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Magnetically Separable Mesoporous Fe$_3$O$_4$/Silica Catalysts with very low Fe$_3$O$_4$ Content

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Abstract

Two magnetically separable Fe$_3$O$_4$/SiO$_2$ (aerogel and MSU-X) composites with very low Fe$_3$O$_4$ content (<1 wt%) have been successfully prepared at room temperature by co-condensation of MPTES-functionalized Fe$_3$O$_4$ nanoparticles (NPs) with a silicon alkoxide. This procedure yields a homogeneous incorporation of the Fe$_3$O$_4$ NPs on silica supports, leading to magnetic composites that can be easily recovered using an external magnetic field, despite their very low Fe$_3$O$_4$ NPs content (ca. 1 wt%). These novel hybrid Fe$_3$O$_4$/SiO$_2$ materials have been tested for the oxidation reaction of 3,3',5,5'-tetramethylbenzidine (TMB) with hydrogen peroxide showing an enhancement of the stability of the NPs in the Fe$_3$O$_4$/silica aerogel as compared to the Fe$_3$O$_4$ NPs alone, even after five catalytic cycles, no leaching or agglomeration of the Fe$_3$O$_4$/SiO$_2$ systems.

Keywords: magnetic materials, porous materials, silica, magnetite nanoparticles, peroxidase-like activity

1. Introduction

Fe$_3$O$_4$, magnetite, nanoparticles (NPs) have many applications. However, their use is limited by their tendency to agglomerate, their susceptibility to oxidation to maghemite and hematite, and their low stability in acidic media. Different strategies have been explored to protect these NPs against agglomeration and oxidation [1-9], one of the most promising being the use of silica as protecting material due to its inertness and biocompatibility, featuring excellent stability and controllable surface chemistry and porosity [1-14]. Usually, the synthesis of Fe$_3$O$_4$/silica composites is based on the coating of a magnetic core (Fe$_3$O$_4$ NPs) with a silica layer leading to core-shell morphologies [1-9]. We have recently reported the synthesis of uniform Fe$_3$O$_4$ NPs with improved stability in acidic media, using the NPs as nuclei for the Stöeber synthesis of silica [2]. Those results pointed out that Si:Fe molar ratios ≥ 20 (60 wt% Fe$_3$O$_4$ loading) are needed to get acceptable stability of the NPs. However, few examples are reported on the incorporation of a relative small amount of Fe$_3$O$_4$ NPs in silica aerogels [10] or mesoporous silica [11-14] for magnetic applications. To the best of our knowledge, a minimum loading of 5 wt% of NPs is needed to achieve magnetically separable composites [10-14].

Herein, we describe the incorporation of a very small amount of magnetite NPs (lower than 1 wt%) into two mesoporous silicas, a silica aerogel and a MSU-X type silica, via sol-gel. This method has been proved to be effective for the homogeneous incorporation of different NPs into the structure of silica, reducing the agglomeration and/or leaching of those NPs [15]. In order to test the improved stability of the Fe$_3$O$_4$ NPs once incorporated into the silica matrices, catalytic studies were carried out. Recently, several studies have proven that Fe$_3$O$_4$ NPs possess intrinsic peroxidase-like activity [16-17]. In this sense, our hybrid materials were tested as catalysts in the oxidation reaction of a typical peroxidase substrate 3,3',5,5'-tetramethylbenzidine (TMB).

Several catalytic recycles were performed to study the improved stability and recyclability of the Fe$_3$O$_4$ NPs because of their incorporation in a silica matrix.

2. Experimental part

The synthesis of the Fe$_3$O$_4$ NPs was carried out according to the previously reported procedure (see ESI for details) [18]. The Fe$_3$O$_4$/silica composites (both aerogel and MSU-X morphologies) were synthesized by co-condensation of the 3-mercaptopropyltrimethoxysilane (MPTES)-functionalized Fe$_3$O$_4$ NPs with the tetraethoxysilicate (TEOS) at room temperature. Fluoride was used as a catalyst for the hydrolysis/co-condensation of the silica sources [2] (see Scheme 1 and ESI for details).

The incorporation of the Fe$_3$O$_4$ NPs in the silica matrices was evaluated by FTIR and Raman. The content of the NPs in the final composites was analyzed by ICP-OES. XRD analysis was carried out to analyze the crystalline structure of the NPs and the structure of the siliceous composites. The particle size and shape of the Fe$_3$O$_4$ NPs and the morphology of the mesoporous materials were investigated by transmission electron microscopy (TEM). The porous texture of these samples was characterized by N$_2$ adsorption/desorption isotherms at 77 K and the textural parameters were determined using the software
package AUTOSORB. The magnetization measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer. Catalytic activity of the Fe₃O₄/silica composites was evaluated by using UV spectroscopy. All the equipment and experimental conditions used are described with more detail in the ESI.

3. Results and Discussion

Monodisperse magnetic Fe₃O₄ NPs with typical cubic spinel structure of magnetite (SG: Fd3m, JCPDS no. 89-0691) and an average crystalline size of ca. 10 nm were successfully prepared using a modified technique based on the Bradley reaction (see Fig. 1a-b) [18]. These NPs show superparamagnetic-like behavior at room temperature, with a high saturation magnetization value, ca. 53 emu/g (Fig. 1c). This value is similar to the values obtained for 10 nm Fe₃O₄ NPs synthesized by co-precipitation and higher than NPs synthesized by solvothermal synthesis [2,18-20].

![Fig. 1. a) XRD pattern, b) a representative TEM image (a Fe₃O₄ NPs suspension in EtOH, scale bar = 10 nm), c) the corresponding histogram representing NPs size distribution from the analysis of at least 100 nanoparticles in TEM images and d) magnetization (M) vs. applied field (H) isotherm at 300 K of the synthesized Fe₃O₄ NPs.](image)

The incorporation of the Fe₃O₄ NPs on the silica matrices using the experimental procedure described in Scheme 1 yields brown mesoporous hybrid materials with a homogeneous distribution of the Fe₃O₄ NPs and good textural properties. There is no observation of metal agglomerates by TEM which is consistent with good dispersion of these NPs during their immobilization (Fig. 2, bottom and Fig. S3). TEM, gas adsorption and XRD analyses confirm the non-ordered worm-like mesoporous structure of both composites (Fig. 2 and Fig. S2-S4). BET surface area of the silica aerogel (820 m²/g) is significantly larger than that of the Fe₃O₄/silica aerogel (330 m²/g) suggesting that the presence of the NPs instead of the solvent may decrease the porosity of the sample in absence of any surfactant. For the Fe₃O₄/MSU-X composite, however, both the pore volume (0.78 cm³/g) and the surface area (860 m²/g) are slightly higher than the ones corresponding to the MSU-X silica (0.68 cm³/g and 815 m²/g, respectively). These data suggest that the growth of the silica framework takes place around the functionalized NPs, as described in the Scheme 1, and the textural properties of both MSU-X-based materials are similar.
due to the presence of the surfactant during the whole synthesis process and the low NPs content [15,20].

The incorporation of the functionalized Fe$_3$O$_4$ NPs into the mesoporous silica support was confirmed by FTIR and Raman spectroscopies. The spectra shown in Fig. 2 support the co-condensation of the both silica sources TEOS and MPTES (Si-O-Si). Interestingly, the S-H stretching absorption of MPTES (strong band around 2500 cm$^{-1}$) disappears in the hybrid systems, suggesting the anchoring of Fe$_3$O$_4$ NPs via the thiol group (Fe-S bond), as indicated in the Scheme 1 (see also ESI, section 6) [22].

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![Scheme 1. Schematic representation of the preparation of the Fe$_3$O$_4$/silica aerogel and the Fe$_3$O$_4$/MSU-X composites. The diagram is not to scale.](image)

Fig. 3a and Fig. S5 show magnetic hysteresis loops at 300 K and 10 K, respectively, for both Fe$_3$O$_4$/silica composites. Both samples exhibit zero coercivity and a superparamagnetic behavior at 300 K, which is consistent with the splitting of the ZFC and FC curves at lower temperatures (Fig. S5a and ESI). The coercivity at 10 K is approximately 150 Oe and 280 Oe for the Fe$_3$O$_4$/silica aerogel and the Fe$_3$O$_4$/MSU-X, respectively. Using the saturation magnetization of
the silica-free magnetite NPs at 300 K (53 emu/g), the content of magnetite was estimated to be 0.34 wt% and 0.62 wt% for the Fe$_3$O$_4$/silica aerogel and the Fe$_3$O$_4$/MSU-X, respectively (lower than the nominal 1 wt%). Besides the low NPs content, the Fe$_3$O$_4$/silica composites are readily magnetized and demagnetized. As shown in Fig. 3b, both magnetic composites can be rapidly separated (ca. 10 seconds) and re-dispersed leading to a stable colloidal suspension (Fig. S5b and movie, Fig. S6). These materials thus show outstanding characteristics for applications in magnetically removable catalysts and adsorbents.

The catalytic performance of both composites as compared to that of the Fe$_3$O$_4$ NPs was tested following the catalytic oxidation of TMB by H$_2$O$_2$. The TMB oxidation produces an intense blue color (652 nm) which was monitored by UV-vis over time (Fig 4a). The reaction rates (Fig. 4b) of the Fe$_3$O$_4$ NPs and both composites are very similar, indicating that the Fe$_3$O$_4$ NPs maintain their
catalytic activity when incorporated onto the silica and that they are freely accessible to the reactants. The stability of the Fe₃O₄ NPs alone and once incorporated in the MSU-X silica (Fe₃O₄/MSU-X composite) is very low as the activity of these catalysts greatly decreases after the first catalytic run, due to their leaching and/or aggregation (see Fig. 4c for the NPs alone). Interestingly, the Fe₃O₄/silica aerogel shows outstanding Fe₃O₄ NPs stability. The Fe₃O₄ NPs can keep their activity almost unchanged even after five recycling tests in the Fe₃O₄/silica aerogel composite (Fig 4d) and the solution remains clear indicating negligible NPs leaching. In this composite, the NPs are trapped by the silica framework thus providing more stability than in the case of MSU-X-based system, where the high surface area allows higher mobility of the Fe₃O₄ NPs. The increase of the catalytic activity after the first run can be attributed to the adsorption of TMB in the porous of the Fe₃O₄/silica aerogel during the first run.

![Figure 4](image)

Fig. 4. (a) UV-vis spectra of the reaction solution in the catalytic oxidation reaction of TMB with H₂O₂ using the Fe₃O₄/silica aerogel as catalyst. (b) Maximum absorbance (652 nm) over time reaction using the Fe₃O₄ NPs (black), the Fe₃O₄/silica aerogel (red) and the Fe₃O₄/MSU-X composite (blue) as catalysts. Relative activity of the peroxidase-like activity during 5 catalytic cycles using (c) the Fe₃O₄ NPs and (d) the Fe₃O₄/silica aerogel as catalysts.

4. Conclusions
Two magnetically separable Fe₃O₄/silica catalysts (MSU-X and aerogel morphologies) have been synthesized by co-condensation of the MPTES-functionalized Fe₃O₄ NPs with a silicon alkoxide. Despite the low content of NPs (lower than 1 wt%) incorporated into the silica matrices, both composites are readily magnetized/demagnetized, and are effectively separated from the colloidal suspensions using a neodymium magnet. Their catalytic performance was studied in the catalytic oxidation of TMB with H₂O₂ showing excellent activity, similar to the Fe₃O₄ NPs which indicates that they are accessible and still catalytically active when incorporated into the silica frameworks. The Fe₃O₄ NPs are greatly stabilized by the silica matrix in the Fe₃O₄/silica aerogel composite evidencing high catalytic activity after 5 cycles.

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Notes and references
Highlights

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- An innovative way to prepare magnetically separable composites with < 1wt% NPs
- The Fe₃O₄/silica composites are readily magnetized/demagnetized
- The Fe₃O₄/silica composites can be easily recovered using an external magnetic field
- Excellent catalytic performance and recyclability despite the low Fe₃O₄ NPs content

Graphical abstract

Magnetically Separable Mesoporous Fe₃O₄/Silica Catalysts with very low Fe₃O₄ Content
Legend: Novel magnetically separable mesoporous silica-based composites with very low magnetite content

Figure: Printed version

Figure: On-line version

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