

Magnetically Separable Mesoporous Fe<sub>3</sub>O<sub>4</sub>/Silica Catalysts with very low Fe<sub>3</sub>O<sub>4</sub> Content

A. Grau-Atienza, E. Serrano, N. Linares, P. Svedlindh, G. Seisenbaeva, J. García-Martínez



PII: S0022-4596(15)30291-7  
DOI: <http://dx.doi.org/10.1016/j.jssc.2015.12.026>  
Reference: YJSSC19215

To appear in: *Journal of Solid State Chemistry*

Received date: 15 September 2015

Revised date: 1 December 2015

Accepted date: 22 December 2015

Cite this article as: A. Grau-Atienza, E. Serrano, N. Linares, P. Svedlindh, G. Seisenbaeva and J. García-Martínez, Magnetically Separable Mesoporous Fe<sub>3</sub>O<sub>4</sub>/Silica Catalysts with very low Fe<sub>3</sub>O<sub>4</sub> Content, *Journal of Solid State Chemistry*, <http://dx.doi.org/10.1016/j.jssc.2015.12.026>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Magnetically Separable Mesoporous Fe<sub>3</sub>O<sub>4</sub>/Silica Catalysts with very low Fe<sub>3</sub>O<sub>4</sub> Content

A. Grau-Atienza,<sup>a</sup> E. Serrano,<sup>a</sup> N. Linares,<sup>a</sup> P. Svedlindh,<sup>b</sup> G. Seisenbaeva<sup>c\*</sup> and J. García-Martínez<sup>a\*</sup>

<sup>a</sup> Molecular Nanotechnology Lab., Department of Inorganic Chemistry, University of Alicante, Carretera San Vicente s/n, E-03690, Alicante, Spain. E-mail: [j.garcia@ua.es](mailto:j.garcia@ua.es), URL: [www.nanomol.es](http://www.nanomol.es).

<sup>b</sup> Department of Engineering Sciences, Uppsala University, Box 534, SE-75121 Uppsala, Sweden.

<sup>c</sup> Department of Chemistry and Biotechnology, BioCenter SLU, Box 7015, SE-75007 Uppsala, Sweden. E-mail: [Gulaim.Seisenbaeva@slu.se](mailto:Gulaim.Seisenbaeva@slu.se).

\* Corresponding author: J. García-Martínez, phone number: +34 965903400 ext. 2224, fax: +34 965903454, e-mail: [j.garcia@ua.es](mailto:j.garcia@ua.es). G. Seisenbaeva, phone number +46 018-672994, +46 073-6143161, fax: +46 18672000, e-mail: [Gulaim.Seisenbaeva@slu.se](mailto:Gulaim.Seisenbaeva@slu.se)

## Abstract

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

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

## 1. Introduction

$\text{Fe}_3\text{O}_4$ , 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  $\text{Fe}_3\text{O}_4$ /silica composites is based on the coating of a magnetic core ( $\text{Fe}_3\text{O}_4$  NPs) with a silica layer leading to core-shell morphologies [1-9]. We have recently reported the synthesis of uniform  $\text{Fe}_3\text{O}_4$  NPs with improved stability in acidic media, using the NPs as nuclei for the Stöber synthesis of silica [2]. Those results pointed out that Si:Fe molar ratios  $\geq 20$  (60 wt%  $\text{Fe}_3\text{O}_4$  loading) are needed to get acceptable stability of the NPs. However, few examples are reported on the incorporation of a relative small amount of  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs once incorporated into the silica matrices, catalytic studies were carried out. Recently, several studies have proven that  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs because of their incorporation in a silica matrix.

## 2. Experimental part

The synthesis of the  $\text{Fe}_3\text{O}_4$  NPs was carried out according to the previously reported procedure (see ESI for details) [18]. The  $\text{Fe}_3\text{O}_4$ /silica composites (both aerogel and MSU-X morphologies) were synthesized by co-condensation of the 3-mercaptopropyltriethoxysilane (MPTES)-functionalized  $\text{Fe}_3\text{O}_4$  NPs with the tetraethylorthosilicate (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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs and the morphology of the mesoporous materials were investigated by transmission electron microscopy (TEM). The porous texture of these samples was characterized by  $\text{N}_2$  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  $\text{Fe}_3\text{O}_4$ /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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  NPs synthesized by co-precipitation and higher than NPs synthesized by solvothermal synthesis [2,18-20].

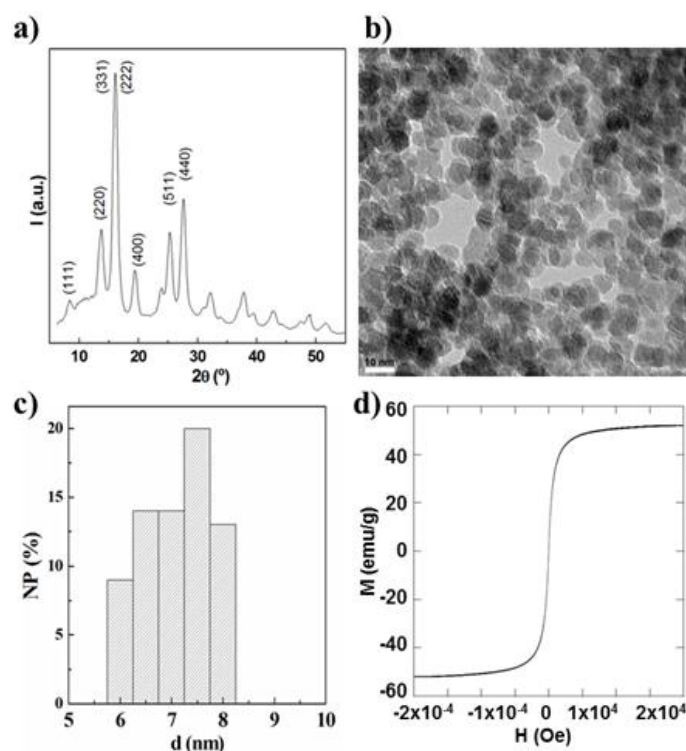


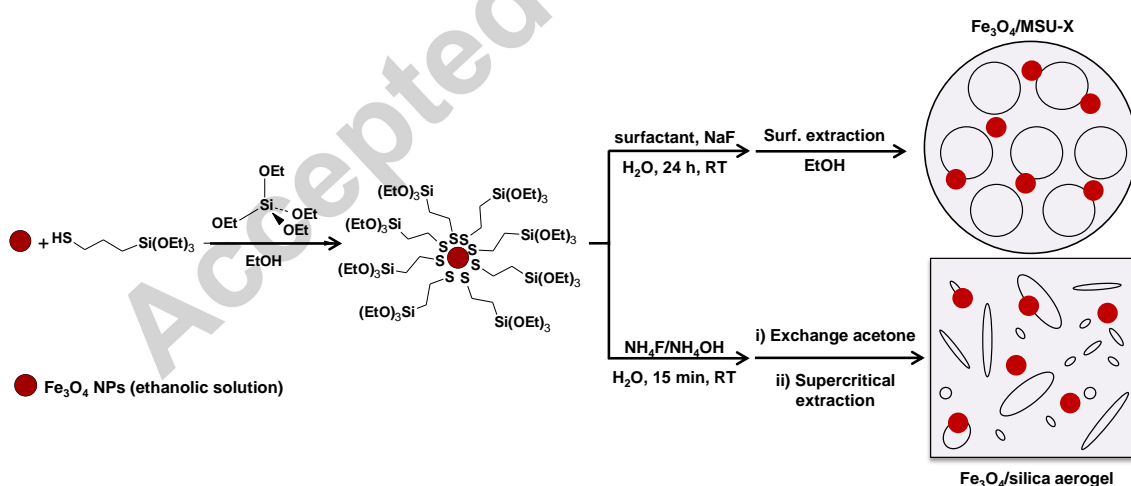
Fig. 1. a) XRD pattern, b) a representative TEM image (a  $\text{Fe}_3\text{O}_4$  NPs suspension in EtOH, scale bar = 10 nm), c) the corresponding histogram representing NPs size distribution from the analysis of at least 100 nanoparticles in TEM images and d) magnetization (M) vs. applied field (H) isotherms at 300 K of the synthesized  $\text{Fe}_3\text{O}_4$  NPs.

The incorporation of the  $\text{Fe}_3\text{O}_4$  NPs on the silica matrices using the experimental procedure described in Scheme 1 yields brown mesoporous hybrid materials with a homogeneous distribution of the  $\text{Fe}_3\text{O}_4$  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  $\text{m}^2/\text{g}$ ) is significantly larger than that of the  $\text{Fe}_3\text{O}_4$ /silica aerogel (330  $\text{m}^2/\text{g}$ ) 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  $\text{Fe}_3\text{O}_4$ /MSU-X composite, however, both the pore volume (0.78  $\text{cm}^3/\text{g}$ ) and the surface area (860  $\text{m}^2/\text{g}$ ) are slightly higher than the ones corresponding to the MSU-X silica (0.68  $\text{cm}^3/\text{g}$  and 815  $\text{m}^2/\text{g}$ , 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  $\text{Fe}_3\text{O}_4$  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  $2500\text{ cm}^{-1}$ ) disappears in the hybrid systems, suggesting the anchoring of  $\text{Fe}_3\text{O}_4$  NPs via the thiol group (Fe-S bond), as indicated in the Scheme 1 (see also ESI, section 6) [22].

The incorporation of the  $\text{Fe}_3\text{O}_4$  NPs on the silica matrices using the experimental procedure described in Scheme 1 yields brown mesoporous hybrid materials with a homogeneous distribution of the  $\text{Fe}_3\text{O}_4$  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 ( $820\text{ m}^2/\text{g}$ ) is significantly larger than that of the  $\text{Fe}_3\text{O}_4$ /silica aerogel ( $330\text{ m}^2/\text{g}$ ) 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  $\text{Fe}_3\text{O}_4$ /MSU-X composite, however, both the pore volume ( $0.78\text{ cm}^3/\text{g}$ ) and the surface area ( $860\text{ m}^2/\text{g}$ ) are slightly higher than the ones corresponding to the MSU-X silica ( $0.68\text{ cm}^3/\text{g}$  and  $815\text{ m}^2/\text{g}$ , 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  $\text{Fe}_3\text{O}_4$  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  $2500\text{ cm}^{-1}$ ) disappears in the hybrid systems, suggesting the anchoring of  $\text{Fe}_3\text{O}_4$  NPs via the thiol group (Fe-S bond), as indicated in the Scheme 1 (see also ESI, section 6) [22].



Scheme 1. Schematic representation of the preparation of the  $\text{Fe}_3\text{O}_4$ /silica aerogel and the  $\text{Fe}_3\text{O}_4$ /MSU-X composites. The diagram is not to scale.

Fig. 3a and Fig. S5 show magnetic hysteresis loops at 300 K and 10 K, respectively, for both  $\text{Fe}_3\text{O}_4$ /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  $\text{Fe}_3\text{O}_4$ /silica aerogel and the  $\text{Fe}_3\text{O}_4$ /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  $\text{Fe}_3\text{O}_4$ /silica aerogel and the  $\text{Fe}_3\text{O}_4$ /MSU-X, respectively (lower than the nominal 1 wt%). Besides the low NPs content, the  $\text{Fe}_3\text{O}_4$ /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.

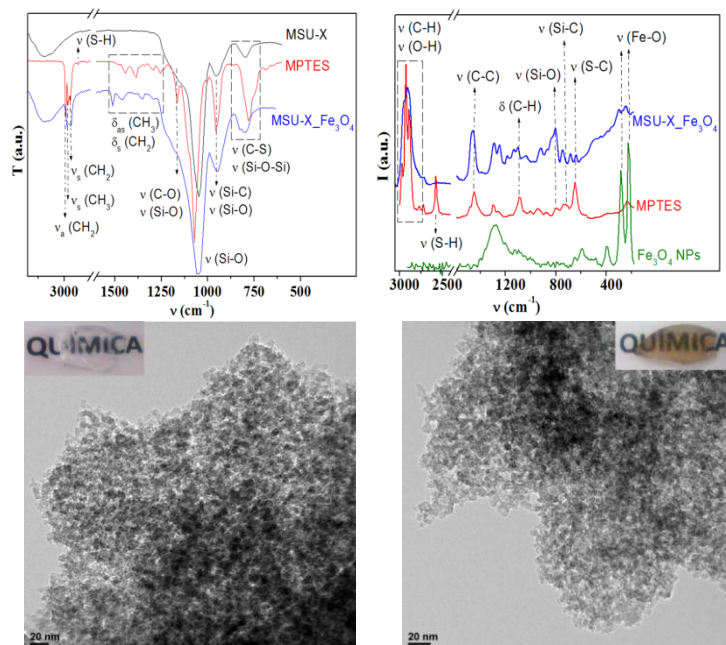


Fig. 2. (Up) FTIR (left) and Raman (right) spectra of the  $\text{Fe}_3\text{O}_4$ /MSU-X composite. For comparison purposes, FTIR spectrum of the  $\text{Fe}_3\text{O}_4$  NPs-free MSU-X silica and the Raman spectrum of the  $\text{Fe}_3\text{O}_4$  NPs are also included. (Bottom) Representative TEM micrographs of the silica aerogel before (left) and after ( $\text{Fe}_3\text{O}_4$ /silica aerogel, right) the incorporation of the NPs. Insets show the photographs of the as-synthesized gels.

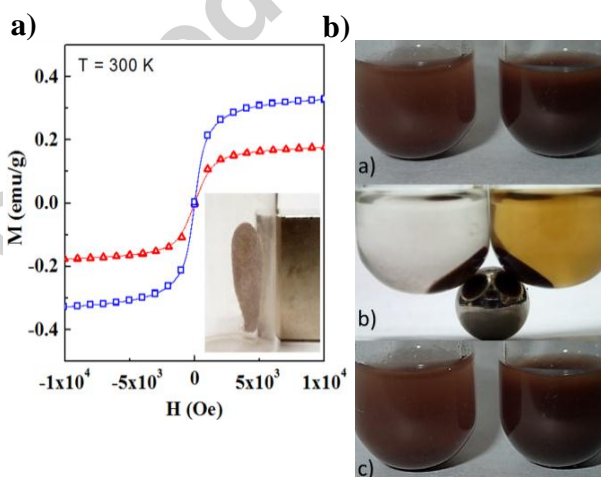


Fig. 3. (a) Magnetization versus field at 300 K. curves of the  $\text{Fe}_3\text{O}_4$ /silica aerogel (red triangles) and the  $\text{Fe}_3\text{O}_4$ /MSU-X (blue squares) composites. The inset in (a) shows a photograph of the  $\text{Fe}_3\text{O}_4$ /MSU-X composite which is being attracted by a magnet after 1 min of contact time. (b) Photographs of the  $\text{Fe}_3\text{O}_4$  NPs (right) and the  $\text{Fe}_3\text{O}_4$ /MSU-X (left) dispersed in ethanol: (a) before being attracted by a magnet, (b) being attracted by a magnet, and (c) after removing the magnet (video in SI).

The catalytic performance of both composites as compared to that of the  $\text{Fe}_3\text{O}_4$  NPs was tested following the catalytic oxidation of TMB by  $\text{H}_2\text{O}_2$ . 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  $\text{Fe}_3\text{O}_4$  NPs and both composites are very similar, indicating that the  $\text{Fe}_3\text{O}_4$  NPs maintain their

catalytic activity when incorporated onto the silica and that they are freely accessible to the reactants. The stability of the  $\text{Fe}_3\text{O}_4$  NPs alone and once incorporated in the MSU-X silica ( $\text{Fe}_3\text{O}_4/\text{MSU-X}$  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  $\text{Fe}_3\text{O}_4/\text{silica}$  aerogel shows outstanding  $\text{Fe}_3\text{O}_4$  NPs stability. The  $\text{Fe}_3\text{O}_4$  NPs can keep their activity almost unchanged even after five recycling tests in the  $\text{Fe}_3\text{O}_4/\text{silica}$  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  $\text{Fe}_3\text{O}_4$  NPs. The increase of the catalytic activity after the first run can be attributed to the adsorption of TMB in the porous of the  $\text{Fe}_3\text{O}_4/\text{silica}$  aerogel during the first run.

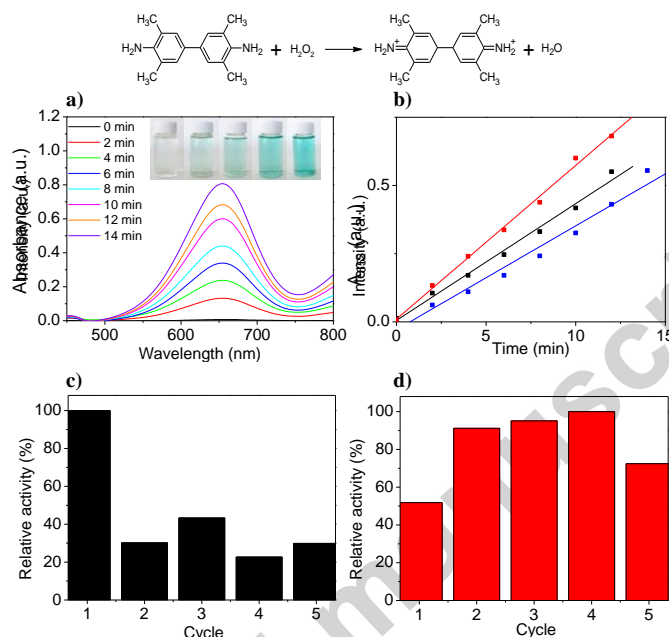


Fig. 4. (a) UV-vis spectra of the reaction solution in the catalytic oxidation reaction of TMB with  $\text{H}_2\text{O}_2$  using the  $\text{Fe}_3\text{O}_4/\text{silica}$  aerogel as catalyst. (b) Maximum absorbance (652 nm) over time reaction using the  $\text{Fe}_3\text{O}_4$  NPs (black), the  $\text{Fe}_3\text{O}_4/\text{silica}$  aerogel (red) and the  $\text{Fe}_3\text{O}_4/\text{MSU-X}$  composite (blue) as catalysts. Relative activity of the peroxidase-like activity during 5 catalytic cycles using (c) the  $\text{Fe}_3\text{O}_4$  NPs and (d) the  $\text{Fe}_3\text{O}_4/\text{silica}$  aerogel as catalysts.

#### 4. Conclusions

Two magnetically separable  $\text{Fe}_3\text{O}_4/\text{silica}$  catalysts (MSU-X and aerogel morphologies) have been synthesized by co-condensation of the MPTES-functionalized  $\text{Fe}_3\text{O}_4$  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  $\text{H}_2\text{O}_2$  showing excellent activity, similar to the  $\text{Fe}_3\text{O}_4$  NPs which indicates that they are accessible and still catalytically active when incorporated into the silica frameworks. The  $\text{Fe}_3\text{O}_4$  NPs are greatly stabilized by the silica matrix in the  $\text{Fe}_3\text{O}_4/\text{silica}$  aerogel composite evidencing high catalytic activity after 5 cycles.

#### Acknowledgements

We thank the Spanish MINECO (Project CTQ2014-60017-R) for financial support. E.S. acknowledges financial support from GV (GV/2014/093) and UA (GRE12-39). G.S. expresses her gratitude to the Swedish Research Council for support to the project "Molecular precursors and molecular models of nanoporous materials".

#### Notes and references



Electronic Supplementary Information (ESI) available: Experimental procedures and additional characterization results. See DOI: xxxxx

- 1 X. Zhao, Y. Shi, T. Wang, Y. Cai, G. Jiang, *J. Chromatogr. A* 2008, 1188, 140; b) M. Kokate, K. Garadkar, A. Gole, *J. Mater. Chem. A* 2013, 1, 2022.
- 2 R.P. Pogorilyi, I.V. Melnyk, Y.L. Zub, S. Carlson, G. Daniel, P. Svedlindh, G.A. Seisenbaeva, V.G. Kessler, *RSC Adv.*, 2014, 4, 22606.
- 3 F. Fajaro, H. Setyawan, A. Nur, I. W. Lenggoro, *Adv. Powder Technol.*, 2013, 24, 507.
- 4 F. Dang, N. Enomoto, J. Hojo and K. Enpuku, *Ultrason. Sonochem.*, 2010, 17, 193.
- 5 a) B. P. Wu, J. H. Zhu and Z. H. Xu, *Adv. Funct. Mater.*, 2004, 14, 345; b) D. Lai, L. Deng, B. Liao, Q. Guo, Y. Fu, *ChemSusChem* 2011, 4, 55; c) T. Sen, I.J. Bruce, *Microp. Mesop. Mater.* 2009, 120, 246.
- 6 W. Zhao, J. L. Gu, L. X. Zhang, H. R. Chen and J. L. Shi, *J. Am. Chem. Soc.*, 2005, 127, 8916.
- 7 J. Kim, J. E. Lee, J. Lee, J. H. Yu, B. C. Kim, K. An, Y. Hwang, C. H. Shin, J. G. Park, J. Kim and T. Hyeon, *J. Am. Chem. Soc.*, 2006, 128, 688.
- 8 a) N. Saadatjoo, M. Golshekan, S. Shariati, H. Kefayati, P. Azizi, *J. Mol. Cat.*, 2013, 377, 173; b) A. Kraus, K. Jainae, F. Unob, N. Sukpirom, *J. Coll. Int. Sci.*, 2009, 338, 359; c) O. Hakami, Y. Zhang, C.J. Banks, *Water Res.*, 2012, 46, 3913.
- 9 J. Chung, J. Chun, J. Lee, S.H. Lee, Y.J. Lee, S.W. Hong, *J. Hazard. Mater.*, 2012, 239-240, 183.
- 10 LL. Casas, A. Roig, E. Rodríguez, E. Molins, J. Tejada, J. Sort, *J. Non-Cryst. Solids*, 2001, 285, 37.
- 11 N.A. Fellenz, S.G. Marchetti, J.F. Bengoa, R.C. Mercader, S.J. Stewart, *J. Mag. Magn. Mater.* 2006, 308, 30.
- 12 K.M. Ponvel, Y.-H. Kim, C.-H. Lee, *Mater. Chem. Phys.* 2010, 122, 397.
- 13 M. Anbia, K. Kargosha, S. Khoshbooei, *Chem. Eng. Res. Des.* 2015, 93, 779.
- 14 S. Huang, C. Li, Z. Cheng, Y. Fan, P. Yang, C. Zhang, K. Yang, *J. Coll. Int. Sci.*, 2012, 376, 312.
- 15 E. Serrano, N. Linares, J. García-Martínez et al. *Chem. Cat. Chem.*, 2013, 4, 825
- 16 a) H. Wei, E. Wang, *Chem. Soc. Rev.*, 2013, 42, 6060; b) J. W. Zhang, H. T. Zhang, Z. Y. Du, X. Wang, S. H. Yu, H. L. Jiang, *Chem. Commun.*, 2014, 50, 1092.
- 17 X. He, L. Tan, D. Chen, X. Wu, X. Ren, Y. Zhang, X. Meng, F. Tang, *Chem. Commun.*, 2013, 49, 4643.
- 18 K. Wilkinson, B. Ekstrand-Hammarstrom, L. Ahlinder, K. Guldevall, R. Pazik, L. Kepinski, K.O. Kvashnina, S.M. Buterin, H. Brismar, B. Onfelt, L. Osterlund, G.A. Seisenbaeva, V.G. Kessler, *Nanoscale*, 2012, 4, 7383.
- 19 M. Fang, V. Strom, R.T. Olsson, L. Belova, K.V. Rao, *Nanotechnology* 2012, 23, 145601.
- 20 A. Hilonga, J. K. Kim, P. B. Sarawade, H. T. Kim, *J. Alloys Compd.* 2009, 487, 744.
- 21 a) V. Polshettiwar, B. Baruwati and R.S. Varma, *Chem. Commun.* 2009, 1837–1839; b) S.W. Raso, P.L. Clark, C. Haase-Pettingell, J. King, G.J. Thomas, Jr, *J. Mol. Biol.* 2001, 307, 899.

## Highlights

### Magnetically Separable Mesoporous Fe<sub>3</sub>O<sub>4</sub>/Silica Catalysts with very low Fe<sub>3</sub>O<sub>4</sub> Content

A. Grau-Atienza,<sup>a</sup> E. Serrano,<sup>a</sup> N. Linares,<sup>a</sup> P. Svedlindh,<sup>b</sup> G. Seisenbaeva<sup>c\*</sup> and J. García-Martínez<sup>a\*</sup>

- An innovative way to prepare magnetically separable composites with < 1wt% NPs
- The Fe<sub>3</sub>O<sub>4</sub>/silica composites are readily magnetized/demagnetized
- The Fe<sub>3</sub>O<sub>4</sub>/silica composites can be easily recovered using an external magnetic field
- Excellent catalytic performance and recyclability despite the low Fe<sub>3</sub>O<sub>4</sub> NPs content

## Graphical abstract

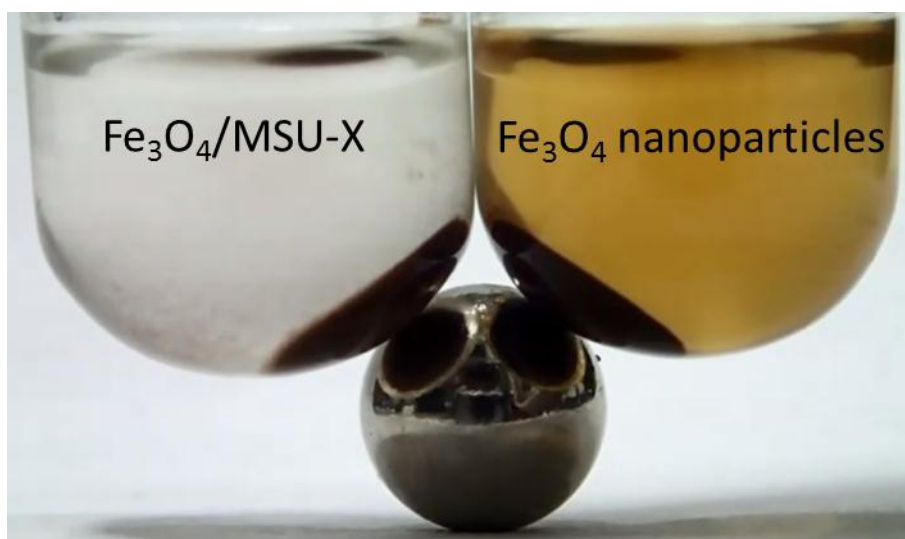
### Magnetically Separable Mesoporous Fe<sub>3</sub>O<sub>4</sub>/Silica Catalysts with very low Fe<sub>3</sub>O<sub>4</sub> Content



A. Grau-Atienza,<sup>a</sup> E. Serrano,<sup>a</sup> N. Linares,<sup>a</sup> P. Svedlindh,<sup>b</sup> G. Seisenbaeva<sup>c\*</sup> and J. García-Martínez<sup>a\*</sup>

**Legend:** Novel magnetically separable mesoporous silica-based composites with very low magnetite content

**Figure: Printed version**



**Figure: On-line version**



GraphAbstract\_Movie\_xvid.avi