Fig. 1. FTIR spectra of samples S1, S6, S7 and S9, recorded in KBr matrix at room temperature.

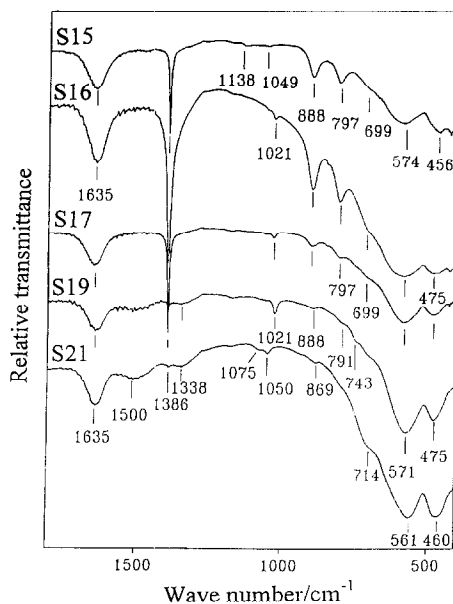Fig. 3. FTIR spectra of samples S15, S16, S17, S19 and S21, recorded in KBr matrix at room temperature.

The results of the present work indicated structural stability of β-FeOOH in decomposing urea up to pH 7.55. In the presence of a small amount of α-FeOOH, the phase transformation β-FeOOH $\rightarrow$ α-Fe_2O_3 is accelerated. At higher pH values there is greater probability of the formation of α-FeOOH from $FeCl_3$ solution. The formation of α-FeOOH is accompanied with dissolution of β-FeOOH and α-Fe_2O_3 crystallization. The importance of α-FeOOH in the phase transformation, β-FeOOH $\rightarrow$ α-Fe_2O_3, was observed in previous works [13,14]. It was also found that α-FeOOH seeding had an influence on this phase transformation. The mechanism of the phase transformation β-FeOOH $\rightarrow$ α-Fe_2O_3 in aqueous medium differs from that occurring in the solid state during the calcination of β-FeOOH [15].

Fig. 2 illustrates the effect of temperature on the phase composition of samples S10 to S12, produced for an initial 5.5 M urea. On the basis of the band at 1024 cm^{-1} and shoulder at 745 cm^{-1}, a conclusion can be made about the presence of a small amount of γ-FeOOH (lepidocrocite) in sample S10. In previous work [16], it was proven that FTIR spectroscopy has a high capability for the detection of small amounts of α-FeOOH and γ-FeOOH in mixtures of Fe-oxides.
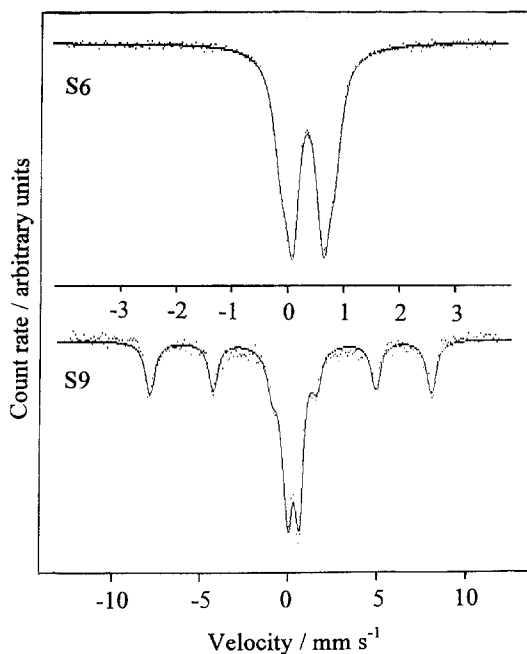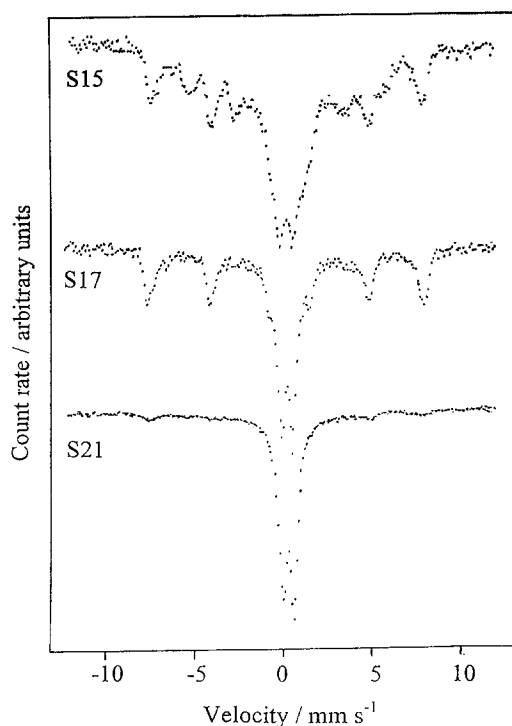

Fig. 5. [57]Fe Mössbauer spectra of samples S15, S17 and S21, recorded at room temperature.

FTIR spectra of samples S11 and S12 show pronounced bands at 556 and 474 cm^{-1}, corresponding to α-Fe_2O_3 and the very small intensity bands at 894 and 794 cm^{-1} are due to the presence of α-FeOOH.

FTIR spectra of samples S15 to S21, shown in Fig. 3, illustrate the effect of nitrate anions on the hydrolysis of Fe^{3+} ions in decomposing urea. The spectra of samples S15 and S16 showed a mixture of α-Fe_2O_3 and α-FeOOH. From samples S16 to S21, a tendency for α-Fe_2O_3 formation, as the end-product (sample S21), was observed.

Fig. 4 and Fig. 5 show the Mössbauer spectra of selected samples. Sample S6 is characterized at RT with the superposition of two quadrupole doublets ($\Delta_1 = 0.55$ and $\Delta_2 = 0.96$ mm s^{-1}) indicating two nonequivalent iron environments in β-FeOOH [14]. The Mössbauer spectrum of sample S9 is characterized, at RT, by a central quadrupole doublet and hyperfine magnetic splitting component. Taking into account the FTIR spectrum of sample S9, the reduced hyperfine magnetic field, $H = 494$ kOe, central quadrupole doublet, $\Delta = 0.64$ mm s^{-1}, and

Fig. 4. [57]Fe Mössbauer spectra of samples S6 and S9, recorded at room temperature.

line-width of the sextet, $\Gamma = 0.65$ mm s^{-1}, can be ascribed to fine α-Fe$_2$O$_3$ particles, which are probably not well-crystallized. It is generally known that imperfections in α-Fe$_2$O$_3$ crystallite can reduce the value of the hyperfine magnetic field.

The Mössbauer spectrum of sample S15 shows superposition of two sextets with reduced hyperfine magnetic fields, $H_1 = 477$ and $H_2 = 338$ kOe, and central quadrupole doublet, $\Delta = 0.67$ mm s^{-1}. The measured values of H_1 and H_2 can be ascribed to

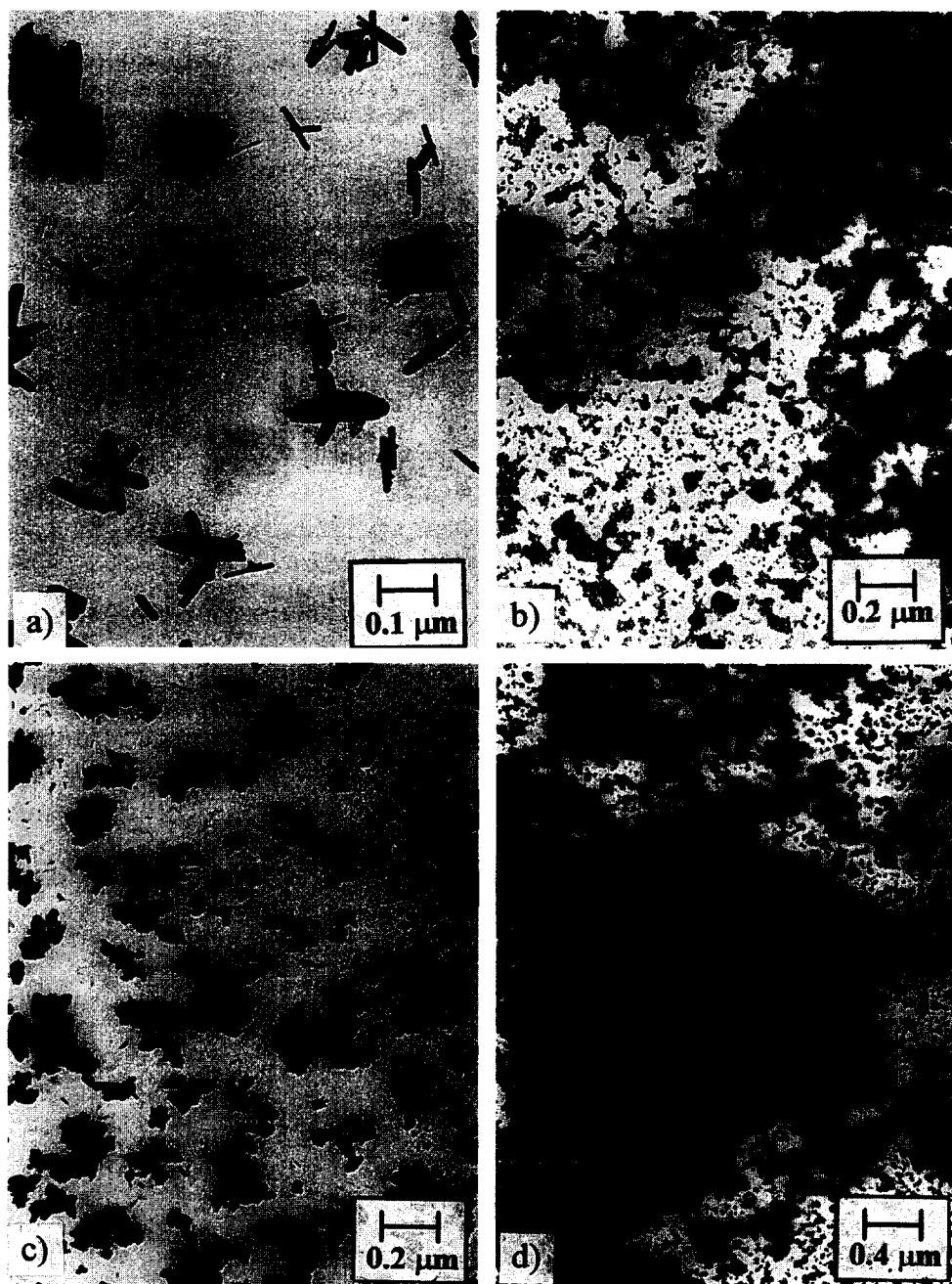Fig. 6. TEM microphotographs of samples (a) S6, (b) S9, (c) S15 and (d) S21.

α-Fe$_2$O$_3$ and α-FeOOH, respectively. However, the Mössbauer parameters and the shape of the spectrum of sample S15 suggests the presence of Fe-oxide particles of small size and probably of poor crystallinity. The Mössbauer spectrum of sample S17 was fitted by the superposition of one sextet ($H = 478$ kOe) and central quadrupole doublet ($\Delta = 0.64$ mm s^{-1}). The spectrum of sample S21 showed significant decrease of the relative intensity of the hyperfine magnetic splitting component ($H = 467$ kOe) in relation to the previous spectra for a given series of the samples.

A TEM microphotograph of sample S6 (Fig. 6a) shows X-, Y- and star-shaped particles. These morphologies are typical of β-FeOOH colloids. The TEM microphotograph of sample S9 (Fig. 6b) shows very small particles and this is in agreement with the shape of the corresponding Mössbauer spectrum in Fig. 4. Sample S15 shows two kinds of particles (Fig. 6c) corresponding to α-Fe$_2$O$_3$ (relatively larger particles) and α-FeOOH (very small rods). Sample S21 (Fig. 6d) shows a significant decrease in size of the particles in relation to sample S15 and this observation is in agreement with Mössbauer spectra as shown in Fig. 5.

Acknowledgements

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