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Room temperature one-pot preparation of magnetically ordered iron(III) oxide from aerated aqueous solutions of Fe^{II} salts in the presence of 2-hydroxypropyl-β-cyclodextrin

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Magnetically ordered γ-Fe_2O_3 was obtained by the interaction of $Fe(NH_4)_2(SO_4)_2$ and NaH_2PO_2 in aerated aqueous alkaline solution in the presence of 2-hydroxypropyl-β-cyclodextrin at room temperature; the only crystal phase (maghemite) was detected in the sample.

It is a challenge to prepare magnetically ordered iron(III) oxide (maghemite, γ-Fe_2O_3) directly from the aqueous solutions of iron salts. In general, maghemite can be obtained by the synthesis and decomposition of iron compounds in air. The low-temperature dry synthesis gives nonmagnetic Fe_2O_3, and high temperature recrystallization is required to obtain magnetically ordered γ-Fe_2O_3.

Here, we report a wet approach to the preparation of magnetically ordered γ-Fe_2O_3 at room temperature.[1] Maghemite was obtained from the aerated aqueous solutions of Fe^{2+} in the presence of NaH_2PO_2 and 2-hydroxypropyl-β-cyclodextrin (HP-β-CD).†

To understand the role of HP-β-CD, the reaction of Fe^{2+} ions with NaH_2PO_2 in alkaline aerated solution was carried out. Brown nonmagnetic Fe_2O_3 was detected in the absence of HP-β-CD. The precipitation of Fe_2O_3 occurred upon the oxidation of metallic iron formed by the reaction of Fe^{2+} with NaH_2PO_2, which is known to reduce effectively metal ions, *e.g.*, Sn^{2+}, Pb^{2+}, Ni^{2+} and Ag^+ in aqueous solutions.

The formation of Fe_2O_3 in the above process results from the oxidation of metallic iron rather than $Fe(OH)_3$ decomposition which does not occur at room temperature. It is reasonable to assume that Fe^{2+} ions in solution or $Fe(OH)_2$ precipitate undergo the following reactions with NaH_2PO_2 to form metallic iron:

$$2\,FeSO_4 + NaH_2PO_2 + 4\,NaOH = \\ = 2\,Fe + 2\,Na_2SO_4 + NaH_2PO_4 + 2\,H_2O, \quad (1)$$

$$2\,Fe(OH)_2 + NaH_2PO_2 = 2\,Fe + NaH_2PO_4 + 2\,H_2O. \quad (2)$$

This indicates that metallic iron itself is the only substance to form Fe_2O_3 in solution. The subsequent spontaneous oxidation of metallic iron in aerated aqueous solution leads to Fe_2O_3 (or hydrated Fe_2O_3):

$$4\,Fe + 3\,O_2 = 2\,Fe_2O_3. \quad (3)$$

Reactions (1)–(3) in the absence of HP-β-CD lead to the formation of nonmagnetic Fe_2O_3 in aqueous solutions. However, the same reactions being carried out at room temperature in the presence of HP-β-CD gave brownish-black compound **1**, which exhibited unequivocal magnetism.

In both cases (with or without HP-β-CD), according to the elemental analysis data, the product was Fe_2O_3. There is a slight difference in IR spectra of the substances obtained.‡ The band at ~590 cm^{-1} in the IR spectrum of **1** (Figure 1) was earlier attributed to the Fe–O stretching vibrations of γ-Fe_2O_3.[2,3] There are no bands at 1000–1100 cm^{-1} due to HP-β-CD stretching vibrations indicating its absence from the oxide.

Thus, HP-β-CD plays a critical role in the direct formation of magnetically ordered Fe_2O_3 in aqueous solutions at room temperature.

According to the XRD data, no crystalline phases other than maghemite were detected. The cell parameter a = 8.3607(6) Å is in good agreement with known data [8.3515(22) Å].

The average crystal size of the particles estimated by the Debye–Scherrer equation was 62(7) nm. The large standard deviation is probably indicative of either a wide size distribution or highly anisotropic crystal shapes.

In order to understand the reason of maghemite formation, the brownish-black solid **2** was isolated from aqueous solutions after 8 h of stirring at room temperature. The intermediate was dried at room temperature and identified as Fe_2O_3.

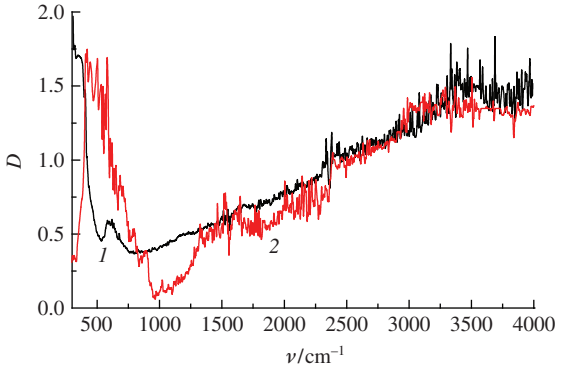

Figure 1 IR spectra of Fe_2O_3 obtained (*1*) in the presence and (*2*) in the absence of HP-β-CD in the initial mixture.

† In a typical experiment, to a solution containing 0.5 mmol of Mohr's salt [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], 0.005 mmol of HP-β-CD, and 1 mmol of NaOH in 50 ml of distilled water, 0.5 mmol of NaH_2PO_2 was added dropwise. The mixture was stirred in air for 24 h at room temperature. The brownish-black residue was isolated from the solution, washed with water and dried in air. In accordance with elemental analysis data, the sample contained 69.50 wt% iron as Fe_2O_3.

‡ The IR spectra were recorded in KBr on Specord M-80 (Carl Zeiss, Germany) in a range of 4000–400 cm^{-1}.

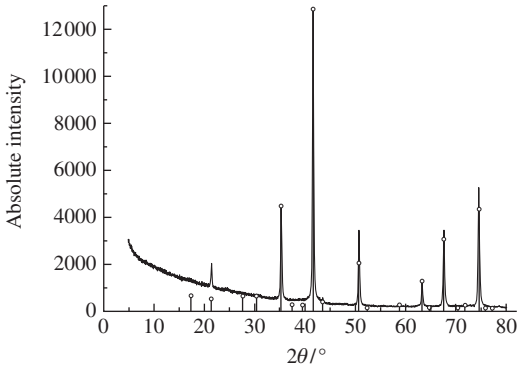

Figure 2 XRD patterns of compound **1** and γ-Fe_2O_3, maghemite (reflection positions from PDF 39-1346).

The XRD data for compound **2** indicate the absence of intermediates on the oxidation of iron with oxygen in the solution. The direct oxidation of iron nuclei to yield Fe_2O_3 rather than FeO, FeO(OH) or Fe_3O_4 was observed earlier on the oxidation of iron species with Me_3NO.[4–6]

This observation was supported by the preparation of Fe/Fe_3O_4 nanoparticles in a solution of cyclodextrin.[7] No oxidation of Fe/Fe_3O_4 nanoparticles to Fe_2O_3 proceeded at room temperature in the presence of γ-cyclodextrin. The magnetite (Fe_3O_4) formed on the surface of metal particles is stable to oxidation with oxygen at room temperature. The conversion of Fe_3O_4 into γ-Fe_2O_3 occurs at 350 K on exposure to atmospheric O_2.[8]

The self-assembling of cyclodextrins to produce nanoparticles of the core–shell type in the presence of metal or metal oxide species in solution is the reason for the inhibition of the spontaneous oxidation of iron metal to nonmagnetic Fe_2O_3. The formation of magnetically ordered γ-Fe_2O_3 is probably due to the oxidation of iron with O_2 within capsules formed by self-assembled HP-β-CD molecules.

The magnetic properties of compounds **1** and **2** at 78 and 300 K were studied.[§] The temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) magnetization for **1** and **2** are shown in Figures 4 and 5. As can be seen in Figure 3, the magnetization patterns of **1** and **2** at 300 K are similar. For comparison, the magnitization of Fe_3O_4 is also presented. The saturation magnetizations of the samples of **1** and **2** were close (74 and 65 emu g^{-1}) at 300 K, and they increased slightly with decreasing temperature. The value of M_s for **1** is somewhat lower than the saturation magnetization of bulk γ-Fe_2O_3 at 300 K (87,[6] 76[9] emu g^{-1}). Coercive forces for the samples of **1** and **2** are 114 and 86 Oe at room temperature and 163 and 158 Oe at 78 K, respectively.

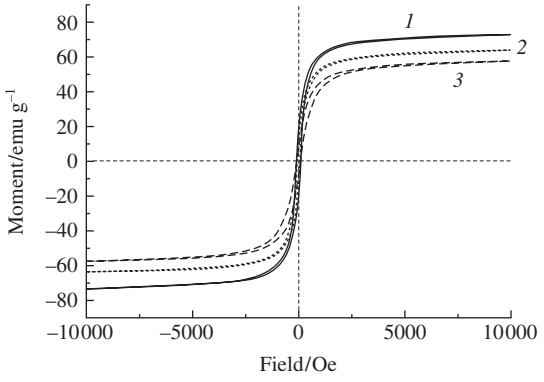

Figure 3 Room temperature magnetization of the samples of (*1*) **1** (γ-Fe_2O_3), (*2*) **2** obtained in aqueous solutions in the presence of HP-β-CD and (*3*) Fe_3O_4.

§ The magnetization measurements were carried out on a Lake Shore 7307 vibration magnetometer at 78–330 K.

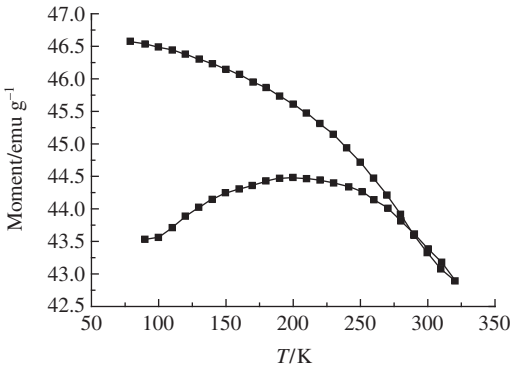

Figure 4 ZFC-FC temperature dependence of the magnetization of **2** measured at 500 Oe.

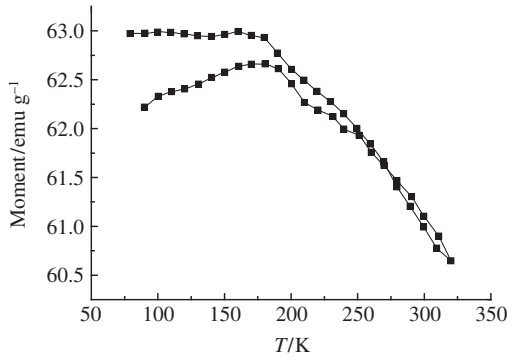

Figure 5 ZFC-FC temperature dependence of the magnetization of **1** measured at 1000 Oe.

The XRD and magnetization data for the sample of **1** are consistent with the results obtained by Mössbauer spectroscopy (Table 1, Figure 6).[¶] The Mössbauer spectra are superpositions of three sextets. The parameters of two principal sextets are close to those of the spectra of Fe^{3+} ions in tetrahedral (A) and octahedral (B) positions (or sublattice) of the γ-Fe_2O_3 structure.[10–14] The third sextet is likely due to the agglomerates of γ-Fe_2O_3 nanoparticles (10–30 nm).[8,15,16] Note that there is no dublet typical of small nanoparticles ($d < 10$ nm) in the spectrum recorded at 299 K. Thus, it is likely that the sample of **1** contains particles with a wide granulometric distribution (XRD and Mössbauer spectroscopic data).

Table 1 Hyperfine parameters obtained from the Mössbauer spectra of the sample of **1** (γ-Fe_2O_3).[a]

T/K	δ/mm s^{-1} (±0.01)	B_{ef}/kOe (±3)	Γ/mm s^{-1} (±0.02)	*S* (%) (±5)	Fe site
299	0.31	479	0.51	35	Fe^{3+}_{tetr} (A)
	0.34	495	0.46	42	Fe^{3+}_{oct} (B)
	0.34	432	0.76	23	Fe^{3+}
78	0.40	510	0.42	34	Fe^{3+}_{tetr} (A)
	0.47	528	0.47	49	Fe^{3+}_{tetr} (B)
	0.46	481	0.72	17	Fe3+

[a] δ is the isomer shift; B_{ef} is the magnetic hyperfine field; Γ is the full width at half height; and *S* is the relative subspectral area; quadrupole shift of the lines $\varepsilon \leqslant |0.02|$.

¶ The Mössbauer spectra were recorded at 299 and 78 K using a conventional spectrometer (MC-1014EM) operating in a constant acceleration mode with a ^{57}Co(Rh) source at 295 K. Isomeric shifts are referred to α-Fe at 295 K.

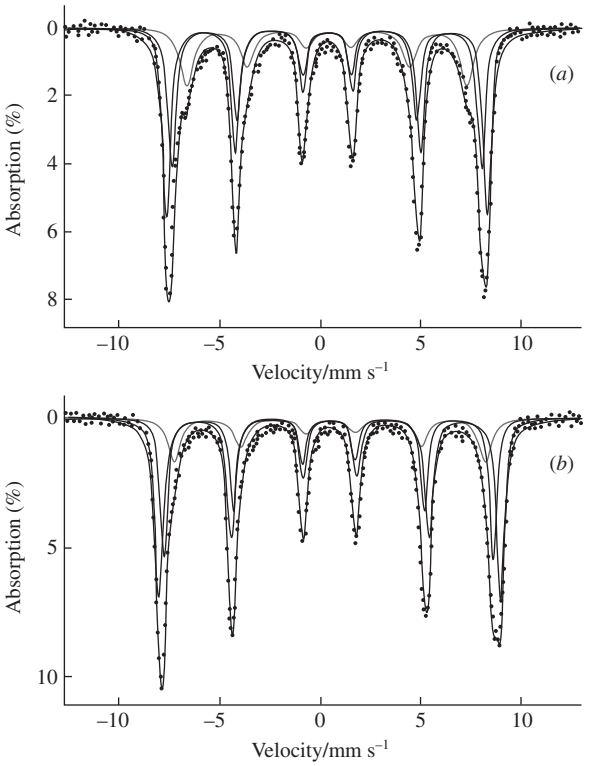

Figure 6 Mössbauer spectra of **1** at (*a*) 299 and (*b*) 78 K.

The direct formation of γ-Fe_2O_3 in aerated aqueous alkaline solutions of Fe^{II} salts in the presence of NaH_2PO_2 and HP-β-CD at room temperature was observed by Mössbauer spectroscopy, XRD and magnetization measurements. The maghemite particle size was about 62(7) nm. HP-β-CD inhibited the spontaneous oxidation of iron to nonmagnetic Fe_2O_3.

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