

PROPERTIES OF MESOPOROUS Fe₂O₃-SiO₂ COMPOSITES AS DEPENDENT ON PREPARATION METHOD

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The method for template hydrothermal synthesis (HTS method) with use of various precursors of iron oxide, namely with iron sulfate and iron chloride salts mixed at ratios of 1:1 and 1:2, iron nitrate, goethite, and γ -Fe₂O₃ stabilized with oleic acid, was applied to synthesize iron-silica composites containing [Fe] and [Si] components at ratios of 0.025-0.2.

To prepare mesoporous Fe₂O₃-SiO₂ systems featured by high proportions of the iron-oxide component (up to [Fe] : [Si] =1) and by high values of specific surface area during the THS process, a “fractional precipitation” method was proposed.

Textural-structural characteristics of the obtained materials were comparatively appraised.

Introduction

Currently, highly dispersive silica doped with magnetic sorts of iron oxides is regarded as a promising material for biomedical applications. High stability and biological compatibility of magnetic silicates, as well as a possibility of modifying Fe₂O₃-SiO₂ surfaces with various functional groups – due to the presence of reactive silanol groups – enables controlling electro-surface properties of materials, their aggregate stability and porous structure. The indubitable interest of researchers is generated by a possible use of magnetic silicate materials in strong drug delivery systems, especially in cases of local effect in a pathogenic focus. As time progresses, a growing number of research works related to the use of magnetic silicate materials in other biomedical applications, such as hyperthermia mediators in treatment of oncologic diseases, in diagnostic procedures, in bioseparation processes of, e.g., protein molecules, etc., evidences this interest [1-11].

Experimental

Preparation of Fe₂O₃-SiO₂ composites was performed by means of template hydrothermal synthesis in an alkaline medium, in the presence of cetyltrimethylammonium bromide (CTAB, Aldrich) as a structure-forming agent. Tetraethoxysilane (TEOS, Aldrich) and tris(trimethylsiloxy)silane (TTSS, Aldrich) were used as sources of silica. Preparation of

mesoporous silicate materials was performed in accord with the earlier designed and tested methods [12].

Molar ratios of basic components for synthesis were opted as follows: TEOS 1 : CTAB 0.04 : TTSS 0.03 : NaOH 0.4 : H₂O 100. The mix comprised of iron sulfate (FeSO₄·7H₂O) and iron chloride (FeCl₃·6H₂O) salts at molar ratio of 1:2 and 1:1, of iron nitrate (Fe(NO₃)₃·9H₂O), goethite, and the nano-sized -form of iron(III) oxide stabilized with oleic acid was used as precursors of the metal-oxide component. Molar ratios of components in the specimens under investigation were varied from [Fe] : [Si] = 0.025 up to [Fe] : [Si] = 1.

Results and discussion

The produced specimens were investigated with use of various physic-chemical methods. X-Ray phase analysis and FTIR-spectroscopy were used to investigate the structure of the obtained materials.

The X-ray analysis was performed with use of the XRD-7000 diffractometer (Shimadzu, Japan) using CuK_α - radiation ($\lambda_{av} = 1.54184 \text{ \AA}$) in angular intervals $2\Theta = 1.4-10^\circ$ and $10-80^\circ$ with $0.01-0.005^\circ$ step and storage time of signal 1.5-2 sec. The signals were identified with use of the JSPDS Card Index. In accord with these findings, the specimens with low contents of iron ([Fe] : [Si] = 0.025-0.05) were ascertained to be X-ray-amorphous. In small-angular interval 2Θ , these specimens evince reflexes confirming availability of the ordered hexagonal structure of mesopores (MCM-41).

The FTIR-spectra were registered with use of the IFS-66/S spectrometer (Bruker, Germany) at room temperature, with 100 scans and 2 cm^{-1} resolution. The spectra of the specimens with low contents of iron oxide (by the example of Fe₂O₃-SiO₂ composites at [Fe] : [Si] = 0.1) evince, apart from adsorption bands characteristic of FTIR spectra of silica ($\sim 450, \sim 800, \sim 1080, \sim 1240 \text{ cm}^{-1}$), availability of adsorption bands characteristic of the Fe-O-Si bond, irrespectively of the nature of precursor introduced during synthesis. Low intensive adsorption bands at $535-630 \text{ cm}^{-1}$ evince existence of Fe-O-Fe bonds in the structures of iron oxide (Fig. 1).

Textural parameters of specimens (specific surface area, volume, pore diameter, pore size distribution) were determined with use of nitrogen sorption at $-196 \text{ }^\circ\text{C}$ on the ASAP 2020 device (Micrometrics, USA) after degassing the material under vacuum at $350 \text{ }^\circ\text{C}$ for 3 h.

Specific surface area (S_{BET}) and total pore volume (V_{tot}) of the specimens were measured with use of the BET method. Pore size distribution was calculated from desorption isotherms with use of the BJH method in 1.7-300 nm interval.

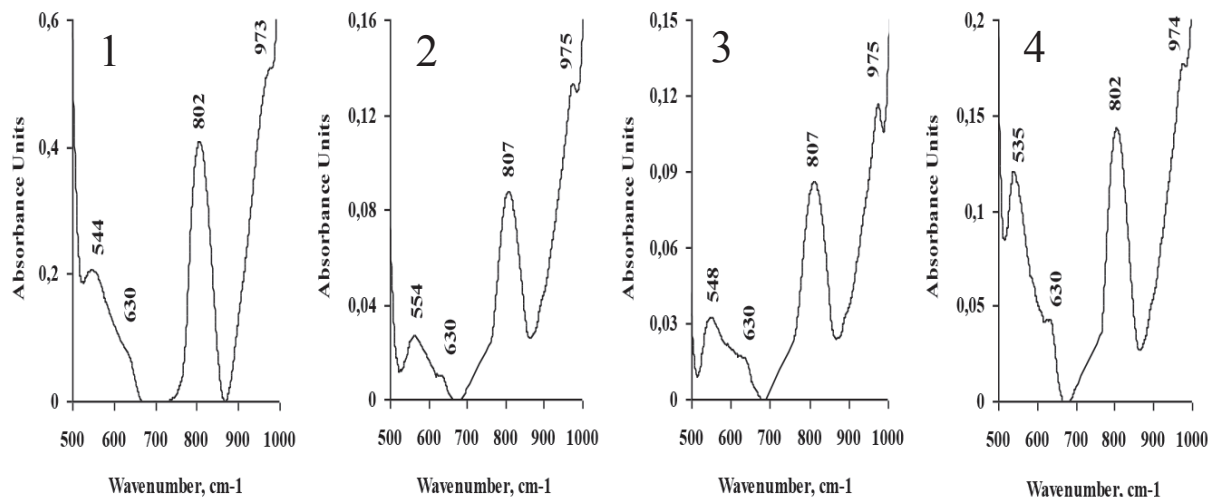


Fig. 1. FTIR-spectra of specimens at $[Fe] : [Si] = 0.1$ obtained with use of:
 1 – $FeSO_4$ and $FeCl_3$ salts mixed at the ratio of 1:2; 2 – iron nitrate nonahydrate; 3 – goethite;
 4 – $\gamma-Fe_2O_3$

Basic textural characteristics of the specimens under investigation at $[Fe] : [Si] = 0.1$ as influenced upon by the nature of iron oxides' precursors are shown in Fig. 2 and in Table 1.

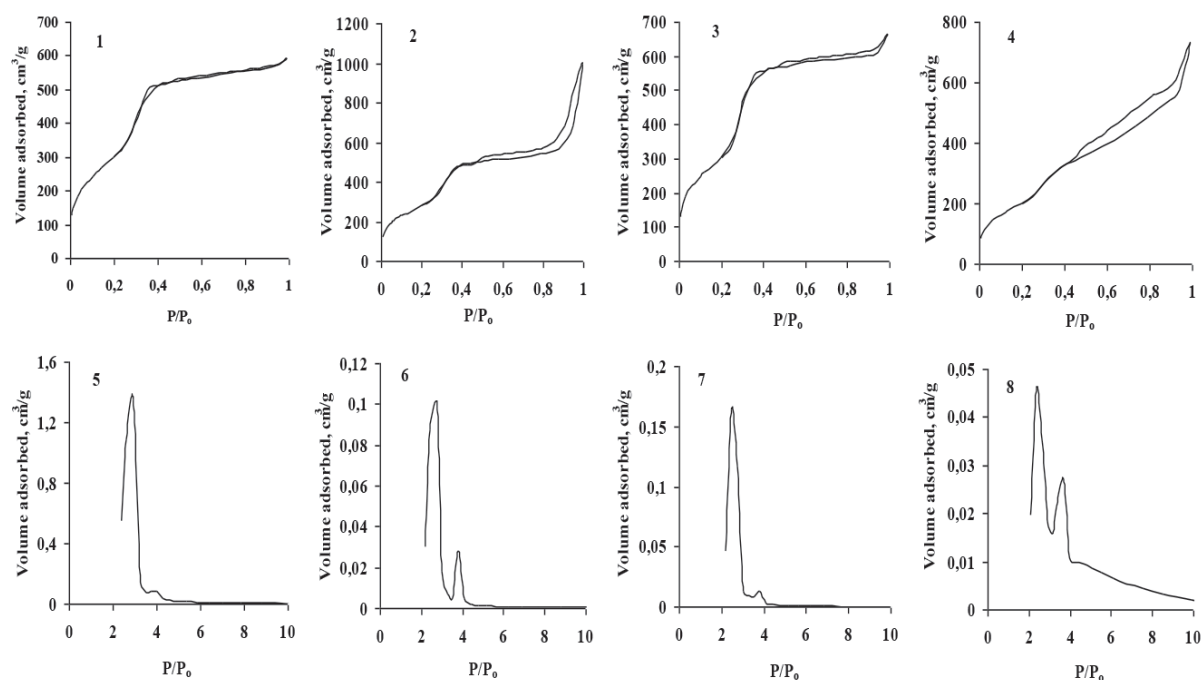


Fig. 2. Sorption isotherms (1-4) and pore size distribution curves (5-8) of the specimens at $[Fe] : [Si] = 0.1$ obtained with use of:
 1,5 – the mix of $FeSO_4$ and $FeCl_3$ salts at ratio of 1:2; 2,6 – iron nitrate nanohydrate; 3,7 – goethite;
 4,8 – $\gamma-Fe_2O_3$ as precursors of iron oxide phase

As is apparent from Fig. 2, sorption isotherms of all the specimens under investigation have the shape characteristic of the ordered mesoporous structures (type IV, in accord with the IUPAC classification), namely isotherms with the markedly expressed part corresponding to nitrogen capillary condensation. The pore size distribution in the specimens is determined in a narrow diapason.

The curves mirroring pore size distribution in the specimens obtained with use of iron nitrate nonahydrate exhibit two maximums that are attributed to availability of “bottle-shaped” pores, i.e. pores with narrow necks and wide cavities. The pore size distribution in the specimen obtained with use of γ -Fe₂O₃ (Fig. 2 [8]) is not homogeneous.

As is apparent from Table 1, the specimens containing minor portions of iron oxide exhibit high textural parameters, independently of the nature of precursors used.

Table 1

Textural characteristics of iron-oxide – silica composites at ratio of components [Fe] : [Si] = 0.025-0.2.

№	Ratio [Fe] : [Si]	1FeSO ₄ ·2FeCl ₃			Fe(NO ₃) ₃ ·9H ₂ O			FeOOH (гётит)			γ -Fe ₂ O ₃		
		S _{BET} , m ² /g	V _{tot} , cm ³ /g	D, nm	S _{BET} , m ² /g	V _{tot} , cm ³ /g	D, nm	S _{BET} , m ² /g	V _{tot} , cm ³ /g	D, nm	S _{BET} , m ² /g	V _{tot} , cm ³ /g	D, nm
1	0.025	1462	0.92	2.5	1368	1.54	4.5	1578	1.03	2.6	1475	1.07	2.9
2	0.05	1124	0.87	3.1	1027	1.16	4.5	1314	1.03	3.1	910	1.01	3.1
3	0.1	626	1.04	6.6	676	1.00	5.9	1337	1.15	3.4	418	0.91	8.7
4	0.2	224	0.45	13.4	434	0.85	7.8	1013	0.99	3.9	63	0.30	19.4

The molar fraction of iron increased up to 0.2 as compared with the silica-oxygen matrix leads to a marked decrease in specific surface area and to an increase in average pore size diameter in the specimens obtained with use of FeSO₄ and FeCl₃ salts mixed at ratio of 1:2, iron nitrate nanohydrate, γ -Fe₂O₃. The specimen obtained with use of goethite exhibits high textural parameters, up to the 0.2 increase of molar fraction in the composite. In accord with data of X-ray phase analysis, the ordered mesoporous structure (MCM-41) is preserved in this specimen, but iron (III) oxide is present as paramagnetic α -form.

The Fe₂O₃-SiO₂ composite with molar fraction of iron up to 0.2 and over, while usable as iron nitrate precursor, is difficult enough to obtain. Aliquation of reaction mix and coagulation of sediment are observable. The reason is, most probably, a decreased pH value of medium caused by an increased concentration of nitrate-ions. With nano-sized iron (III) γ -oxide as precursor, the same processes are observable.

Therefore, to elaborate the template HTS methods for Fe₂O₃-SiO₂ composites containing high proportions of iron (III) oxide at [Fe] : [Si] = 0.2-1, the mix comprised of iron sulfate (FeSO₄·7H₂O) and iron chloride (FeCl₃·6H₂O) at molar ratios of 1:2 and 1:2 was used as precursor of the iron oxide component.

To obtain composites containing high proportions of the iron oxide component, peculiarities of synthesis of composites containing low proportions of iron were taken into account. In this case, an increased molar fraction of iron up to 0.2, as compared with silica, generated degradation of mesoporous structure and considerable impairment of basic textural parameters. To overcome this problem, the “fractional precipitation” method was proposed. The method implied increased portions of both alkaline agent (NaOH) and aqueous phase requisite to dissolve iron oxide precursors.

To opt ratios of salts – of iron (III) chloride and iron (II) sulfate – with the aim to obtain magnetic composites, the formation processes of iron-oxide-silica mesoporous structures by the example of specimens with [Fe] : [Si] = 0.6 were comparatively appraised with use of FTIR-spectroscopy (Fig. 3).

As follows from Fig. 3, formation of goethite structure (α -FeOOH, adsorption band at 619 cm⁻¹) occurs at intermediate stage of synthesis of Fe₂O₃-SiO₂ composites (after hydrothermal treatment of reaction mix and before its baking). Adsorption bands at 637 (628) and 695 (694) cm⁻¹ characteristic of magnetic forms of iron oxide – maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄), and lepidocrocite (γ -FeOOH) – appear in FTIR spectra after thermal destruction of the organic constituent and of acid residues in the specimens under investigation.

The mentioned adsorption bands are assigned to both valence vibrations of Fe-O-Fe bonds in spinel structures of iron oxides, and stretch vibrations of δ (Fe-O-H) in OH-groups directly bonded to iron ions. At this point, for the specimen *3a* containing FeSO₄ and FeCl₃ salts at ratio of 1:1, the spectral pattern at 695-561 cm⁻¹ characteristic of the maghemite structure is more markedly expressed as compared with the one for specimen *3b* containing iron sulfate and iron chloride at ratio of 1:2.

The “fractional precipitation” method enables obtaining materials featured by good values of specific surface area and total pore volume, even if

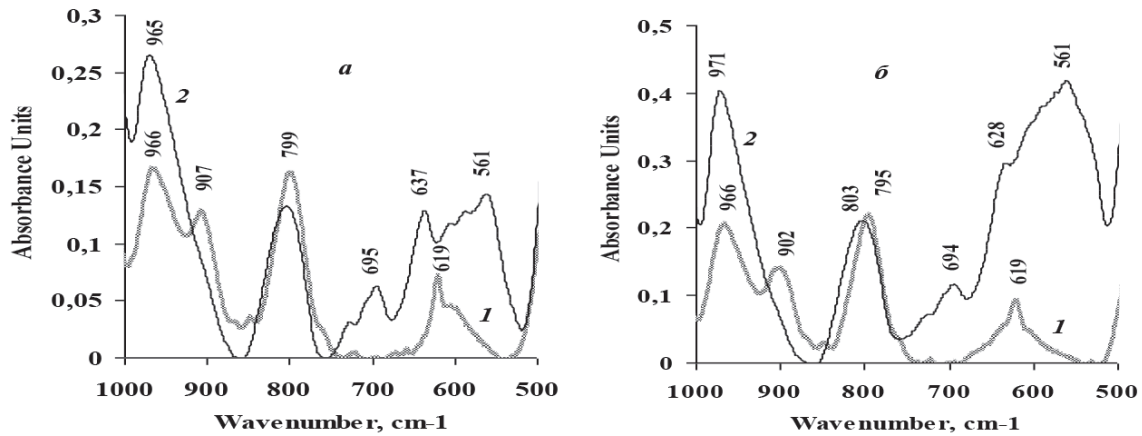


Fig. 3. FTIR-spectra of specimens at $[Fe] : [Si] = 0.6$ obtained with use of $FeSO_4$ and $FeCl_3$ salts as precursors mixed at the ratio of 1:1 (a), and 1:2 (b):
 1 – intermediate stage of synthesis (before baking), 2 – after baking

these materials contain large proportions of iron (III) oxide. The specimens containing $[Fe]$ and $[Si]$ components at ratio of 0.2-0.3 exhibit largest value of total pore volume ($1.19 \text{ cm}^3/\text{g}$). With increasing iron oxide fraction in specimens obtained with use of the “fractional precipitation” method, the following phenomena occur: (a) values of specific surface area increase to some extent ($SBET = 849 \text{ m}^2/\text{g}$); (b) values of pore diameter decrease, with minimal values of 3-3.5 nm for specimens at $[Fe] : [Si] = 0.6-0.9$.

Phase composition of the specimens comparatively analyzed with use of the X-ray phase method has shown the HTS method as fit to produce specimens containing predominantly the γ -phase of iron(III) oxide. In accord with the method, components are used at the computational ratio of $[Fe] : [Si] = 0.4-0.7$, with $FeSO_4$ and $FeCl_3$ salts (as precursors of iron(III) oxide) mixed at ratio of 1:1. The specimens obtained with use of $FeSO_4$ and $FeCl_3$ salts mixed at ratio of 1:2 contain a mix of α - and γ -phases of iron(III) oxide with the predominant hematite fraction.

Conclusions

The Fe_2O_3 - SiO_2 composites featured by high contents of the iron oxide component and good textural parameters are obtained with use of the “fractional precipitation” method. Ratios of $[Fe] : [Si] = 0.4-0.7$ are regarded as optimal values contributing to formation of ferrimagnetic γ -phase of iron oxide.

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