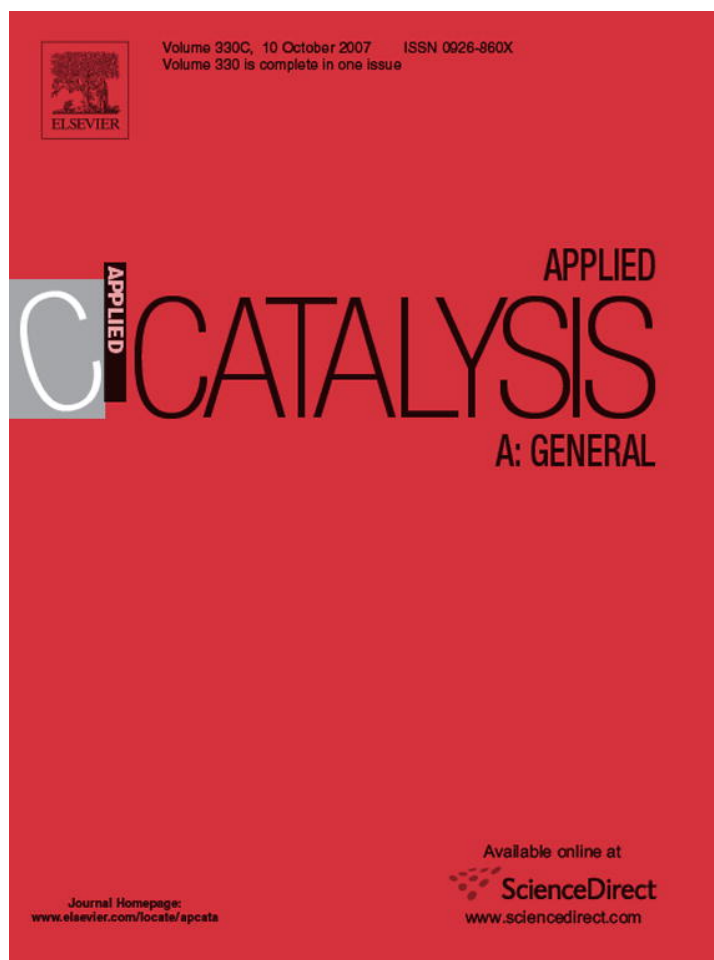


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article was published in an Elsevier journal. The attached copy is furnished to the author for non-commercial research and education use, including for instruction at the author's institution, sharing with colleagues and providing to institution administration.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



## A magnetically recoverable scavenger for palladium based on thiol-modified magnetite nanoparticles

Liane M. Rossi <sup>a,b,\*</sup>, Lucas L.R. Vono <sup>a</sup>, Fernanda P. Silva <sup>a</sup>,  
Pedro K. Kiyohara <sup>c</sup>, Evandro L. Duarte <sup>c</sup>, Jivaldo R. Matos <sup>a</sup>

<sup>a</sup> *Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Preste, 748 São Paulo 05508-000, SP, Brazil*

<sup>b</sup> *CEPEMA-USP, Cubatão, SP, Brazil*

<sup>c</sup> *Institute of Physics, University of São Paulo, Rua do Matão Travessa R, 187 São Paulo 05508-090, SP, Brazil*

Received 17 April 2007; received in revised form 6 July 2007; accepted 13 July 2007

Available online 19 July 2007

### Abstract

Modification of magnetite nanoparticles surfaces with thiol groups leads to a magnetically recoverable scavenger for metals. The magnetic solid removed Pd<sup>2+</sup> ions from aqueous and non-aqueous solutions, and it was easily recovered with a magnet with no need of additional separation procedures. Scavenging efficiency of >99% was demonstrated. The magnetically recovered solid containing palladium-catalyzed the conversion of cyclohexene to cyclohexane for at least five successive reactions with TON ~800 each. Magnetic separation capabilities greatly facilitate the recovery of the metal scavenger and catalyst.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Magnetic nanoparticles; Functionalization; Scavenger; Metals; Palladium; Hydrogenation

### 1. Introduction

Magnetite, Fe<sub>3</sub>O<sub>4</sub>, is a magnetic iron oxide that has a superparamagnetic behavior under certain particle size, meaning that it can be easily magnetized with an external magnetic field and redispersed immediately once the magnet field is removed [1]. Magnetic separation technology, using magnetic nanoparticles, is far known in biomedical application as a quick and easy method for sensitive and reliable capture of specific proteins, genetic material and other biomolecules [2–4]. This non-laborious, cheap and often highly scalable separation technique, that offers many advantages over filtration and other purification methods, is much less used in the recovery of valuables or catalysts [5,6]. We here investigate the use of magnetic nanoparticles with appropriated chemical surface modification for recovery of valuables, such as metals or residual catalysts, using magnetic separation techniques. The

removal and recovery of residual metals from solutions and organic products have become important issues, due to the high cost of noble metals and the decreasing regulatory limit of this kind of residues in food and drug products [7]. The use of palladium-catalyzed reactions in organic synthesis, including reactions involving C–C and C–X bond formations as well as hydrogenations, has been well known [8–10]. Although palladium is recognized as an efficient and selective catalyst, removing it from the product is a drawback of practical use of homogeneous transition metal catalysis in industry. For example, active pharmaceutical products must contain palladium levels below a few parts per million [11]. General techniques for reducing the concentration of Pd to acceptable levels are distillation or crystallization, not very often applicable, and extraction or chromatography, which can be labor and solvent-consuming procedures. A very promising technique for purifying Pd-catalyzed reactions is the use of scavenging agents for metal adsorption by means of organic or inorganic solid supports, followed by filtration steps [7]. Attention has been paid to the preparation of scavengers for palladium, which includes several functionalized polymeric resins containing chelating polyamines [12], phosphines [13], 2,4,6-trimercaptotriazine [14] and dithiothreitol [15], or glass

\* Corresponding author at: Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Preste, 748 São Paulo 05508-000, SP, Brazil.

Tel.: +55 11 30912181; fax: +55 11 38155579.

E-mail address: [lrossi@iq.usp.br](mailto:lrossi@iq.usp.br) (L.M. Rossi).

beads modified with sulfonated triphenylphosphine analogues [16], to say some. Mesoporous silica modified with thiol groups has also been shown as a remarkable scavenger for palladium [17–19]. The palladium-loaded solid obtained by Crudden et al. [17] was also used as a heterogeneous and reusable catalyst for coupling reactions with no leaching of palladium to products (<3 ppb of Pd in the filtrates). All these adsorbents remove palladium efficiently from organic and aqueous solutions by filtration or centrifugation. Herein, we report the use of thiol-functionalized magnetic nanoparticles as a magnetically recoverable scavenger for palladium, which is also active as a catalyst for alkenes hydrogenation.

## 2. Experimental

### 2.1. Materials and instrumentation

Iron(II) chloride hydrate, iron(III) chloride hydrate, palladium(II) chloride, palladium(II) acetate, 3-mercaptopropionic acid and cyclohexene were purchased from Aldrich Chemical Co. Gas chromatography analyses were performed on a Shimadzu GC 17A, equipped with a 30 m capillary column with a dimethylpolysiloxane stationary phase, using the following parameters: initial temperature, 50 °C; initial time, 5 min; ramp, 10 °C min<sup>-1</sup>; final temperature, 250 °C; final time, 5 min; injector and detector temperature, 250 °C; injection volume, 2 µL.

Transmission electron microscopy (TEM) micrographs were taken on a Philips CM 200 microscope operating at an accelerating voltage of 200 kV. The samples for TEM were prepared by dispersion of the nanoparticles in toluene solution at room temperature and then collected on a carbon-coated copper grid.

Thermogravimetry (TG) curves were obtained with a thermobalance model TGA 50 (Shimadzu) in the temperature range of 25–700 °C, using Pt crucibles with ~5 mg of samples, under dynamic N<sub>2</sub> atmosphere (50 mL min<sup>-1</sup>) and heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) curves were obtained in a DSC-50 cell (Shimadzu), under dynamic N<sub>2</sub> atmosphere (50 mL min<sup>-1</sup>), heating rate of 10 °C min<sup>-1</sup> in the temperature range from 25 to 600 °C using Al crucibles with 2 mg of samples. The DSC cell was calibrated with indium (m.p. 156.6 °C;  $\Delta H_{\text{fus}} = 28.54 \text{ J g}^{-1}$ ) and zinc (m.p. 419.6 °C).

A VSM was used to obtain the magnetization versus magnetic field loop at room temperature up to  $H = 20 \text{ kOe}$ . The apparatus was calibrated with a Ni pattern. The magnetization measurements were carried out on a known quantity of powder samples, slightly pressed and conditioned in a cylindrical holders of Lucite.

### 2.2. Synthesis of oleic acid coated magnetic nanoparticles (FF)

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by co-precipitation method [20]: 10 mL of an aqueous solution of FeCl<sub>3</sub> (1 mol L<sup>-1</sup>) were mixed with 2.5 mL of FeCl<sub>2</sub> (2 mol L<sup>-1</sup>)

dissolved in HCl 2 mol L<sup>-1</sup>. Both solutions were freshly prepared with deoxygenated water before use. Immediately after mixed under nitrogen, the solution containing the iron chlorides was added to 125 mL of ammonium hydroxide solution (0.7 mol L<sup>-1</sup>, deoxygenated water) under vigorous mechanical stirring (10,000 rpm, Ultra-Turrax T18 Homogenizer, IKA Works) under nitrogen atmosphere. After 30 min, the black precipitated formed was separated magnetically and redispersed in a new portion of water (3 × 250 mL). Oleic acid (5 mmol) dissolved in 5 mL of acetone was drop wise added. The solution was heated at 80 °C for 30 min under stirring. The resulting precipitate was separated magnetically, washed with acetone and redissolved in 50 mL of toluene. The resulting solution was centrifuged at 2000 rpm for 1 h to separate any precipitates and the supernatant collected. The solid content is the resulting solution is 25 g L<sup>-1</sup>.

### 2.3. Preparation of thiol-modified magnetic particles (FFMPA)

To 90 mL toluene solution containing magnetic particles was added 54 µL of 3-mercaptopropionic acid (MPA) dissolved in toluene. The solution was heated at 80 °C for 30 min under stirring. The resulting precipitate, no longer soluble in toluene, was washed with acetone and isolated as a powder. Sulfur contents analyzed by ICP-AES: 1.30%

### 2.4. Scavenging experiments

Dispersions of the magnetic solid FFMPA (25 mg) were stirred with palladium(II) solutions prepared from PdCl<sub>2</sub> and Pd(OAc)<sub>2</sub>. An aqueous stock solution was prepared dissolving PdCl<sub>2</sub> (2.6 mg) by addition of NaCl in distilled water (4 mL) and heating. A toluene stock solution was prepared dissolving Pd(OAc)<sub>2</sub> (5 mg) in toluene (10 mL) under inert atmosphere. Solutions of different concentrations of palladium were prepared and treated with FFMPA. The magnetic material was recovered from the solution with a permanent magnet and the palladium concentration in the supernatant solution was determined by ICP-AES.

### 2.5. Preparation of the catalyst (FFMPAPd)

To a solution containing 520 mg of FFMPA was added 18.7 mg of PdCl<sub>2</sub> (PdCl<sub>2</sub> was dissolved in water by addition of NaCl and heating). After stirring overnight at room temperature, the resulting solid was separated magnetically, washed with acetone and isolated as a powder.

### 2.6. Hydrogenation experiments

The catalytic reactions were carried out in a 100 mL stainless steel autoclave reactor. In a typical experiment, FFMPAPd (150 mg, 0.03 mmol Pd) and 2.46 g of cyclohexene (0.03 mol) are added to the reactor under inert atmosphere. The reactor is loaded with hydrogen (10 atm) and placed in an oil bath at 75 °C under stirring (700 rpm). The consumption of

hydrogen was monitored by the drop of the reactor pressure. At the desired time, the reactor was cooled down in an ice bath, the remaining hydrogen relieved and the catalyst recovered magnetically by placing a magnet in the reactor wall. The products were collected and analyzed by GC. The isolated catalyst could be reused by addition of new portions of substrate.

### 3. Results and discussion

Co-precipitation of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions under alkaline conditions followed by oleic acid coating was the method of choice for the synthesis of soluble iron oxide nanoparticles used in this study. TEM image of the oleic acid coated nanoparticles is shown in Fig. 1(a). Analysis of the TEM micrographs, by measuring the diameter of 600 randomly selected particles in enlarged TEM

images, resulted in the particle size distribution histogram shown in Fig. 1(b). The size distribution was found to be well described by a lognormal distribution function from which we obtained the median particles diameter of 10 nm and the distribution width of 0.36. A lognormal distribution is widely used for describing the polydispersity of very small particles, where the lower particle size is usually more difficult to measure and shows some aggregation, in metallic nanoparticle systems [21].

The functionalization of the magnetic particles surfaces was achieved by a substitution reaction in which oleate molecules were substituted by 3-mercaptopropionic acid (MPA) resulting in thiol-modified magnetite nanoparticles, designated as FFMPA (Scheme 1). The reaction was performed in toluene under stirring and heating at 80 °C for 30 min. The product was decanted with acetone and isolated as a powder. Functionalization of the solid surfaces leads to a thiol loading of 1.3% as determined by ICP-AES analysis.

The TG and DSC curves of the oleic acid coated magnetic nanoparticles, shown in Fig. 2 (top), revealed a strong interaction between oleic acid and magnetite. This strong interaction was evidenced from the observed thermal decomposition shift to higher temperature range of bound oleic acid compared to free oleic acid (Fig. 2, top, curves b and c). The mass loss of 13.5%, due to the thermal decomposition of oleic acid, estimated by TG curve is in good agreement with the

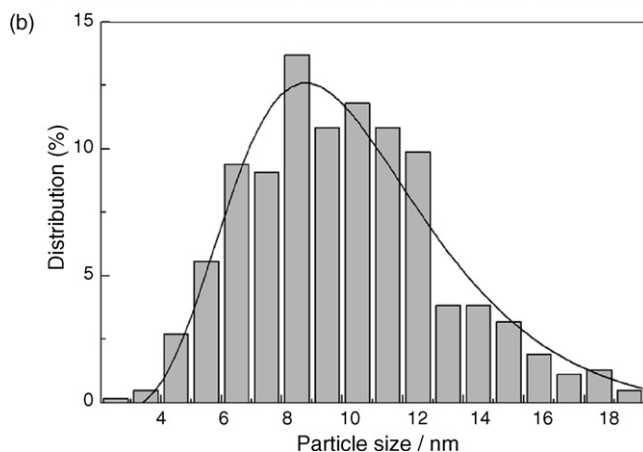
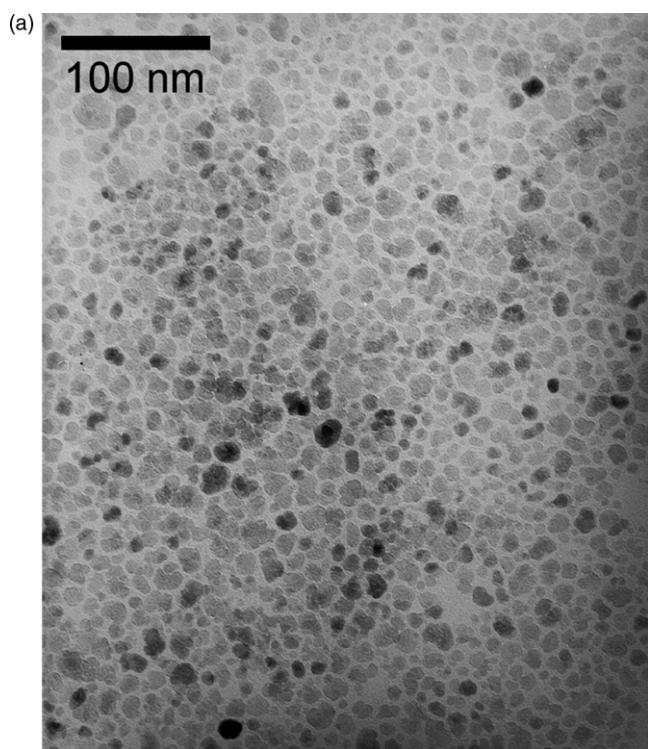


Fig. 1. (a) Transmission electron microscopy of oleic acid coated magnetite nanoparticles and (b) histogram showing particle size distribution.

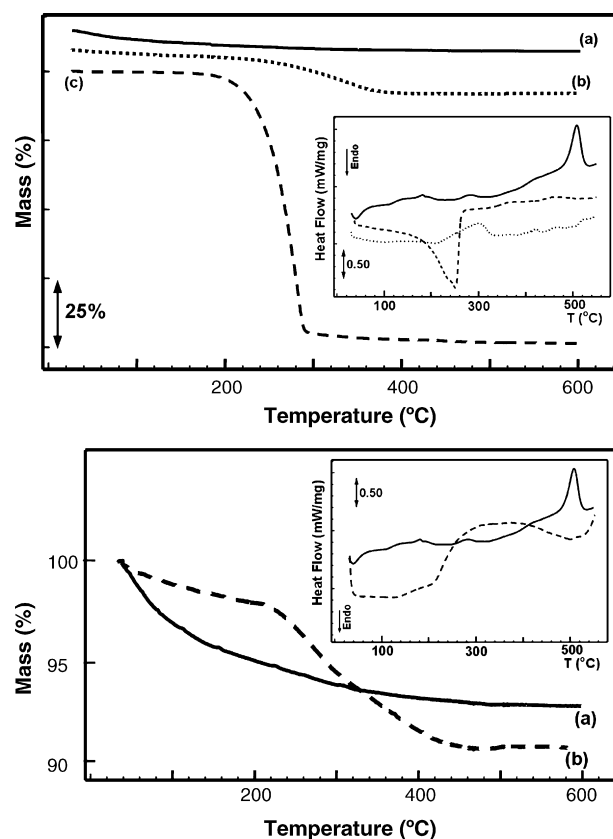
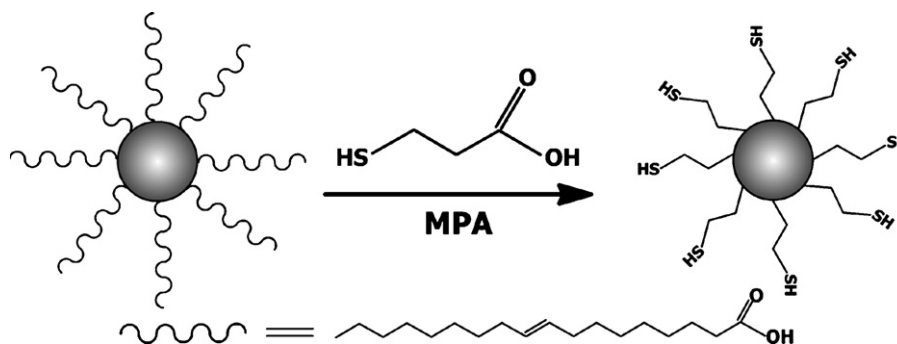


Fig. 2. Top: TG curves of decomposition of (a) magnetite, (b) oleic acid-coated magnetite and (c) oleic acid at 10 °C min<sup>-1</sup>. Bottom: TG curves of decomposition of (a) magnetite, (b) FFMPA at 10 °C min<sup>-1</sup>. Inset: Shows the corresponding DSC curves.



Scheme 1. Preparation of thiol-modified magnetic nanoparticles (FFMPA).

amount of oleic acid in the solid of 13.8% obtained from CHN elemental analysis (10.5% C; 1.6% H). The DSC curve of the oleic acid coated magnetic particles (Fig. 2, top, inset) showed an exothermic decomposition ( $T_{\text{peak}} = 300.5\text{ }^{\circ}\text{C}$ ) of the bound oleic acid, whereas thermal decomposition of free oleic acid is an endothermic process ( $T_{\text{peak}} = 251\text{ }^{\circ}\text{C}$ ), such behavior indicates a strong chemical interaction between oleate groups and  $\text{Fe}_3\text{O}_4$ . Moreover, the TG curves of pure magnetite (curve a) did not show mass loss in the temperature range from 200 to 600  $^{\circ}\text{C}$ , while the DSC curves indicated an exothermic event with peak temperature at 508.5  $^{\circ}\text{C}$  that can be associated with phase transition of the iron oxide [1]. A mass loss of 7.3% and also an exothermic decomposition process in the temperature range from 140 to 500  $^{\circ}\text{C}$  ( $T_{\text{peak}} = 372\text{ }^{\circ}\text{C}$ ), coincident with the mass loss observed in the TG curve (Fig. 2, bottom), were observed when oleic acid was substituted by 3-mercaptopropionic acid (MPA). This mass loss is lower than that of the original oleate coated magnetic particles, but still higher than the value of 4.3% estimated by means of the amount of sulfur determined by ICP-AES. This difference can be attributed to a remaining amount of oleate at the nanoparticles surfaces.

The palladium uptake capacity of the thiol-modified magnetic particles (FFMPA) was examined and the results are shown in Table 1. A portion of 25 mg of FFMPA was added to aqueous or non-aqueous solutions containing different concentrations of palladium, the solid was recovered by placing

a permanent magnet to the flask wall and the amount of palladium remaining in the supernatant was determined by ICP-AES. An aqueous solution containing 90 ppm of Pd was treated with FFMPA, the solid was separated magnetically and the remaining metal concentration in the solution is less than 0.9 ppm, which corresponds to a 100-fold reduction in Pd content after the treatment or an uptake of 99% of the Pd from the solution. The magnetic scavenger was also effective in reducing the concentration of palladium in toluene solution from 12 to <0.1 ppm and in THF solution from 30 to <10 ppm. At low initial concentrations of palladium, the magnetic scavenger is more effective for removing Pd from aqueous solution than organic solvents. At high initial concentration of palladium, however, metal uptake is more effective in THF (38.5  $\text{mg}_{\text{Pd}}/\text{g}_{\text{FFMPA}}$ ), followed by water (31.4  $\text{mg}_{\text{Pd}}/\text{g}_{\text{FFMPA}}$ ), and toluene (23.9  $\text{mg}_{\text{Pd}}/\text{g}_{\text{FFMPA}}$ ). These experiments showed that it is possible to obtain magnetic solids with palladium loadings of 1–4 wt% in the conditions studied, which can be eventually used as catalyst precursors.

We next examined the ability of the palladium-loaded magnetic nanoparticles to catalyze hydrogenation reactions. The catalyst was prepared according to entry 2 of Table 1. That condition was found to be advantageous because it guarantees a good palladium uptake (2 wt%) and it also minimizes the metal content left in the residual solution. Also, in this condition the molar ratio of Pd:S is 1:2 which has been suggested as critical to

Table 1  
Palladium uptake from aqueous and non-aqueous solutions by FFMPA

Entry	Solvent	mol Pd:mol S	[Pd] <sub>initial</sub> (ppm)	[Pd] <sub>final</sub> (ppm)	Pd loading ( $\text{mg}_{\text{Pd}}/\text{g}_{\text{FFMPA}}$ )	Pd uptake (%)
1	$\text{H}_2\text{O}^{\text{a}}$	1:1	360	98.68	31.4	72.6
2		1:2	180	6.51	20.8	96.4
3		1:4	90	0.90	10.7	99.0
4	THF <sup>b</sup>	1:1	120	23.84	38.5	80.1
5		1:2	60	21.48	15.4	64.2
6		1:4	30	6.28	9.5	79.1
7	Toluene <sup>c</sup>	1:1	124	64.16	23.9	48.3
8		1:2	62	22.85	15.7	63.2
9		1:4	31	6.59	9.8	78.8
10		1:10	12	0.11	4.8	99.1

<sup>a</sup>  $\text{Na}_2\text{PdCl}_4$  aqueous solution (3 mL) treated with 25 mg of FFMPA for 24 h and separated magnetically.

<sup>b</sup>  $\text{Pd}(\text{OAc})_2$  THF solution (10 mL) treated with 25 mg of FFMPA for 2 h and separated magnetically.

<sup>c</sup>  $\text{Pd}(\text{OAc})_2$  toluene solution (10 mL) treated with 25 mg of FFMPA for 2 h and separated magnetically.



Table 2  
Hydrogenation<sup>a</sup> of olefins by FFMPAPd magnetic catalyst

Entry	Substrate	Product	Time [h]	Conv. <sup>b</sup> [%]	TON	TOF <sup>c</sup> [h <sup>-1</sup> ]
1	1-Hexene	Hexane	2.0	>99	1000	500
2	Cyclohexene	Cyclohexane	2.5	61	610	244
3	Cyclohexene	Cyclohexane	2.5	78	780	312
4	Cyclohexene	Cyclohexane	2.5	86	860	344
5	Cyclohexene	Cyclohexane	2.5	87	870	348
6	Cyclohexene	Cyclohexane	2.5	77	770	308
7 <sup>d</sup>	Cyclohexene	Cyclohexane	2.5	2.7	27	14

<sup>a</sup> Conditions: Catalyst/substrate ratio = 1/1000, temperature = 75 °C, hydrogen pressure = 10 atm.

<sup>b</sup> Measured by GC.

<sup>c</sup> Catalytic turnover frequency: moles of substrate transformed per mole of catalyst per hour.

<sup>d</sup> Reaction performed with FFMPA without palladium.

obtain a catalyst with minimal leaching of metal to the solution [17]. The catalytic activity of the isolated solid (designated as FFMPAPd) was investigated in hydrogenation reactions of olefins. In a typical experiment, solid FFMPAPd and the olefin (palladium/olefin molar ratio 1/1000) were added to the reactor under inert atmosphere. The reactor was loaded with hydrogen at 10 atm and placed in an oil bath at 75 °C under stirring (700 rpm). The consumption of hydrogen was monitored by the drop of the reactor pressure. At the desired time, the reactor was cooled down in an ice bath, the remaining hydrogen relieved and the catalyst recovered magnetically placing a magnet in the reactor wall. The organic phase was easily separated and analyzed by gas chromatography. Table 2 summarizes the results of the hydrogenation reactions. The hydrogenation of 1-hexene was complete (>99% of conversion) after 2 h of reaction, corresponding to a turnover frequency (TOF) of 500 h<sup>-1</sup>. The hydrogenation of cyclohexene converted 61% of product in 2.5 h of reaction, corresponding to a TOF of 244 h<sup>-1</sup>. The catalyst was recovered magnetically placing a magnet in the reactor wall and the magnetically recovered catalyst was reused in five successive runs, by addition of new portions of cyclohexene. It was possible to calculate a partial turnover (TON) of 4000 in 12.5 h, but since the catalyst showed no apparent deactivation at the end of the fifth run, this is not the optimized total turnover number. The organic products were

collected and the Pd content was <0.01 ppm (ICP-AES analysis). When the hydrogenation reaction was performed under lower hydrogen pressure ( $P_{H_2} = 6$  atm,  $T = 75$  °C), we observed isomerization of 1-hexene.

The magnetic properties of the solids FFMPA and FFMPAPd were investigated. Magnetization curves shown in Fig. 3 confirmed the superparamagnetic behavior of both solids. The thiol-modified magnetic nanoparticles (FFMPA) presented a saturation magnetization of 62 emu g<sup>-1</sup> and the solid loaded with palladium (FFMPAPd) presented a saturation magnetization of 56 emu g<sup>-1</sup>. This slightly reduction of the saturation magnetization for the metal loaded solid was expected. Those values are smaller than that of bulk magnetite (92 emu g<sup>-1</sup>) [1], which is consistent with the presence of diamagnetic components, but the solid can still be efficiently separated from solution with a small neodymium permanent magnet.

#### 4. Conclusions

In summary, we have prepared a magnetic scavenger highly effective in reducing the concentration of palladium in aqueous and non-aqueous solutions that could be easily separated magnetically from solution as an alternative for solvent-consuming extraction and filtration procedures. Also, the recovered palladium-loaded magnetic solid showed catalytic activity in hydrogenation of olefins and could be readily recycled by magnetic separation and used for successive hydrogenation reactions.

#### Acknowledgments

We are grateful to FAPESP, CNPq and TWAS for financial support. We also thank the Laboratory of Magnetism of IF-USP for VSM measurements.

#### References

- [1] R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, VCH, Weinheim, 1996.
- [2] Q.A. Pankhurst, J. Connolly, S.K. Jones, J. Dobson, *J. Phys. D Appl. Phys.* 36 (2003) R167–R181, and references therein.
- [3] Z.M. Saiyed, S.D. Telang, C.N. Ramchand, *Biomag. Res. Technol.* 1 (2003) 1–17.

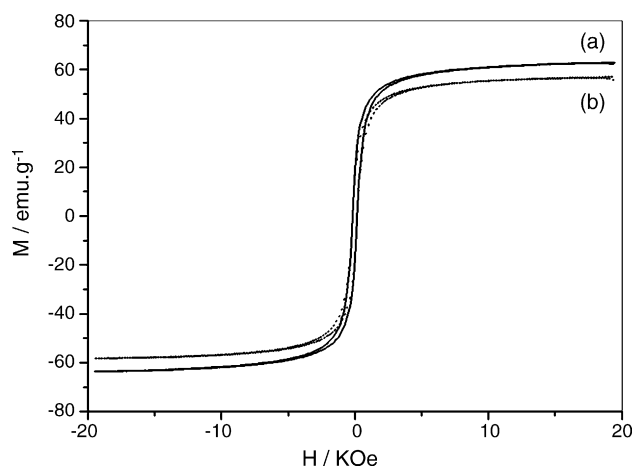


Fig. 3. Magnetization curves of (a) FFMPA and (b) FFMPAPd at 300 K.

- [4] S.K. Sahoo, V. Labhasetwar, *Drug Discovery Today* 8 (2003) 1112–1120.
- [5] L.M. Rossi, F.P. Silva, L.L.R. Vono, P.K. Kiyohara, E.L. Duarte, R. Itri, R. Landers, G. Machado, *Green Chem.* 9 (2007) 379–385, and references therein.
- [6] D. Guin, B. Baruwati, S.V. Manorama, *Org. Lett.* 9 (2007) 1419–1421.
- [7] C.E. Garrett, K. Prasad, *Adv. Synth. Catal.* 346 (2004) 889–900.
- [8] R.F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, New York, 1985.
- [9] J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, New York, 1995.
- [10] E. Negishi, in: A. de Meijere (Ed.), *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley, New York, 2002.
- [11] C. Chen, P. Dagneau, E.J.J. Grabowski, R. Oballa, P. O'Shea, P. Prasit, J. Robichaud, R. Tillyer, X. Wang, *J. Org. Chem.* 68 (2003) 2633–2638.
- [12] Y. Urawa, M. Miyazawa, N. Ozeki, K. Ogura, *Org. Process Res. Dev.* 7 (2003) 191–195.
- [13] M. Guino, K.K.M. Hii, *Tetrahedron Lett.* 46 (2005) 6911–6913.
- [14] K. Ishihara, M. Nakayama, H. Kurihara, A. Itoh, H. Haraguchi, *Chem. Lett.* (2000) 1218–1219.
- [15] R. Winder, *Chem. Ind.* 14 (2004) 7.
- [16] M.S. Anson, M.P. Leese, L. Tonks, J.M.J. Williams, *J. Chem. Soc., Dalton Trans.* (1998) 3529–3538.
- [17] C.M. Crudden, M. Sateesh, R. Lewis, *J. Am. Chem. Soc.* 127 (2005) 10045–10050.
- [18] T. Kang, Y. Park, J.C. Park, Y.S. Cho, J. Yi, *Stud. Surf. Sci. Catal.* 146 (2003) 527–530.
- [19] T. Kang, Y. Park, J. Yi, *Ind. Eng. Chem. Res.* 43 (2004) 1478–1484.
- [20] A.P. Philipse, M.P.B. van Bruggen, C. Pathmamanoharan, *Langmuir* 10 (1994) 92–99.
- [21] F.C. Fonseca, G.F. Goya, R.F. Jardim, N.L.V. Carreño, R. Muccillo, E. Longo, E.R. Leite, *Phys. Rev. B* 66 (2002) 104406.