

Synthesis of Polymeric Sorbents with Magnetic Properties

OLEG MANAENKOV, OLGA KISLITSA

Department of biotechnology, chemistry and standardization
Tver State Technical University
Tver, Af. Nikitina, 22
RUSSIA

Abstract: In this work, a procedure for the synthesis of polymeric sorbents based on hypercrosslinked polystyrene (HPS) with magnetic properties was developed. The technique is based on the reduction of iron salts with polyhydric alcohols at high temperature in an inert atmosphere. The resulting sorbents retain their original characteristics: an extended specific surface area, micro-mesoporous structure, acquiring magnetic properties, which makes it possible to use them as magnetically separable sorbents, supports for the active phase of heterogeneous catalytic systems etc.

Key-Words: hypercrosslinked polystyrene, sorbent, magnetite, materials with magnetic properties.

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1 Introduction

Hypercrosslinked polystyrene (HPS) is a porous structure spontaneously formed during synthesis. This polymer is characterized by the presence of rigid cavities with a diameter of about 2–3 nm, and has a high degree of crosslinking (more than 100 %) [1]. The micro-mesoporous structure of the HPS polymer matrix, and an extended specific surface area (usually about 1000 m²/g) determine the excellent sorption properties of the material. Sorbents based on HPS simultaneously combine high adsorptive capacity, the ability to swell in solvents of various nature, high molecular-size selectivity with easy regeneration, good kinetic characteristics, stability in aggressive medium, and the absence of volumetric changes varying ionic strength, pH, or type of solvent [2, 3].

Other advantages of HPS include its mechanical strength, chemical and thermal (up to 400 °C) stability. It makes the HPS an excellent alternative to traditional supports (C, Al₂O₃, SiO₂, etc.) used for the synthesis of heterogeneous catalytic systems [2-4].

Structural features of HPS provide wide opportunities for its use as a matrix for nanocomposites. The movement and agglomeration of particles embedded in HPS cavities is difficult due to the small size of the pores and channels of the polymeric network. Since the network parameters are determined by the synthesis conditions, the pore size differs insignificantly. This fact is of the great importance when developing different materials, in particular, catalysts, since the enlargement of particles decreases the inner surface

of the particles, and, consequently, the activity of the catalyst [5-7].

In this regard, the modification of HPS in order to impart magnetic properties is of high interest. Sorbents with magnetic properties can be very useful in various industries due to its ability to be quickly and easily separated by a magnetic field [8].

There are two methods for obtaining magnetic polymeric sorbents: the synthesis of magnetic nanoparticles (MNPs) in pores of the matrix and the synthesis of a polymer in the presence of MNPs. The first method seems to be the simplest. It includes the chemical precipitation of magnetite (Fe₃O₄) from iron (II) and (III) salts [9]. For example, Pastukhov and colleagues [10] developed a magnetic nanocomposite material based on MN200 HPS. To introduce iron hydroxide nanoparticles, the above neutral polymers were impregnated with a solution of Fe (II) and Fe (III) salts and then treated with an aqueous solution of ammonia. It was shown that the impregnated magnetite nanoparticles were found to have a particle size up to 6 nm in microporous composites, while for the biporous HPS (with micro-mesoporous structure), magnetite nanoparticles were about 16 nm. According to the results of sorption studies, the developed nanocomposite magnetic sorbents have high capacity with respect to some physiologically active compounds along with the original HPS.

Another approach was implemented in [11]. Preliminarily synthesized magnetite nanoparticles were introduced into the polymer matrix at the stage of hypercrosslinking. The resulting magnetic sorbent showed high sorption capacity to antibiotics.

The approach based on the in-situ synthesis of magnetic nanoparticles showed a better distribution of nanoparticles in the porous structure of resins, while no agglomeration phenomena were detected [2]. On the contrary, the ex-situ method revealed in some cases of magnetite nanoparticles agglomeration on the surface of resin supports [12].

In the present work, we propose a new method for the synthesis of magnetically recoverable composites with high saturation of magnetization based on MN270 HPS (non-functionalized), which can be used directly as sorbents or as supports for heterogeneous catalytic systems.

2 Experimental

Fe₃O₄/HPS MN270 composites were synthesized according to the following procedure. FeCl₃·H₂O was dissolved in 95 wt.% ethanol. As received HPS MN270 was added to the resulting solution, mixed thoroughly and left for 15 min for impregnation. Then, a calculated portion of sodium acetate was added dropwise to the solution. The mixture was dried at a temperature of 70 °C until complete removal of ethanol. The powder was wetted with ethylene glycol and placed in a quartz tube purged with an argon. The tube was heated in an electric furnace up to 300 °C and kept for 5 h in an argon flow. The synthesized Fe₃O₄/HPS MN270 powder was washed several times with water, then with ethanol, and dried to constant weight in an oven at a temperature of 70 °C.

The thermal stability of the initial HPS MN270 sample was studied using a TG 209 IRIS thermogravimetric analyzer (NETZSCH, Germany). The values of the specific surface area of the samples were determined by the method of low-temperature nitrogen physisorption using a Beckman Coulter^{SA} 3100 surface analyzer (USA). Transmission electron microscopy (TEM) was performed using a JEM1010 microscope (USA). The magnetic properties of the samples were determined using a VIBRACH vibrating magnetometer (TVGU, Russia). X-ray fluorescence analysis was performed on a Zeiss Jena VRA-30 spectrometer (Germany).

3 Results and discussion

To estimate the thermal stability of the HPS polymer matrix, a thermogravimetric (TG) study of the prepared and crushed polymer (particle size less than 60 μm) was carried out. The results of thermogravimetric analysis of the initial HPS MN270 sample are shown in Figure 1.

An intense, multi-stage decomposition of the polymer probably associated with the destruction of methylene crosslinks seems to begin at a temperature of about 450 °C. This temperature corresponds to the maximum rate of polymer weight loss, 10 %/min. The resulting weight loss was approximately 55 %. These facts confirmed the possibility of synthesizing magnetite particles in the pores of the HPS matrix by thermal reduction of iron salts at temperatures up to 400 °C.

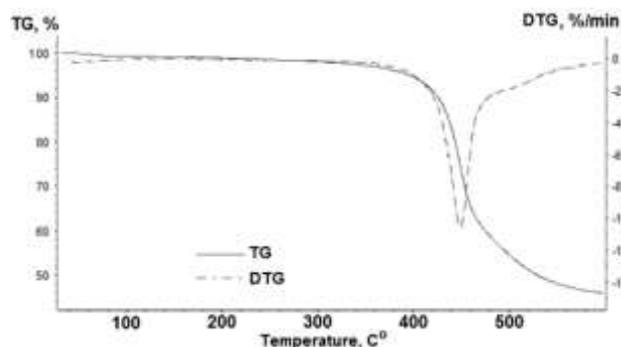


Fig. 1 Results of thermogravimetric analysis of HPS MN270.

In the study, the method for synthesizing magnetite particles in HPS pores was optimized. The use of iron (III) nitrate as a precursor was found to be unacceptable due to the formation of a significant amount of oxygen during the nitrate thermal decomposition, as it was shown in the previous study [13].



The high amount of oxygen formed can lead to the destruction of the porous structure HPS due to its oxidation (Table 1).

Table 1. Specific surface area of samples.

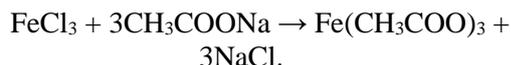
#	Sample	S _{BET} , m ² /g	S _L , m ² /g	S _t , m ² /g
1	HPS MN270	1075	1191	265 ¹ ; 807 ²
2	Fe ₃ O ₄ /HPS MN270	450	480	160 ¹ ; 289 ²
3	Fe ₃ O ₄ /HPS MN270	11	9	30 ¹ ; 0 ²

S_{BET} is the specific surface area (BET model); S_L is the specific surface area (Langmuir model); S_t is the specific surface area (t-plot); ¹specific surface area of micropores; ²specific surface area according to a t-plot model.

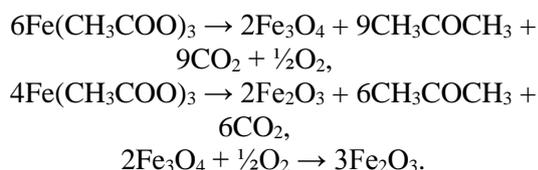
It can be seen from the data in the table that the specific surface area of a sample obtained using iron

(III) nitrate (Entry 3) is by 45-50 times less than that for the sample synthesized using FeCl₃ (Entry 2) as a precursor.

Thus, for the synthesis of Fe₃O₄/HPS MN270 composites, iron (III) chloride was used as a precursor. Then the reactions occurring during the synthesis according to the above method can be represented by the equation below. As a result of the exchange reaction, Fe(CH₃COO)₃ is formed in the pores of the polymer:



In this case, it is important to use 95 % ethanol as a solvent to prevent the hydrolysis of the resulting iron acetate. In the case when hydrolysis does not occur, the subsequent thermal decomposition of acetate at 300 °C proceeds according to the following mechanism [14]:



It should be noted that in these reactions, a much smaller amount of oxygen is formed. It can be quickly removed from the reaction zone by constant purging with an inert gas (argon). Thus, the oxygen destructive effect on the polymer matrix is significantly reduced.

The synthesized samples of Fe₃O₄/HPS MN270 composites were characterized by physicochemical methods. Table 2 presents the results of elemental analysis, which shows that the developed synthesis procedure makes it possible to obtain samples with desired iron content in the magnetite composition.

Table 2. Results of elemental analysis of Fe₃O₄/HPS MN270 samples.

Sample	Fe, %
Fe ₃ O ₄ /HPS MN270 (1:1)*	17.1
Fe ₃ O ₄ /HPS MN270 (1:2)	19.6
Fe ₃ O ₄ /HPS MN270 (1:3)	25.4

* - parentheses indicate the mass ratio of the initial HPS and FeCl₃.

The results of the study by the method of low-temperature nitrogen adsorption showed that the synthesized composites seem to be micro-mesoporous. The ratio of micro- and mesopores and their specific surface area are significantly affected

by the introduction of magnetite particles into the polymer matrix (Table 3).

Table 3. Specific surface area and pore volume of samples with different iron contents.

Sample	S _{BET} , m ² /g	S _L , m ² /g	S _t , m ² /g	V, cm ³ /g
HPS MN270	1075	1191	265 ¹ ; 807 ²	0.37
Fe ₃ O ₄ /HPS MN270 (1:1)	730	825	224 ¹ ; 506 ²	0.22
Fe ₃ O ₄ /HPS MN270 (1:2)	656	752	158 ¹ ; 498 ²	0.23
Fe ₃ O ₄ /HPS MN270 (1:3)	450	480	160 ¹ ; 289 ²	0.13

S_{BET} is the specific surface area (BET model); S_L is the specific surface area (Langmuir model); S_t is the specific surface area (t-plot); ¹specific surface area of micropores; ²specific surface area according to a t-plot model.; V – micropores volume.

It was assumed that the formation of magnetite particles occurs mainly on the HPS surface and at the mouths of the pores. The last ones can be blocked by the magnetite nanoparticles and, as a result, a decrease in the specific surface area and a change in the ratio of micro-, meso-, and macropores of the samples can be observed. This assumption was confirmed by the TEM results. It is shown that (Figure 2) the formation of Fe₃O₄ actually occurs mainly on the surface, at the mouths of the pores of the HPS polymer matrix. The particle size of magnetite was found to be 40 ± 5 nm.

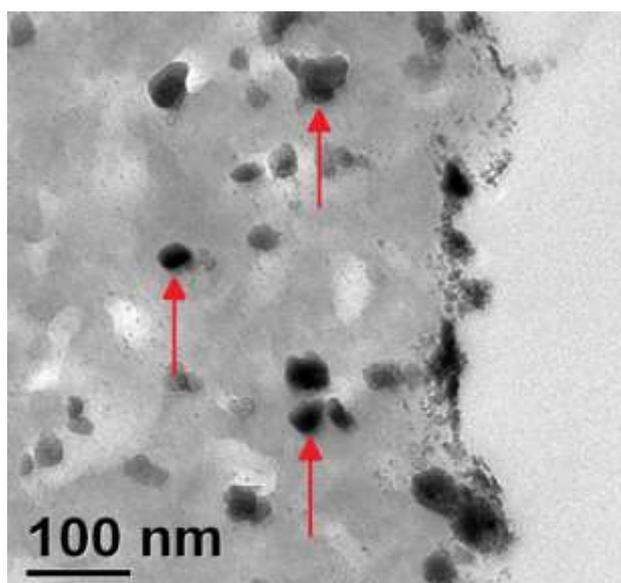


Fig. 2 TEM images of the Fe₃O₄/HPS MN270 sample.

The composition of the surface of nanocomposites was determined by X-ray photoelectron spectroscopy (XPS) (Table 4).

Table 4. Surface composition of Fe₃O₄/HPS MN270 based on XPS analysis results.

Element	at%	wt%
C 1s	66.8	45.5
O 1s	25.8	23.5
N 1s	0.2	0.2
Cl 2p	0.4	0.8
Fe 2p _{3/2}	3.5	11.1

The magnetic properties of Fe₃O₄/HPS MN270 were also studied.

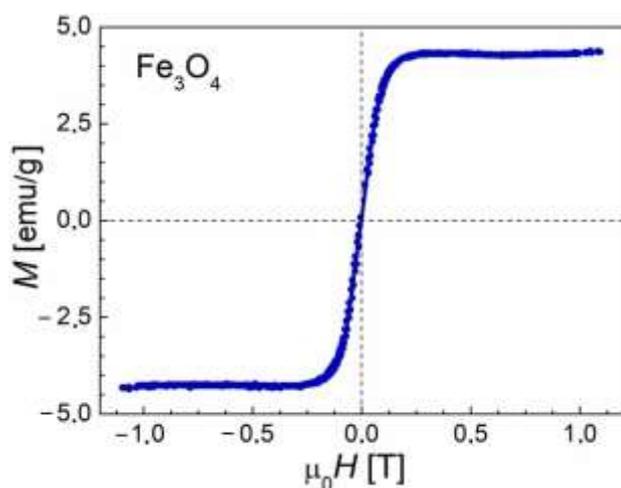


Fig. 3 Magnetization curves Fe₃O₄/HPS MN270 (1:3).

It has been shown that the experimental samples have a five times higher saturation magnetization (about 4.0 ± 0.5 emu/g, Figure 3) than the value for magnetically separable catalysts based on mesoporous silicon dioxide developed by us in previous studies [13]. Such magnetization allows the composite to be easily separated from the liquid phase by external magnetic field.

The characteristic shape of the magnetization curves indicates the superparamagnetic nature of the sample and confirms the formation of magnetite particles in the pores of the HPS polymer matrix.

The magnetite nature of the magnetic particles was also confirmed by X-ray powder diffraction (Figure 4). The diffraction pattern of Fe₃O₄/HPS MN270 contains a set of clear Bragg reflections, the intensity and position of which are typical for magnetite.

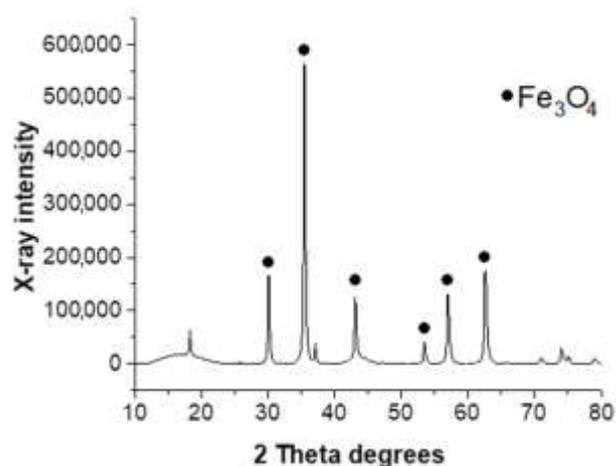


Fig. 4 XRD pattern of the Fe₃O₄/HPS MN270 (1:3).

4 Conclusion

Based on the results of the study, the following conclusions can be done:

- a new method for the synthesis of sorbents based on a polymer matrix of hypercrosslinked polystyrene with magnetic properties (saturation magnetization of at least 4.0 ± 0.5 emu/g) was proposed. This method is characterized by the absence of processes of destruction of the porous polymer structure;
- the magnetite nature of the particles formed in the pores of HPS during the synthesis was confirmed by the various methods;
- the synthesized composites can be used directly as sorbents or as support for heterogeneous catalytic systems.

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