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Short Communication

Iron(III)-substituted polyoxotungstates immobilized on silica nanoparticles: Novel oxidative heterogeneous catalysts

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ABSTRACT

Silica nanoparticles supporting polyoxometalates (POMs), namely an iron(III) mono-substituted Keggin-type polyoxotungstate of formula α-$[PW_{11}Fe^{III}(H_2O)O_{39}]^{4-}$ and a sandwich-type tungstophosphate with the formula B-α-$[(PW_9O_{34})_2Fe^{III}_4(H_2O)_2]^{6-}$ were synthesized. The POM/SiO_2 nanocomposites were obtained by alkaline hydrolysis of tetraethoxysilane using a reverse micelle and sol–gel technique. The spectroscopic studies suggest that the POMs were successfully immobilized on the silica nanoparticles. The catalytic activity of POM/SiO_2 nanomaterials was tested in the epoxidation of geraniol using H_2O_2 as oxygen donor. The α-$[PW_{11}Fe^{III}(H_2O)O_{39}]^{4-}$/$SiO_2$ nanocomposite was the most efficient catalyst with high geraniol conversion and good regioselectivity for 2,3-epoxygeraniol.

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1. Introduction

The most important reasons for the on-going research on oxidation reactions are the effective transformation of cheap natural compounds into valuable intermediates for organic synthesis as well as the development of environmentally benign oxidation procedures [1]. Recently, there has been an increase in research for new catalytic processes for the production of fine chemicals from renewable resources [2]. Geraniol is an example of a monoterpene available from essential oils of some plants, widely used as a fragrance in several commercially available cosmetics and toiletries [3]. This allylic alcohol offers several possible sites of oxidative attack, namely at the two double bonds, at the allylic carbon centres and at the carbon of the CH_2OH group.

Transition metal-substituted POMs are efficient catalysts for the oxidation of organic compounds in homogeneous conditions [4–6]. The immobilization of POMs in solid supports brings advantages to the oxidation reactions, in particular the easier catalyst recovery and its possible reutilization in new catalytic cycles. Silica is one of the most attractive supports, because it is chemically inert, thermally stable, harmless and inexpensive [7]. Some recent papers report the incorporation of transition metal-substituted POMs into silica matrices for several applications [8–21], including heterogeneous oxidative catalysis using silica nanoparticles [10,11,14]. However, to our knowledge, only our group has prepared silica nanoparticles as a support for POMs by the present method [16,21].

Following our previous studies in oxidative catalysis with hydrogen peroxide using transition metal-substituted POMs as homogeneous catalysts [22–25], we report here the development of new heterogeneous catalysts based on POM/SiO_2 nanomaterials. The polyoxometalates investigated were an iron(III) mono-substituted Keggin-type polyoxotungstate of formula α-$[PW_{11}Fe^{III}(H_2O)O_{39}]^{4-}$ (abbreviated to $PW_{11}Fe$) and a sandwich-type tungstophosphate with the formula B-α-$[(PW_9O_{34})_2Fe^{III}_4(H_2O)_2]^{6-}$ (abbreviated to $(PW_9)_2Fe_4$). The catalytic activity of these nanocomposites was studied in the epoxidation of geraniol using H_2O_2 as the oxidizing agent and CH_3CN as solvent, in a heterogeneous system.

2. Experimental

2.1. Synthesis of POM/SiO_2 nanocomposites

The potassium salts of the POMs (K-POM) were prepared by adaptation of known procedures: $[PW_{11}Fe^{III}(H_2O)O_{39}]^{4-}$ **$PW_{11}Fe$** [26] and $[(PW_9O_{34})_2Fe^{III}_4(H_2O)_2]^{6-}$ **$(PW_9)_2Fe_4$** [27] (Appendix A).

The following procedure for the preparation of POM/SiO_2 nanocomposites was adapted from the literature [21]. A microemulsion containing 2.38 g of Triton X-100, 1.88 g of 1-octanol, 7.25 g of cyclohexane, 233 μL of TEOS (tetraethoxysilane) and 60 mg of K-POM

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Table 1
Spectroscopic data (FT-IR and FT-Raman) for the POMs used as starting materials and the corresponding silica nanocomposites.

Compound	Vibrational spectra (cm^{-1})[a]		
	ν(P—O)	ν(W=O)	ν(W—O—W)
K-$PW_{11}Fe$	1086 s, 1058 s	961 vs	892 s, 808 vs, 731 vs
	1053 vw	*994 vs, 980 vs*	*906 m, 848 w, 805 sh*
$PW_{11}Fe/SiO_2$		950 m	880 m, 737 m
		969 sh, 949 vs	*870 m, 860 m, 804 sh*
$PW_{11}Fe/SiO_2$		954 m	917 sh,722 sh
after catalysis		*965 vs, 948 sh*	*883 sh, 864 sh, 807 sh*
K-$(PW_9)_2Fe_4$	1054 vs, 1035 sh	951 vs	875 vs, 805 vs, 734 vs
	1044 vw	*970 vs*	*896 m, 884 sh, 808 vw*
$(PW_9)_2Fe_4/SiO_2$		952 m	879 m, 738 m
	1045 vw	*966 vs*	*880 w, 800 vw*
$(PW_9)_2Fe_4/SiO_2$		952 m	878 m, 738 m
after catalysis		*969 vs*	*887 w, 810 vw*

[a] Raman data in italic; v: very, s: strong, m: medium, w: weak, sh: shoulder.

(potassium salt of the respective POM) dissolved in 1.16 mL of water was prepared. Another microemulsion containing 2.38 g of Triton X-100, 1.88 g of 1-octanol, 7.25 g of cyclohexane and 233 μL of aqueous 25 wt.% NH_3 was also prepared. After vigorous stirring for 30 min, the two microemulsions were mixed and the resulting mixture was stirred at r.t. for 48 h. Acetone was then added and a precipitate was obtained. The mixture was kept standing for 24 h. The solid obtained was centrifuged, washed with ethanol and ethanol:H_2O (4:1 v/v), and dried under vacuum.

Silica nanoparticles containing 43.6 wt.% of K-$PW_{11}Fe$ and 41.3 wt. % of K-$(PW_9)_2Fe_4$ were obtained by this method.

2.2. Oxidation procedure

Geraniol and 30 wt.% H_2O_2 were purchased from Aldrich and Riedel-de Häen, respectively, and used as received.

Heterogeneous reactions were performed as follows: POM/SiO_2 nanomaterials (25 mg) dispersed in acetonitrile (1.8 mL), substrate (1.2 mmol) and 30 wt.% H_2O_2 (3.6 mmol) were placed in a closed reactor, and the mixture stirred at r.t. in the absence of light. At regular intervals, the reaction mixture was centrifuged and an aliquot of 1 μL was taken directly from the supernatant with a microsyringe and injected into the gas chromatograph (GC). At the end of the reaction, the reaction mixture was centrifuged and the heterogeneous catalyst was recovered, washed with ethanol or acetonitrile and dried under vacuum.

For the reactions in homogeneous phase, a typical oxidation procedure was performed as follows: the catalyst (TBA-$PW_{11}Fe$, 3.82 μmol or TBA-$(PW_9)_2Fe_4$, 2.08 μmol; TBA- indicates that the tetrabutylammonium salt of the POM, prepared as in Appendix A, was used) dissolved in acetonitrile (1.8 mL), substrate (1.2 mmol) and 30 wt.% H_2O_2 (3.6 mmol) were placed in a closed reactor, and the mixture stirred at r.t. in the absence of light. After 3 or 5 h of reaction, an aliquot of 1 μL was taken directly from the reaction mixture with a microsyringe and injected into the GC.

3. Results and discussion

3.1. Preparation and characterization of POM/SiO_2 nanomaterials

The silica nanoparticles supporting the potassium salts of the polyoxoanions $[PW_{11}Fe^{III}(H_2O)O_{39}]^{4-}$ and $[(PW_9O_{34})_2Fe^{III}{}_4(H_2O)_2]^{6-}$ were prepared by alkaline hydrolysis of TEOS, using the sol–gel method within reverse micelles. This is a system based on water-in-oil (w/o) microemulsions [21], each microemulsion being composed by an aqueous phase (NH_3 25 wt.% solution in water or an aqueous solution of polyoxoanion and TEOS), a surfactant (Triton X-100), a co-surfactant (1-octanol) and an organic phase (cyclohexane) [28]. Acetone was added in order to disaggregate the micelles and to promote the precipitation of a solid with variable colour depending on the supported POM. These nanosized materials were characterized by FT-IR and FT-Raman spectroscopy and by transmission electron microscopy (TEM).

The presence of polyoxotungstates in the POM/SiO_2 nanocomposites is shown by several bands in the 700–1100 cm^{-1} range in the infrared and Raman spectra (Table 1, and Figs. 1 and 2). The infrared spectrum of nanosized silica (Fig. 1c) prepared in the absence of POM (by the same method as the POM/SiO_2 nanocomposites) shows four characteristic bands at 1095, 957, 798 and 468 cm^{-1} assigned to ν_{as}(Si—O—Si), ν(Si—OH), ν_s(Si—O—Si) and δ(Si—O—Si), respectively [29]. The infrared spectra of the POM/SiO_2 nanomaterials are dominated by the intense and broad bands of silica, which prevent the observation of most of the POM characteristic vibrational modes, as shown in Fig. 1b. The opposite is observed in the Raman spectra (Fig. 2), in which the bands of the POM supported on silica are clearly visible and silica does not show any signal in the 1100–100 cm^{-1}

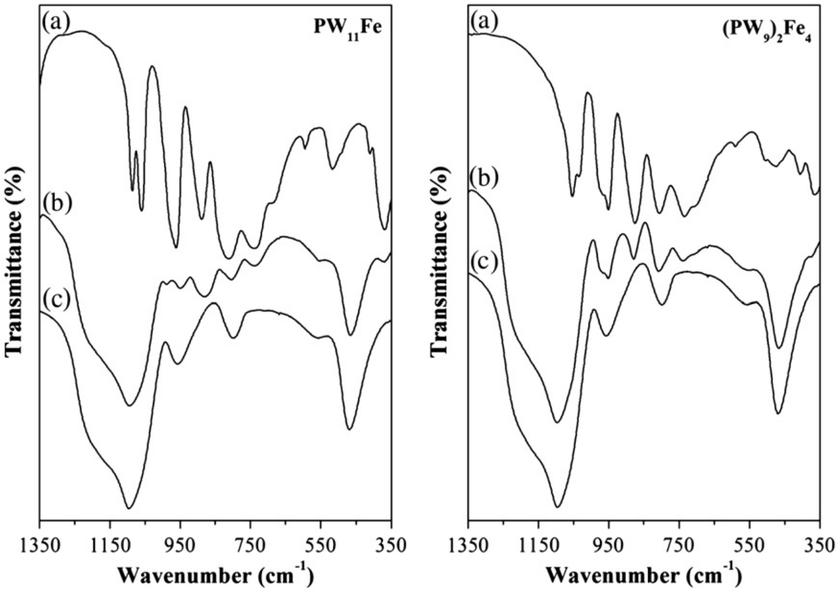


Fig. 1. FT-IR spectra of K-POM (a), POM/SiO_2 nanocomposite (b) and nanostructured silica (c), for the POMs $PW_{11}Fe$ and $(PW_9)_2Fe_4$.

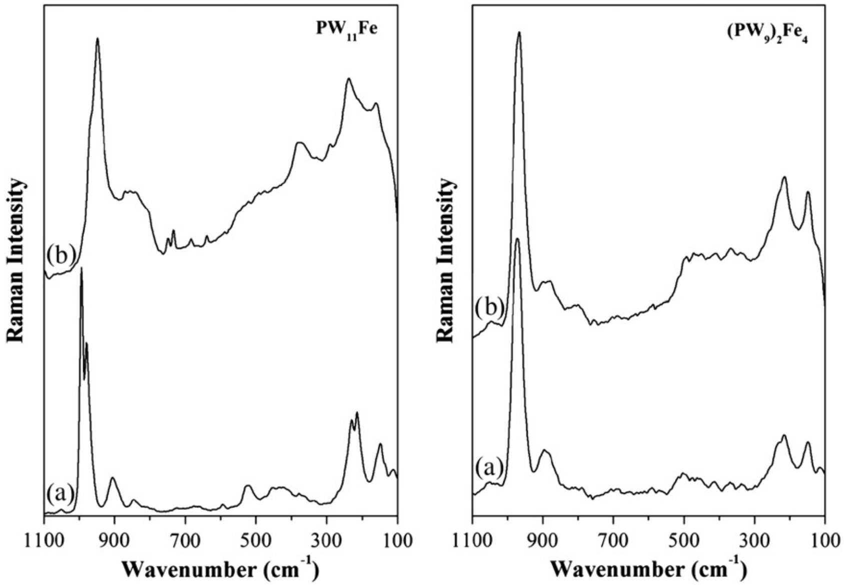


Fig. 2. FT-Raman spectra of K-POM (a) and corresponding POM/SiO_2 nanomaterial (b), for the POMs $PW_{11}Fe$ and $(PW_9)_2Fe_4$.

region. The POM bands are assigned to the terminal W=O stretches (949–994 cm^{-1}) and W—O—W stretching modes in edge-shared WO_6 octahedra (701–894 cm^{-1}) [30] as shown in Table 1. Overall, these results suggest that the polyoxotungstates are effectively immobilized on silica nanoparticles. Structure maintenance of the POM on the silica support could not be completely demonstrated by the vibrational spectra. Though in the case of $(PW_9)_2Fe_4$ there are strong similarities in the Raman spectra of both starting POM and POM/SiO_2 material (Fig. 2), for $PW_{11}Fe$ there is a shift in the position of the most intense bands.

Fig. 3 shows TEM images of the two silica nanomaterials with immobilized $(PW_9)_2Fe_4$ or $PW_{11}Fe$, respectively. These silica nanoparticles have a spherical form and similar diameters (between 25 and 35 nm). In the nanocomposites $(PW_9)_2Fe_4/SiO_2$ (Fig. 3A) the POM is assigned to the inner dark core, which is encapsulated by the silica forming core/shell nanoparticles. In $PW_{11}Fe/SiO_2$ the POM is scattered in the nanoparticles (Fig. 3B). Energy dispersive X-ray spectroscopy (EDX) confirmed the presence of tungsten in the two POM/SiO_2 nanomaterials.

Raman spectroscopy was also used to characterize the recovered material after catalysis. The Raman spectra for both POM/SiO_2 materials before and after catalysis (Fig. 4A and Table 1) are very similar, which indicates that the materials are not destroyed during catalysis neither by leaching of the POM from SiO_2 support or by POM decomposition. This is confirmed by the infrared spectra (Fig. 4B), and also by the TEM image of the $(PW_9)_2Fe_4/SiO_2$ nanocomposite after catalysis (Fig. 4C) that shows that the morphology is identical to that of the starting material (Fig. 3A).

3.2. Catalytic studies

The properties of the two prepared POM/SiO_2 nanocomposites as catalysts were evaluated in the oxidation of geraniol with H_2O_2. It was found by GC analysis that geraniol is preferentially epoxidized at the 2,3-position yielding 2,3-epoxygeraniol as the main product. Other minor products were observed, namely the 6,7-epoxide and the diepoxide (Scheme 1). The results are presented in Table 2. The highest catalytic activity was obtained in the presence of the $PW_{11}Fe/SiO_2$ nanomaterial (96% of conversion after 3 h of reaction), whereas 81% of conversion after 5 h of reaction was obtained with $(PW_9)_2Fe_4/SiO_2$. In the absence of catalyst but in the presence of the support (nanostructured silica), the epoxidation of geraniol led to 12% of

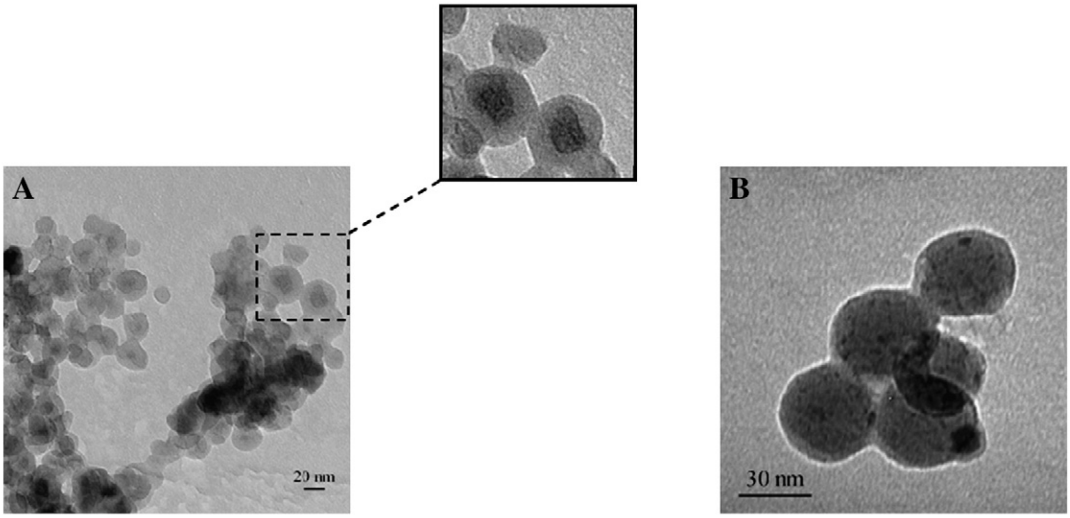


Fig. 3. TEM images of $(PW_9)_2Fe_4/SiO_2$ (A) and $PW_{11}Fe/SiO_2$ (B) nanocomposites.

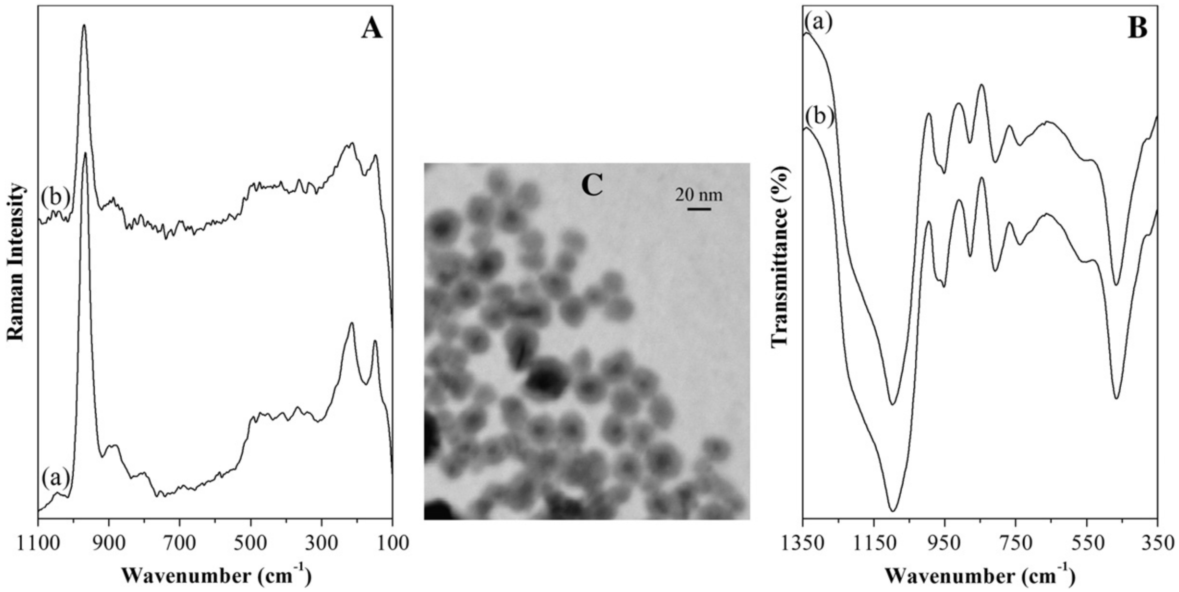
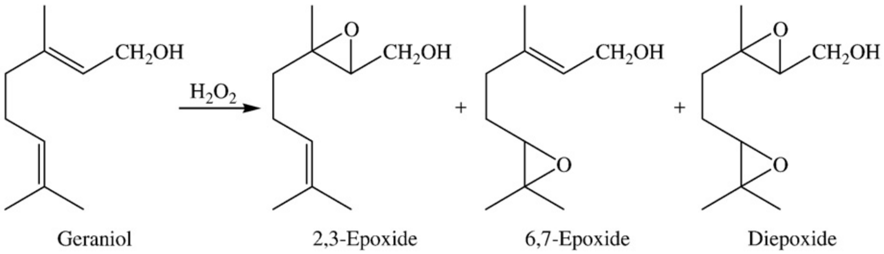


Fig. 4. FT-Raman (A) and FT-IR (B) spectra of $(PW_9)_2Fe_4/SiO_2$ before (a) and after (b) the first catalytic cycle, and TEM image (C) of this material after catalysis.



Scheme 1.

conversion after 3 h of reaction. The selectivity obtained for the 2,3-epoxygeraniol was 88% and 91% for $PW_{11}Fe/SiO_2$ and $(PW_9)_2Fe_4/SiO_2$, respectively. Catalyst nanomaterials were reused through two other catalytic runs and continued to show catalytic activity.

The consumption of H_2O_2 during the oxidation of geraniol is also presented in Table 2. Overall, about 60–70% of the initial added H_2O_2 was not consumed. However, when the stoichiometric quantities of H_2O_2 were used, the conversion of geraniol was very low, reaching conversion values of 11% and 20% after 3 h and 5 h of reaction, respectively.

There are only a few reports on the oxidation of geraniol in the presence of transition metal-substituted POMs, where 2,3-epoxygeraniol is generally obtained, along with high conversion values [22,31–35].

It is possible to compare the catalytic results obtained in this heterogeneous system with the results achieved with the tetrabutylammonium (TBA) salts of the same anions in homogeneous systems, in identical reaction conditions. In the case of the heterogeneous catalyst $(PW_9)_2Fe_4/SiO_2$, a significant selectivity improvement occurred over the behaviour of the corresponding TBA salt (Table 2).

To evaluate the possible effect of oxygen in the head-space reactor, tests under argon atmosphere were carried out in the reaction catalysed by $PW_{11}Fe/SiO_2$. Similar results were obtained, in comparison with those in the presence of air. Thus, the possibility of autoxidation appears to be ruled out. The epoxidation of geraniol by H_2O_2 catalysed by $PW_{11}Fe/SiO_2$ does not seem to be a radical process, because the addition of about 1.0 mmol of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a radical scavenger, did not inhibit the formation of any product in the epoxidation of geraniol.

The solid recovered after the first catalytic cycle with $(PW_9)_2Fe_4/SiO_2$ was characterized by TEM, FT-Raman and FT-IR spectroscopy. This heterogeneous catalyst presents a core/shell structure (Fig. 3A), which remained unchanged after the catalytic reactions (Fig. 4C). The spectroscopic studies (Figs. 4A and B) suggest that the POM in the silica nanocomposites was not destroyed and there is no evidence of POM leaching during the oxidation process under the conditions used in our catalytic studies.

In Fig. 5, the evolution of geraniol epoxidation in the presence of the $PW_{11}Fe/SiO_2$ catalyst is compared with that observed after removal of the catalyst after 15 min of reaction. There is a large

Table 2
Catalytic results for the epoxidation of geraniol with H_2O_2[a].

Catalyst	Time (h)	Conversion (%)	2,3-epoxide Selectivity[b] (%)	H_2O_2 Consumed (%)
$PW_{11}Fe/SiO_2$	3	96	88	30.9 ± 1.9
TBA-$PW_{11}Fe$	3	98	83	33.5 ± 2.2
$PW_{11}Fe/SiO_2$[c]	3	11	100	–
	5	20	100	28.1 ± 0.5
$(PW_9)_2Fe_4/SiO_2$	5	81	91	35.5 ± 1.1
TBA-$(PW_9)_2Fe_4$	5	99	81	51.1 ± 1.4
None	3	12	69	–
$(CH_3CN + \text{geraniol} + H_2O_2)$	5	17	73	–
None	3	12	68	–
$(SiO_2 + CH_3CN + \text{geraniol} + H_2O_2)$	5	21	77	–

[a] Reaction conditions: heterogeneous (POM/SiO_2, 25 mg) or homogeneous (TBA-$PW_{11}Fe$, 3.82 µmol; or TBA-$(PW_9)_2Fe_4$, 2.08 µmol) catalyst, CH_3CN (1.8 mL), substrate (1.2 mmol), 30 wt.% H_2O_2 (3.6 mmol), were stirred at r.t. and in the absence of light.
[b] Based on the amount of consumed substrate;
[c] H_2O_2/substrate molar ratio of 1.

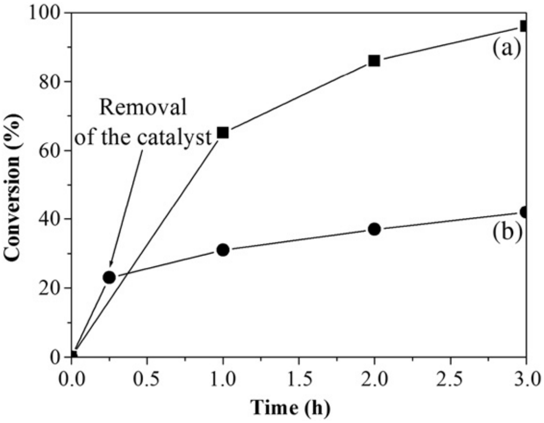


Fig. 5. Time course for the epoxidation of geraniol in the presence of $PW_{11}Fe/SiO_2$ (a) and with the removal of the catalyst after 15 min of reaction (b).

difference between final conversion values, which are significantly lower in the experiments with removal of the catalyst, suggesting that this epoxidation process is truly heterogeneous. The slight increase on geraniol conversion after the removal of the catalyst can be due to the presence of some nanoparticles that might remain in the solution or to some leaching of the POM into the solution.

4. Conclusions

This paper presents the preparation and characterization of silica nanoparticles supporting iron(III) containing POMs (of Keggin-type, $PW_{11}Fe/SiO_2$, and sandwich-type, $(PW_9)_2Fe_4/SiO_2$). POM/SiO_2 composites were synthesized by a system of reverse micelles giving rise to nanoscale spherical particles, with diameters between 25 and 35 nm. It was found that core/shell structures could form, with the POM encapsulated by the silica, while in other cases the POM was dispersed in the nanoparticles.

The nanocomposites synthesized were tested as heterogeneous catalysts in the epoxidation of geraniol with H_2O_2. The catalyst that showed the best catalytic activity for this oxidation reaction was $PW_{11}Fe/SiO_2$, with 96% of geraniol conversion after 3 h of reaction. Selectivities of 88–91% for 2,3-epoxygeraniol were found. Globally, the new nanostructured catalysts seemed to be more selective than the corresponding TBA salts used in homogeneous conditions, with the advantage of ease of separation and reuse.

Supplementary materials related to this article can be found online at doi:10.1016/j.catcom.2010.11.005.

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References

[1] R.A. Sheldon, Chem. Commun. (2008) 3352–3365.
[2] J.L.F. Monteiro, C.O. Veloso, Top. Catal. 27 (2004) 169–180.
[3] L. Hagvall, C. Bäcktorp, S. Svensson, G. Nyman, A. Börje, A.-T. Karlberg, Chem. Res. Toxicol. 20 (2007) 807–814.
[4] N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944–1956.
[5] R. Neumann, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, 47, John Wiley & Sons, Inc, 1998, pp. 317–370.
[6] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407–455.
[7] A.B.D. Nandiyanto, S.-G. Kim, F. Iskandar, K. Okuyama, Micropor. Mesopor. Mater. 120 (2009) 447–453.
[8] B.J.S. Johnson, A. Stein, Inorg. Chem. 40 (2001) 801–808.
[9] Y. Guo, Y. Yang, C. Hu, C. Guo, E. Wang, Y. Zou, S. Feng, J. Mater. Chem. 12 (2002) 3046–3052.
[10] N.M. Okun, T.M. Anderson, C.L. Hill, J. Am. Chem. Soc. 125 (2003) 3194–3195.
[11] N.M. Okun, T.M. Anderson, C.L. Hill, J. Mol. Catal. A: Chem. 197 (2003) 283–290.
[12] Y. Guo, C. Hu, C. Jiang, Y. Yang, S. Jiang, X. Li, E. Wang, J. Catal. 217 (2003) 141–151.
[13] O.A. Kholdeeva, M.P. Vanina, M.N. Timofeeva, R.I. Maksimovskaya, T.A. Trubitsina, M.S. Melgunov, E.B. Burgina, J. Mrowiec-Bialon, A.B. Jarzebski, C.L. Hill, J. Catal. 226 (2004) 363–371.
[14] N.M. Okun, M.D. Ritorto, T.M. Anderson, R.P. Apkarian, C.L. Hill, Chem. Mater. 16 (2004) 2551–2558.
[15] L. Li, C. Liu, A. Geng, C. Jiang, Y. Guo, C. Hu, Mater. Res. Bull. 41 (2006) 319–332.
[16] M.S.S. Balula, H.I.S. Nogueira, A.M.V. Cavaleiro, Mater. Sci. Forum 514–516 (2006) 1206–1210.
[17] N.V. Maksimchuk, M.S. Melgunov, Y.A. Chesalov, J. Mrowiec-Bialon, A.B. Jarzebski, O.A. Kholdeeva, J. Catal. 246 (2007) 241–248.
[18] L. Chen, K. Zhu, L.-H. Bi, A. Suchopar, M. Reicke, G. Mathys, H. Jaensch, U. Kortz, R.M. Richards, Inorg. Chem. 46 (2007) 8457–8459.
[19] J.A.F. Gamelas, D.V. Evtuguin, A.P. Esculcas, Transition Met. Chem. 32 (2007) 1061–1067.
[20] H. Hamidi, E. Shams, B. Yadollahi, F.K. Esfahani, Electrochim. Acta 54 (2009) 3495–3500.
[21] C.M. Granadeiro, R.A.S. Ferreira, P.C.R. Soares-Santos, L.D. Carlos, T. Trindade, H.I.S. Nogueira, J. Mater. Chem. 20 (2010) 3313–3318.
[22] I.C.M.S. Santos, M.M.Q. Simões, M.M.M.S. Pereira, R.R.L. Martins, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, J. Mol. Catal. A: Chem. 195 (2003) 253–262.
[23] A.C. Estrada, M.M.Q. Simões, I.C.M.S. Santos, M.G.P.M.S. Neves, A.M.S. Silva, J.A.S. Cavaleiro, A.M.V. Cavaleiro, Catal. Lett. 128 (2009) 281–289.
[24] A.C. Estrada, M.M.Q. Simões, I.C.M.S. Santos, M.G.P.M.S. Neves, A.M.S. Silva, J.A.S. Cavaleiro, A.M.V. Cavaleiro, Appl. Catal. A: Gen. 366 (2009) 275–281.
[25] I.C.M.S. Santos, M.M.Q. Simões, M.S.S. Balula, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, Synlett (2008) 1623–1626.
[26] T.J.R. Weakley, S.A. Malik, J. Inorg. Nucl. Chem. 29 (1967) 2935–2944.
[27] X. Zhang, Q. Chen, D.C. Duncan, R.J. Lachicotte, C.L. Hill, Inorg. Chem. 36 (1997) 4381–4386.
[28] Z. Ye, M. Tan, G. Wang, J. Yuan, J. Mater. Chem. 14 (2004) 851–856.
[29] R.C. Schroden, C.F. Blanford, B.J. Melde, B.J.S. Johnson, A. Stein, Chem. Mater. 13 (2001) 1074–1081.
[30] A.M.V. Cavaleiro, J.D.P. Jesus, H.I.S. Nogueira, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Molecular Clusters in Chemistry, 1, Wiley-VCH, 1999, pp. 444–458.
[31] A.J. Stapleton, M.E. Sloan, N.J. Napper, R.C. Burns, Dalton Trans. (2009) 9603–9615.
[32] P. Liu, C. Wang, C. Li, J. Catal. 262 (2009) 159–168.
[33] K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno, Chem. Eur. J. 13 (2007) 639–648.
[34] W. Adam, P.L. Alsters, R. Neumann, C.R. Saha-Möller, D. Sloboda-Rozner, R. Zhang, J. Org. Chem. 68 (2003) 1721–1728.
[35] R. Neumann, A.M. Khenkin, D. Juwiler, H. Miller, M. Gara, J. Mol. Catal. A: Chem. 117 (1997) 169–183.