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Synthesis, structure and magnetic properties of porous magnetic composite, based on MCM-41 molecular sieve with Fe_3O_4 nanoparticles

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Abstract

Porous magnetic composites were prepared by the synthesis of molecular sieve MCM-41 in the presence of Fe_3O_4 nanoparticles with average diameter of 15 nm. Nanoparticles were captured by porous silica matrix MCM-41, which resulted in their incorporation, as it was confirmed by TEM, SEM and X-ray diffraction. The materials possessed high surface area (392–666 $m^2\,g^{-1}$), high pore volume (0.39–0.73 $cm^3\,g^{-1}$) along with high magnetic response (M_S up to 28.4 emu g^{-1} at 300 K). Calcination of samples resulted in partial oxidation of Fe_3O_4 to α-Fe_2O_3. The influence of nanoparticles content on sorption and magnetic properties of the composites was shown. No hysteresis was found for the samples at 300 K; at 5 K, H_C was in the range 370–385 G for non-calcinated samples and 350–356 G for calcinated ones.

Keywords: Porous magnetic composites; Molecular sieves; MCM-41; Fe_3O_4 nanoparticles; Sorption properties; Magnetic properties

1. Introduction

Porous materials and molecular sieves attract much attention due to their remarkable characteristics, they possess high surface and high sorption capacity compared to non-porous objects, as well as the possibility to perform selective sorption of various substrates by regulation of pore diameter or easy chemical modification [1–3]. The most studied porous materials are those built from diamagnetic units, such as carbon, oxides of *p* elements, etc. [4,5]. Such porous materials are widely used in various fields, in particular, for sorption of different substrates from liquids with analytical, technical, environmental or biochemical purposes [6–9]. Creation of porous materials, which may be drawn into magnetic field, opens new fields of application of such species—they may be used for magnetic separation (extraction of adsorbed compounds from the solution) or transport of adsorbed compounds in magnetic fields [10–13], as well as for development of magnetochemical sensors [14,15]. Magnetic separation of the compound (porous carrier with adsorbed substrate) may significantly simplify analytical procedures, and in some cases it may provide the best way for separation of the compounds (for example, in the case of colloids, like blood). Some recent examples of such application include extraction of immunoglobulins by modified magnetic nanoparticles [16] and transport of anti-inflammatory agent ibuprofen by silica-coated magnetic microspheres [10].

For this purpose, the material should have significant ferro- or ferrimagnetic response, since "simple" paramagnetism is not sufficient for movement of the particles in magnetic fields, which are created by common permanent magnets. Two approaches may be proposed for the preparation of porous magnetic materials: (i) creation of magnetic particles in already prepared porous matrix and (ii) synthesis of porous component at the surface of magnetic nanoparticles.

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The first approach may be illustrated by several examples. Nanoparticles of paramagnetic α-Fe_2O_3 in pores of SBA-15 were synthesized by thermolysis of $Fe(NO_3)_3$ inside the pores [17]. As expected, partial occupation of pores resulted in decrease of specific surface and volume of pores, giving rise to materials containing about 25% of Fe_2O_3. It should be noted that synthesis of nanoparticles in porous matrix should result in full or at least partial occupation of pores. Ordered material of MCM-41 type, containing 8.2 wt% of Fe, was prepared by introduction of $FeCl_3$ into reaction mixture [18]. Fe^{III} ions occupied tetrahedral positions in silica structure and no clustered Fe oxides were found, hence the material had the properties of simple paramagnet.

Regarding the second approach, superparamagnetic porous aluminosilicate with γ-Fe_2O_3 particles embedded in the walls was prepared by addition of Fe^{III} ethoxide powder to the reaction mixture, followed by calcination of the product [19]. Several methods for the synthesis of nanoparticles, covered by SiO_2, were reported. γ-Fe_2O_3 nanoparticles were covered by SiO_2 shell, forming composite species with an average diameter at 145 nm [20]. SiO_2 dissolution precipitation was used for covering α-Fe_2O_3 nanoparticles [21]. Mixed-oxide SiO_2–Fe_2O_3 nanocomposite was prepared by sol–gel method [22]. None of these materials exhibit magnetic response sufficient for magnetic separation from the solution combined with high sorption capacity.

Porous layer of MCM-41 structure was grown on Fe_3O_4 microparticles (3 μm in average), which allowed to achieve high magnetization ($83\,\mathrm{emu\,g^{-1}}$ at room temperature) along with rather low surface ($52.3\,\mathrm{m^2\,g^{-1}}$) [23]. Very recently, the magnetic porous microspheres were prepared by synthesis of porous silica on 12 nm Fe_3O_4 nanoparticles [10]. Such approach allowed to prepare the composite with high surface ($721\,\mathrm{m^2\,g^{-1}}$) but comparatively low magnetization (about $2\,\mathrm{emu\,g^{-1}}$ at 300 K) [10]. Growth of mesoporous silica layer on Fe_2O_3 nanoparticles followed by reduction of this oxide to Fe_3O_4 also allowed to synthesize porous magnetic microspheres, containing 48-nm particles of Fe_3O_4 [13]. This sample possessed rather high surface ($250\,\mathrm{m^2\,g^{-1}}$) along with high magnetization ($9.8\,\mathrm{emu\,g^{-1}}$) [13]; however, the synthesis was rather complicated.

Notably, magnetic materials may be synthesized by formation of porous structure from paramagnetic building blocks without "special" porous component, which may be illustrated by the synthesis of mesostructured iron oxyhydroxides [24,25] or paramagnetic porous coordination polymers [26]; however, magnetic responses of such compounds at room temperature are quite low for their use as magnetic sorbents.

The aim of this study was to develop a new method of porous magnetic material preparation by growth of porous silica matrix on Fe_3O_4 nanoparticle, and to find how magnetic properties of such materials depend on nanoparticles content and the conditions of sample treatment. The idea of such material preparation was to use magnetic nanoparticles, a priori much larger than pore diameter, in order to avoid pore filling and produce combination of ferrimagnetism with high surface area, capable of sorption of various substrates. For this purpose, we used 15-nm Fe_3O_4 particles (vide infra) and porous MCM-41 material with average pore size of about 3.3 nm. Since the distribution of magnetic nanoparticles by their size has no influence on desired properties of the material, we especially chose the simplest method for preparation of nanoparticles, realizing, however, that such distribution there will be broad. The materials, described in this paper, fill the interval between porous magnetic composites with high surface/low magnetization [10] and low surface/high magnetization [23], as well as allow us to see the influence of Fe_3O_4/Fe_2O_3 content on sorption and magnetic properties of ferrimagnetic porous composites.

2. Experimental

2.1. Starting materials and physical measurements

Commercially available reagents and solvents ("Ukrreakhim", "Aldrich") were used without additional purification. X-ray powder measurements were carried out on DRON-3M diffractometer (Cu$K\alpha$ radiation, filtered by nickel). Since the main expected field for application of MCM-41/Fe_3O_4 composite is extraction of various substrates from the solutions, surface characteristics were determined by sorption of methanol, which is more hydrophilic than nitrogen or argon; methanol sorption on MCM-41 gives surface parameters close to the ones determined by nitrogen sorption [27]. Adsorption isotherms were measured by weight method (methanol, 293 K) [28]. Fe_3O_4 nanoparticles were prepared using standard procedure by addition of the solution, containing equimolar quantities of $Fe_2(SO_4)_3 \cdot 9H_2O$ and $FeSO_4 \cdot 7H_2O$ [29], to hot solution of NaOH. Average size of the particles was estimated by Scherrer equation, which was proven to be correct for similar systems [30] and was independently confirmed by TEM. TEM studies were performed on Philips EM430 ST; instrument, SEM was performed on JEOL F-6301. Magnetic measurements were performed on Quantum design SQUID MPMSXL magnetometer with a maximum of 5 T and operating between 2 and 300 K.

2.2. Synthesis

The procedure for preparation of MCM-41 [31] was modified by introduction of nanoparticles in reaction mixture. Water solution of cetyltrimethylammonium chloride was adjusted to $pH = 10.5$ by ammonia, and then the calculated quantity (Table 1) of Fe_3O_4 colloid was added at vigorous stirring. The reaction mixture was charged with HS-40 silicasol, stirred for 0.5 h at room temperature,