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Structural dependence of the efficiency of functionalization of silica-coated FeO_x magnetic nanoparticles studied by ATR-IR

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ABSTRACT

The efficiency of propylamino functionalization of magnetic silica-coated FeO_x nanoparticles prepared by different methods, including coprecipitation and flame aerosol synthesis, has been evaluated by attenuated total reflection infrared spectroscopy (ATR-IR) combined with a specific surface reaction, thus revealing the availability of the grafted functional groups. Large differences in the population of reactive groups were observed for the investigated materials, underlining the tight relation between the structure of nanoparticles and their suitability for organic functionalization. The materials possessed different core structure, surface area, and porosity, as evidenced by transmission electron microscopy and nitrogen adsorption–desorption isotherms. Grafting of aminopropyl groups using a standard procedure based on reaction with (3-aminopropyl)trimethoxysilane as source of the propylamino groups was performed, followed by classical dry analysis methods to determine the specific concentration of the organic functional groups (in mmol g^{-1} of material). ATR-IR spectroscopy in a specially constructed reactor cell was applied as wet methodology to determine the chemically available amount of such functional groups, showing that the materials possess largely different loading capacity, with a variability of up to 70% in the chemical availability of the organic functional group. The amount of (3-aminopropyl)trimethoxysilane used for functionalization was optimized, thus reaching a saturation limit characteristic of the material.

1. Introduction

Magnetic nanoparticles based on iron oxides have found a broad range of applications in the past decades [1–4]. Biomedical research has shown interest for such materials in the fields of drug delivery [5–10] and hyperthermia [11–13], but they have also been used as contrast agents [14–18], as semiconductors [19–21], and in the development of new catalysts [22–28], only to mention some of the areas of research which were most influenced by their introduction. Functionalized magnetic nanoparticles (FMN) constitute a further development and refinement of such systems. Organic functional groups can in fact be immobilized on the carrier nanoparticles thus generating multifunctional systems that combine in a single material the interesting properties of nanosized systems, magnetism, organic functionality and reactivity. Some of the main features of FMN are the following: (i) unlike molecular systems, which are constituted by unique entities, organically functionalized nanoparticles are usually characterized by a size distribution; (ii) they often possess acid–base properties, as the oxides used for their coating; (iii) organic functionalities grafted on their surface may show chemical behavior dependent on factors such as the length and nature of the anchoring moiety, or their chemical interaction with the surface; (iv) grafted groups have an effect on their aggregation when suspended in a solvent, therefore determining a higher or lesser degree of exposure of the organic groups; (v) they are characterized by superparamagnetism, which makes them respond to external magnetic fields. As we have pointed out, their nature of composite materials makes them interesting, but at the same time rather complex to analyze and use. Only control of such diverse properties can make them apt for optimal applications in catalysis, chemistry or biomedicine.

In the present study we focus on one particular aspect: the population density of chemically available functional groups that can be covalently linked to FeO_x/SiO_2 nanoparticles in relation to their method of preparation. We have shown in a previous contribution [29] that there exists a discrepancy between the theoretical loading of functional groups grafted on silica-coated FeO_x nanoparticles (determined by the total amount of nitrogen by elemental analysis) and the loading of functional groups that is actually available for reactivity. A stoichiometric use of organically

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functionalized magnetic nanoparticles on the other hand requires accurate information about the extent to which organic groups can modify the surface of the carrier particles [30]. The structure of the solid support plays an important role in the determination of such reactivity. Several preparation procedures for silica-coated iron oxide nanoparticles have been published in recent years, each of them yielding a material with different physical and chemical features [31]. Amongst the most diffused of such procedures are co-precipitation and coating using either sodium silicate or tetraethyl orthosilicate (TEOS) as silica precursors. The latter can yield well defined core–shell structures, with a core composed of the iron oxide particles and a shell of silica, for a diameter of 15–20 nm. This results in particles that are three to four times smaller than the ones obtained by the sodium silicate route. Such core–shell particles are better defined, smaller and less porous. Recently Teleki et al., have proposed an interesting dry synthetic approach to silica-coated iron nanoparticles, based on flame spray pyrolysis, which constitutes an alternative to classical wet synthetic approaches [32]. The resulting material shows similarities to that prepared with TEOS, having a well defined core–shell structure and similar dimensions. Among the advantages offered by this synthetic route are tight control of particles properties within a single step synthesis and the scalability of the process [33].

In the present investigation we address the question of the functionalization efficiency of the different materials mentioned above, using propylamino functional groups as organic functionalities. In particular we are interested in the grafting efficiency, that is the amount of chemically available amino groups per surface area or mass, which provides information on the real potential of such composite materials to be used as carriers of organic functions.

2. Experimental

2.1. Materials used, preparation of FeO_x nanoparticles, and silica coating

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$ >98%), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$ >99%), tetraethyl orthosilicate and sodium metasilicate (Na_2SiO_3) were purchased from Sigma–Aldrich; ammonium hydroxide (25%), hydrochloric acid (≥37%), (3-aminopropyl)trimethoxysilane (APTMS) (>97%), 1,4-bis(diphenylphosphino)butane and benzaldehyde (>99%) were purchased from Fluka; anhydrous ethanol was purchased from Scharlab S.L.; toluene from VWR International S.A.S. (99.8%) was used after drying over 4 Å molecular sieves. The iron oxide nanoparticles (IONs) were prepared by chemical coprecipitation according to the synthesis described by Liu et al. [34]. 4.3 g of $FeCl_2{\cdot}4H_2O$ and 11.68 g $FeCl_3{\cdot}6H_2O$ were dissolved in 200 ml deionized water under nitrogen atmosphere and vigorous magnetic stirring at 85 °C. 15 ml of 25% ammonium hydroxide was then rapidly poured into the solution. The solution immediately turned dark brown. After stirring the ferrofluid for 30 min. under nitrogen, the system was cooled down to room temperature. The precipitate was separated by centrifugation at 20,000 rpm, was washed several times with distilled water and dried at 70 °C overnight. As-synthesized IONs were successively coated with silica by means of two different approaches. A first one using Na_2SiO_3 as a source of silica [34]. This procedure yielded material M_1. In the second coating procedure, described by Y.P. He et al., with some modifications, TEOS was used as source of silica [35]. This procedure, applied using two different concentrations of TEOS, yielded what we designate as materials M_2 and M_3. The structural differences between the materials obtained by the two procedures will be elucidated in chapter 3.1. Following the first coating procedure, a portion (5 g) of bare iron oxide nanoparticles, synthesized as described above was covered with silica using sodium metasilicate and the following procedure; first 37% hydrochloric acid was half diluted with distilled water, and at this concentration was used to adjust the pH in the following steps; 47.50 g of Na_2SiO_3 was dissolved in distilled water and successively the pH of the solution was adjusted to 12–13 with hydrochloric acid. The IONs were then added and the suspension was ultrasonicated for 2 h. Under vigorous mechanical stirring the solution was heated to 85 °C and the pH was again adjusted to pH = 6–7 using hydrochloric acid. At this pH the suspension formed a gel and became denser. After 30 min of stirring the suspension was cooled down to r.t., the silica-coated magnetic nanoparticles were filtered off and the coating procedure was repeated. Throughout the text we will refer to the thus obtained material as M_1. Following the second coating procedure, a second portion (5 g) of superparamagnetic FeO_x nanoparticles were ultrasonically dispersed in a 240 ml ethanol and 60 ml water solution and the pH was brought to pH = 9 by means of ammonia. 33 ml of TEOS was added to the particle suspension under vigorous mechanical stirring. Iron oxide nanoparticles were coated with silica by hydrolysis of TEOS on the surfaces of the nanoparticles for 10 h, and further with hydrolysis at 50 °C for 12 h. The coated IONs were then separated by centrifugation and washed with ethanol and distilled water several times. The particles were dried at 60 °C overnight. We will refer to the thus prepared material as M_2. This latter coating procedure using TEOS was repeated with exactly the same amount of reactants, but using a much more diluted system. In fact the solvent used was a solution of 1.6 l of ethanol with 0.4 l of water, for a total of 2 l of solvent system. The higher dilution of reactants and higher dispersion of the ferrofluid are necessary for the formation of a core–shell type of coated nanoparticles. The thus obtained material will be referred to as M_3.

In addition to the materials prepared by wet chemical route, iron oxide nanoparticles coated with 23 wt.% silica by the flame-coating technique described by Teleki et al. [32] were also used for functionalization and this material is designated as M_4.

2.2. Functionalization of the silica-coated IONs

The as-prepared M_1–M_4 materials were functionalized as described in the following. 1 g of the coated nanoparticles was ultrasonically dispersed in 70 ml of toluene. 3 g of APTMS was subsequently added into the particle suspension under mechanical stirring. The solution was heated at 120 °C under reflux conditions and argon atmosphere for 17 h. The functionalized material was then washed with 40 ml of toluene and 10 ml of a 1:1 diethylether and methanol solution and further dried at 60 °C for 2 h [29]. As-prepared functionalized nanoparticles were designated $M_1(1)$, $M_2(1)$, $M_3(1)$ and $M_4(1)$, where the number in parentheses indicates a modification with a defined concentration of APTMS. In the described functionalization procedure the concentration of APTMS was 0.24 mol L^{-1}. The M_1–M_4 materials were also functionalized using higher concentrations of the same reactant. The use of a concentration of APTMS of 0.37 mol L^{-1} resulted in the functionalized materials $M_1(2)$–$M_4(2)$; the use of a concentration of APTMS of 0.49 mol L^{-1} resulted in the materials $M_1(3)$–$M_4(3)$ while the use of a concentration of APTMS of 0.61 mol L^{-1} resulted in the materials $M_1(4)$–$M_4(4)$.

2.3. Characterization techniques

The materials whose preparation has been described above have been first characterized using the classical methods for the analysis of solids. These methods included elemental analysis, powder X-ray diffraction (XRD), nitrogen adsorption–desorption measurements, thermogravimetry (TG), transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS), and magnetization