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Hybrid Polyoxotungstate/MIL-101 Materials: Synthesis, Characterization, and Catalysis of H₂O₂-Based Alkene Epoxidation

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Polyoxotungstates [PW₄O₂₄]^{3−} (PW₄) and [PW₁₂O₄₀]^{3−} (PW₁₂) have been inserted into nanocages of the metal organic framework MIL-101. The hybrid materials PW_x/MIL-101 (*x* = 4 or 12) containing 5–14 wt % of polyoxotungstate have been obtained and characterized by elemental analysis, N₂ adsorption, FT-IR, Raman, and ³¹P NMR MAS spectroscopic techniques. Their catalytic performance was assessed in the selective oxidation of alkenes with aqueous hydrogen peroxide under mild reaction conditions ([H₂O₂] = 0.1–0.2 M, 50 °C, MeCN). PW_x/MIL-101 enclosing 5 wt % of polyoxotungstate demonstrated fairly good catalytic activities in the epoxidation of various alkenes (3-carene, limonene, α-pinene, cyclohexene, cyclooctene, 1-octene), the turnover frequencies (TOF) and alkene conversions were close to the corresponding parameters achieved with homogeneous PW_x. For the oxidation of substrates with aromatic groups (styrene, *cis*- and *trans*-stilbenes), a higher level of olefin conversion was attained using PW₁₂/MIL-101. Moreover, confinement of PW₁₂ within MIL-101 nanocages allowed us to reach higher epoxide selectivities at higher alkene conversions. The hybrid PW_x/MIL-101 materials were stable to leaching, behaved as true heterogeneous catalysts, were easily recovered by filtration, and reused several times with the maintenance of the catalytic performance.

Introduction

Alkene epoxidation is one of the basic reactions in industrial organic synthesis because epoxides are key intermediates for the manufacture of a wide variety of valuable products.^{1–8} The selective epoxidation of alkenes is widely used in the fine chemicals industry and can be successfully achieved by using stoichiometric amounts of peroxy acids.⁹ However, the development and implemen-

tation of catalytic processes which eliminate the use of hazardous reactants and reduce generation of waste is an important goal.^{6–8}

Hydrogen peroxide has attracted great attention as an environmentally benign oxidant because it is quite cheap, readily available, easy to handle, and gives water as the only co-product.^{10–13} Tungsten compounds are well-known as active and selective catalysts for alkene epoxidation with aqueous H₂O₂.^{8,14–21} In the mid of 1980s, highly effective systems based on the use of [PW₄O₂₄]^{3−}

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(1) Franz, G.; Sheldon, R. A. In *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B., Hawkins, S., Shulz, G., Eds.; VCH: Weinheim, Germany, 1991; Vol. A(18), pp 261–311.

(2) *Kirk-Othmer Encyclopedia of Chemical Technology*; Interscience: New York, 1985; Vol. 7, pp 239, 263.

(3) Siemel, G.; Rieth, R.; Rowbottom, K. T. In *Ullmann's Encyclopedia of Industrial Chemistry*; Gerhartz, W., Ed.; VCH Publishers: New York, 1985; Vol. A(9), pp 531–545.

(4) Dusi, M.; Mallat, T.; Baiker, A. *Catal. Rev. Sci. Eng.* **2000**, *42*, 213–278.

(5) Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance and Flavor Materials*; Wiley-VCH: New York, 1997.

(6) Sheldon, R. A.; van Vliet, M. C. A. In *Fine Chemicals through Heterogeneous Catalysis*; Sheldon, R. A., van Bekkum, H., Eds.; Wiley: Weinheim, Germany, 2001; pp 473–551.

(7) *Handbook of Heterogeneous Catalysis*, 2nd ed.; Ertl, G., Knözinger, H., Schütt, F., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, Germany, 2008.

(8) Adolfsen, H. In *Modern Oxidation Methods*; Bäckvall, J.-E., Ed.; Wiley-VCH: Weinheim, Germany, 2004; pp 21–49.

(9) *Organic Peroxides*; Swern, D., Ed.; Wiley Interscience: New York, 1971; Vol. 2.

(10) Jones, C. W. *Application of Hydrogen peroxide and Derivatives*; Royal Society of Chemistry: Cambridge, U.K., 1999.

(11) *Catalytic Oxidations with Hydrogen peroxide as Oxidant*; Strukul, G., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992.

(12) Hudlucky, M. *Oxidations in Organic Chemistry*, ACS Monograph Series; American Chemical Society: Washington, DC, 1990.

(13) Hill, C. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: London, 1988; Vol. 1, pp 1–30.

(14) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431–458.

(15) Hoegaerts, D.; Sels, B. F.; De Vos, D. E.; Verpoort, F.; Jacobs, P. A. *Catal. Today* **2000**, *60*, 209–218.

(16) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. *Green Chem.* **2003**, *5*, 1–7.

(17) Brégeault, J.-M. *Dalton Trans.* **2003**, 3289–3302.

(18) Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457–2473.

(19) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977–1986.

(20) Kamata, K.; Yonehara, K.; Sumida, Y.; Yamaguchi, K.; Hikichi, S.; Mizuno, N. *Science* **2003**, *300*, 964–966.

(21) Mizuno, N.; Yamaguchi, K.; Kamata, K. *Coord. Chem. Rev.* **2005**, *249*, 1944–1956.

(PW₄) and [PW₁₂O₄₀]^{3−} (PW₁₂) polyoxometalates (POMs) were developed independently by the Venturello^{22–23} and Ishii^{24–26} groups. The major drawback of the Venturello–Ishii epoxidation systems is the use of toxic chlorocarbons as solvents to obtain high reaction rates and yields of epoxides. An improved ternary catalytic system for the selective epoxidation of simple alkenes has been suggested by Noyori and co-workers.^{27,28} This entirely free of organic solvents and halides system consists of Na₂WO₄, (aminomethyl)phosphonic acid and Q⁺HSO₄[−]. The use of lipophilic quaternary ammonium hydrogen sulfate significantly enhances the yield of epoxide. However, this catalytic system can not be employed for the production of acid sensitive epoxides because epoxide ring-opening occurs under acidic conditions. Furthermore, both the Venturello–Ishii and Noyori systems have drawbacks typical of homogeneous catalysts, such as complexity of the catalyst separation from the reaction mixtures and contamination of products with traces of transition metals (even if two-phase conditions are employed).

Immobilization of active homogeneous catalysts on solid supports has attracted a lot of research interest because solid catalysts have the advantages of being easier to recover and to recycle. Many research papers were dedicated to immobilization of the 12-tungstophosphoric acid, H₃PW₁₂O₄₀, on different solid supports, such as amorphous silica,^{29–41}

mesostructured silicates,^{31,42–47} layered double hydroxides (LDH),^{48,49} active carbon,⁵⁰ metal oxides,^{29,51–54} and polymers.^{55,56} Silica has been widely used as supporting material for PW₁₂ since it interacts weakly with the PW₁₂ anion, thereby preserving its structure in the supported form. However, PW₁₂ immobilized by weak interaction is easily leached out of the support in polar reaction media.^{39–41} On the contrary, strong interaction, for example, with alumina, may result in PW₁₂ destruction in the course of immobilization.⁵⁴

Supported PW₁₂ catalysts were mainly examined as acid catalysts,^{44,45,47,53} but a few examples of using immobilized PW₁₂ in alkene epoxidation with H₂O₂ were also reported. Thus, LDH intercalated PW₁₂ was found to be almost inactive in cyclohexene epoxidation with 10% H₂O₂.⁴⁹ On the other hand, the catalyst prepared by supporting PW₁₂ on mesoporous silica preliminary modified with Ph₃SiOEt and Me₃NCH(OCH₂Ph)₂ groups produced epoxides from different alkenes with the yields up to 97% using aqueous 15% H₂O₂ without an organic solvent.³³ However, no data on the catalysts stability, recyclability, metal leaching, and the nature of catalysis were reported for this system.

Different low nuclearity oxo- and peroxotungstic species, such as WO₄[−],⁵⁷ WO₅^{3−},^{58–61} W₇O₂₄^{6−},⁶² [W₂O₃(O₂)₄]^{2−},⁶³ and [(HPO₄)₂{WO(O₂)₂}]^{2−} (PW₂),^{64–66} were immobilized on solid supports by anion exchange with LDH^{57,62} or Amberlyst A26,⁶⁵ adsorption onto silica supports^{64–66} and binding with organophosphorous groups on the surface of functionalized silica,^{58,63} resin,⁵⁹ hydroxyapatite⁵⁹ or porous polymers.⁶¹ A mixed-valence oxotungsten-silica mesoporous W-SBA-15 material prepared by the sol-gel technique using tetraethyl orthosilicate and Na₂WO₄ was reported as well.^{64,67} The supported materials catalyzed selective oxidation of olefins,^{57–60,62,64,65} allylic alcohols⁵⁷ and sulfides⁶³ with aqueous H₂O₂. Silica-supported WO₅^{3−}⁵⁸ and PW₂^{64,65}

(22) Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107–110.
 (23) Venturello, C.; D'Aloisio, R. *J. Org. Chem.* **1988**, *53*, 1553–1557.
 (24) Matoba, Y.; Inoue, H.; Akagi, J.; Okabayashi, T.; Ishii, Y.; Ogawa, M. *Synth. Commun.* **1984**, *14*, 865–873.
 (25) Ishii, Y.; Yamawaki, K.; Yoshida, T.; Ura, T.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 1868–1870.
 (26) Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587–3593.
 (27) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 8310–8311.
 (28) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Panyella, D.; Noyori, R. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905–915.
 (29) Mohana Rao, K.; Gobetto, R.; Iannibello, A.; Zecchina, A. *J. Catal.* **1989**, *119*, 512–516.
 (30) Mastikhin, V. M.; Kulikov, S. M.; Nosov, A. V.; Kozhevnikov, I. V.; Mudrakovsky, I. L.; Timofeeva, M. N. *J. Mol. Catal.* **1990**, *60*, 65–70.
 (31) Kozhevnikov, I. V.; Kloestera, K. R.; Sinnema, A.; Zandbergen, H. W.; van Bekkum, H. *J. Mol. Catal. A: Chem.* **1996**, *114*, 287–298.
 (32) Lefebvre, F. *J. Chem. Soc., Chem. Commun.* **1992**, 756–757.
 (33) Sakamoto, T.; Pac, C. *Tetrahedron Lett.* **2000**, *41*, 10009–10012.
 (34) Mrovec-Bialoń, J.; Turek, W.; Jarzebski, A. B. *React. Kinet. Catal. Lett.* **2002**, *76*, 213–219.
 (35) Kim, H.-J.; Shul, Y.-G.; Han, H. *Appl. Catal., A* **2006**, *299*, 46–51.
 (36) Zhang, Q.; Tan, Y.; Yang, C.; Han, Y.; Shamoto, J.; Tsubaki, N. *J. Nat. Gas Chem.* **2007**, *16*, 322–325.
 (37) Izumi, Y.; Hisano, K.; Hida, T. *Appl. Catal., A* **1999**, *181*, 277–282.
 (38) Izumi, Y.; Ono, M.; Kitagawa, M.; Yoshida, M.; Urabe, K. *Microporous Mesoporous Mater.* **1995**, *5*, 255–262.
 (39) Vázquez, P.; Pizzio, L.; Romanelli, G.; Autino, J.; Cáceres, C.; Blanco, M. *Appl. Catal., A* **2002**, *235*, 233–240.
 (40) Marme, F.; Coudurier, G.; Védrine, J. C. *Microporous Mesoporous Mater.* **1998**, *22*, 151–163.
 (41) Haber, J.; Pamin, K.; Matachowski, L.; Mucha, D. *Appl. Catal., A* **2003**, *256*, 141–152.
 (42) Li, W.; Li, L.; Wang, Z.; Cui, A.; Sun, C.; Zhao, J. *Mater. Lett.* **2001**, *49*, 228–234.
 (43) Damyanova, S.; Dimitrov, L.; Mariscal, R.; Fierro, J. L. G.; Petrov, L.; Sobrados, I. *Appl. Catal., A* **2003**, *256*, 183–197.
 (44) He, N.-Y.; Woo, C.-S.; Kim, H.-G.; Lee, H.-I. *Appl. Catal., A* **2005**, *281*, 167–178.
 (45) Sawant, D.; Vinu, A.; Lefebvre, F.; Halligudi, S. B. *J. Mol. Catal. A: Chem.* **2007**, *262*, 98–108.
 (46) Yang, L.; Li, J.; Yuan, X.; Shen, J.; Qi, Y. *J. Mol. Catal. A: Chem.* **2007**, *262*, 114–118.
 (47) Herrera, J. E.; Kwak, J. H.; Hu, J. Z.; Wang, Y.; Peden, C. H. F. *Top. Catal.* **2008**, *49*, 259–267.
 (48) Kwon, T.; Pinnavaia, T. J. *Chem. Mater.* **1989**, *1*, 381–383.

(49) Gardner, E.; Pinnavaia, T. J. *Appl. Catal., A* **1998**, *167*, 65–74.
 (50) Kozhevnikov, I. V.; Sinnema, A.; Jansen, R. J. J.; van Bekkum, H. *Catal. Lett.* **1994**, *27*, 187–197.
 (51) Gómez-García, M. A.; Pitchon, V.; Kiennemann, A. *Appl. Catal., B* **2007**, *70*, 151–159.
 (52) Qu, X.; Guo, Y.; Hu, C. *J. Mol. Catal. A: Chem.* **2007**, *262*, 128–135.
 (53) Rajkumar, T.; Ranga Rao, G. *J. Mol. Catal. A: Chem.* **2008**, *295*, 1–9.
 (54) Hodjati, S.; Vaezzadeh, K.; Petit, C.; Pitchon, V.; Kiennemann, A. *Top. Catal.* **2001**, *16/17*, 151–155.
 (55) Hasik, M.; Turek, W.; Stochmal, E.; Lapkowski, M.; Pron, A. *J. Catal.* **1994**, *147*, 544–551.
 (56) Stochmal-Pomarzanska, E.; Hasik, M.; Turek, W.; Pron, A. *J. Mol. Catal. A: Chem.* **1996**, *114*, 267–275.
 (57) Sels, B. F.; De Vos, D. E.; Jacobs, P. A. *Tetrahedron Lett.* **1996**, *37*, 8557–8560.
 (58) Gelbard, G.; Gauduchau, T.; Vidal, E.; Parvulescu, V. I.; Crosman, A.; Pop, V. M. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 257–266.
 (59) Gelbard, G.; Breton, F.; Quenard, M.; Sherrington, D. C. *J. Mol. Catal. A: Chem.* **2000**, *153*, 7–18.
 (60) Crosman, A.; Gelbard, G.; Poncelet, G.; Parvulescu, V. I. *Appl. Catal., A* **2004**, *264*, 23–32.
 (61) Gelbard, G. *C. R. Acad. Sci. Chem.* **2000**, *3*, 757–764.
 (62) Palomeque, J.; Figueras, F.; Gelbard, G. *Appl. Catal., A* **2006**, *300*, 100–108.
 (63) Xian-Ying, S.; Jun-Fa, W. *J. Mol. Catal. A: Chem.* **2008**, *280*, 142–147.
 (64) Brégeault, J.-M.; Piquemal, J.-Y.; Briot, E.; Duprey, E.; Launay, F.; Salles, L.; Vennat, M.; Legrand, A.-P. *Microporous Mesoporous Mater.* **2001**, *44–45*, 409–417.
 (65) Brégeault, J.-M.; Thouvenot, R.; Zoughebi, S.; Salles, L.; Atlamsani, A.; Duprey, E.; Aubry, C.; Robert, F.; Chottard, G. *Stud. Surf. Sci. Catal.* **1994**, *82*, 571–581.
 (66) Duprey, E.; Maquet, J.; Man, P. P.; Manoli, J.-M.; Delamar, M.; Brégeault, J.-M. *Appl. Catal., A* **1995**, *128*, 89–96.
 (67) Cheng, C.-Y.; Lin, K.-J.; Prasad, M. R.; Fu, S.-J.; Chang, S.-Y.; Shyu, S.-G.; Sheu, H.-S.; Chen, C.-H.; Chuang, C.-H.; Lin, M.-T. *Catal. Commun.* **2007**, *8*, 1060–1064.

were found to be liable to tungsten leaching. The W-SBA-15 catalyst was reused successfully just once;⁶⁷ moreover, the "hot catalyst filtration test"⁶⁸ was not reported, and, hence, the nature of catalysis remained unclear.

By far, only few true heterogeneous and recyclable catalysts have been published for H₂O₂-based alkene epoxidation, and the elaboration of such catalysts is still a challenging goal. Several attempts to heterogenize the Venturello complex, PW₄, have been performed, including anion exchange with Amberlite IRA-900,^{15,69–71} electrostatic binding to a silica xerogel covalently modified with phenyl and quaternary ammonium groups,⁷² and "solvent-anchored" supporting technique when covalently attached to silica surface polyethers acted as a solvent and/or complexing agents for POM.⁷³ The "solvent-anchored" and xerogel-attached PW₄ catalyzed selectively cyclooctene epoxidation with 30% aqueous H₂O₂ without organic solvent at room temperature.^{72,73} The PW₄–Amberlite catalyst showed fairly good selectivity in alkene epoxidations with H₂O₂ (93 and 97% selectivities were reported for limonene and 3-carene at 84 and 55% conversions, respectively, after 24 h at 38 °C).⁶⁹ Both the "solvent-anchored" and PW₄–Amberlite catalysts were recycled several times without loss of the activity, and the results of the hot catalyst filtration experiments pointed out true heterogeneous nature of catalysis. However, it was found that epoxide product deactivates the PW₄–Amberlite catalyst and totally inhibits the reaction at 160 TON.⁷¹

In the past decade, metal-organic frameworks (MOFs) have attracted considerable attention because of their unique combination of properties such as high surface area, crystalline open structures, tunable pore size, and functionality, and so forth.^{74–77} All these properties allow considering MOFs as prospective catalytic materials and supports for

immobilization of homogeneous catalysts.^{77–87} In 2005, Férey and co-workers reported the synthesis of the mesoporous chromium terephthalate coordination polymer MIL-101 which possesses a rigid zeotype crystal structure, extremely large surface area and quasi-spherical cages of two modes (free internal diameters are close to 29 and 34 Å, while the cages are accessible through microporous windows of about 12 and 16 Å).⁸⁸ Importantly, this material is resistant to air, water, common solvents, and thermal treatment (up to 320 °C).^{76,88} Férey and co-workers demonstrated a successful incorporation of the lacunary heteropolytungstate K₇PW₁₁O₃₉ within nanocages of MIL-101.⁸⁸

Recently, we have first prepared composite materials based on the MIL-101 matrix and redox active Keggin heteropolyanions, [PW₁₁CoO₃₉]^{5–} and [PW₁₁TiO₄₀]^{5–}, and explored their catalytic performances in the allylic oxidation of alkenes with O₂ and H₂O₂, respectively.⁸⁹ Both composite materials were proven to be stable to POM leaching, behaved as true heterogeneous catalysts, and could be used repeatedly without suffering a loss of the activity and selectivity under mild reaction conditions. Recently, MIL-101 was used as a stable support for palladium in the Knoevenagel condensation,⁹⁰ Heck coupling reaction,⁸⁶ and alkene hydrogenation.⁹¹ SO₃H-functionalized MIL-101 was active as acid catalyst in the esterification of acetic acid with ethanol,⁸⁶ while L-proline-modified MIL-101 showed remarkable catalytic activities in asymmetric aldol reactions.⁹² Yet, MIL-101 with coordinatively unsaturated chromium sites (after heating under vacuum at 150 °C) was found to be active in cyanosilylation,⁹¹ selective oxidation of tetralin to 1-tetralone with TBHP,⁹³ and sulfoxidation of thioethers to sulfoxides with H₂O₂.⁹⁴ Very recently, a direct encapsulation of phosphotungstic acid into MIL-101 by the addition of PW₁₂ during the synthesis of MIL-101 was reported.⁹⁵ These materials were found to be active in acid-catalyzed reactions, such as the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, esterification of *n*-butanol with acetic acid, and dehydration of methanol to dimethylether.

Here we further explore the potential of the mesoporous MOF MIL-101 for the preparation of heterogeneous selective oxidation catalysts based on catalytically active POMs. Optimal procedures for the incorporation of polyoxotungstates PW₄ and PW₁₂ into the coordination polymer nanocages have been elaborated, and the obtained hybrid materials have been characterized by elemental analysis, N₂ adsorption, FT-IR, Raman, and ³¹P NMR MAS spectroscopic techniques. The catalytic properties of the new hybrid materials were examined in the liquid-phase alkene

(68) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, *31*, 485–493.

(69) Villa de, P. A. L.; Sels, B. F.; De Vos, D. E.; Jacobs, P. A. *J. Org. Chem.* **1999**, *64*, 7267–7270.

(70) Sels, B. F.; Villa, A. L.; Hoegaerts, D.; De Vos, D. E.; Jacobs, P. A. *Top. Catal.* **2000**, *13*, 223–229.

(71) Villa de, P. A. L.; Taborda, F. A.; de Correa, C. M. *J. Mol. Catal. A: Chem.* **2002**, *185*, 269–277.

(72) Neumann, R.; Miller, H. *J. Chem. Soc., Chem. Commun.* **1995**, 2277–2278.

(73) Neumann, R.; Cohen, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1738–1740.

(74) *Handbook of Porous Solids*; Schüth A.; Sing K. S. W.; Weitkamp J., Eds.; Wiley-VCH: Weinheim, Germany, 2002.

(75) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.

(76) Férey, G.; Mellot-Draznieks, C.; Sere, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225.

(77) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191–214.

(78) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Leon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.

(79) Forster, P. M.; Cheetham, A. K. *Top. Catal.* **2003**, *24*, 79–89.

(80) Qiu, L.-G.; Xie, A.-J.; Zhang, L.-D. *Adv. Mater.* **2005**, *17*, 689–692.

(81) Zou, R.-Q.; Sakurai, H.; Zu, Q. *Angew. Chem., Int. Ed.* **2006**, *45*, 2542–2546.

(82) Alaerts, L.; Seguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; De Vos, D. E. *Chem.—Eur. J.* **2006**, *12*, 7535–7563.

(83) Horcajada, P.; Surblé, S.; Serre, C.; Hong, D.-Y.; Seo, Y.-K.; Chang, J.-S.; Grenéche, J.-M.; Margiolaki, I.; Férey, G. *Chem. Commun.* **2007**, 2820–2822.

(84) Wu, C.-D.; Lin, W. *Angew. Chem., Int. Ed.* **2007**, *46*, 1075–1078.

(85) Alkordi, M. H.; Liu, Y.; Larsen, R. W.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 12639–12641.

(86) Hong, D.-Y.; Hwang, Y. K.; Serre, C.; Férey, G.; Chang, J.-S. *Adv. Funct. Mater.* **2009**, *19*, 1537–1552.

(87) Lee, J. Y.; Farha, O. K.; Roberts, J.; Sheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.

(88) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040–2042.

(89) Maksimchuk, N. V.; Timofeeva, M. N.; Melgunov, M. S.; Shmakov, A. N.; Chesalov, Yu. A.; Dybtsev, D. N.; Fedin, V. P.; Kholdeeva, O. A. *J. Catal.* **2008**, *257*, 315–323.

(90) Hwang, Y. K.; Hong, D.-Y.; Chang, J.-S.; Jung, S. H.; Seo, Y.-K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Férey, G. *Angew. Chem.* **2008**, *120*, 4212–4216.

(91) Henschel, A.; Gedrich, K.; Kraehnert, R.; Kaskel, S. *Chem. Commun.* **2008**, 4192–4194.

(92) Banerjee, M.; Das, S.; Yoon, M.; Choi, H. J.; Hyun, M. H.; Park, S. M.; Seo, G.; Kim, K. *J. Am. Chem. Soc.* **2009**, *131*, 7524–7525.

(93) Kim, J.; Bhattacharjee, S.; Jeong, K.-E.; Jeong, S.-Y.; Ahn, W.-S. *Chem. Commun.* **2009**, 3904–3906.

(94) Hwang, Y. K.; Hong, D.-Y.; Chang, J.-S.; Seo, H.; Yoon, M.; Kim, J.; Jung, S. H.; Serre, C.; Férey, G. *Appl. Catal., A* **2009**, *358*, 249–253.

(95) Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Lafont, U.; Gascon, J.; Kapteijn, F. *J. Catal.* **2010**, *269*, 229–241.

epoxidation with aqueous H_2O_2 and compared with the catalytic performance of the corresponding homogeneous POM catalysts. The critical issues on the catalysts stability, reusability, and the nature of catalysis have been addressed.

Experimental Section

Materials. Hydrogen peroxide was used as 30 wt % solution in water; its concentration was determined iodometrically prior to use. Heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ was a commercial product and was purified by extraction with diethyl ether. The compound purity was confirmed by ^{31}P NMR (a single peak at -15.0 ppm in H_2O). All other reactants were obtained commercially and used without further purification.

Synthesis of MIL-101. MIL-101 was prepared by a hydrothermal reaction of terephthalic acid with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, HF, and H_2O following the procedure reported by Férey et al.⁸⁸ In a typical synthesis, chromium nitrate (1.2 g, 3 mmol), terephthalic acid (500 mg, 3 mmol), 3 M HF (1 mL, 3 mmol), and H_2O (15 mL, 0.833 mol) were mixed in a Teflon linear and kept at 220°C during 6 h. The crystalline MIL-101-as product in the solution was twice filtered off using a glass filter with the pore size $160\ \mu\text{m}$ to remove free terephthalic acid and then through a paper filter. The purification of the rude MIL-101-as product was carried out in four steps: double treatment in *N,N*-dimethylformamide (DMF) at 60°C during 6 h and then double treatment in hot ethanol at 70°C during 6 h. After drying in air at 70 – 80°C overnight, the X-ray diffraction (XRD) analysis confirmed the structure of pure MIL-101. MIL-101-B with increased surface area was prepared by solvothermal treatment of the rude MIL-101-as with ethanol at 80°C for 24 h.^{90,94}

PW₄ Synthesis. The Venturello complex $[\text{PW}_4\text{O}_{24}]^{3-}$ (PW_4) was prepared by the peroxide mediated decomposition of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ following the slightly modified published procedure.²⁶ To a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (720 mg, 0.25 mmol) in of 30% H_2O_2 (15 mL, 150 mmol) was added 5 M aqueous solution of H_3PO_4 (0.1 mL, 0.5 mmol). The solution was stirred for 4 h at 40°C to give PW_4 , which was confirmed by ^{31}P NMR spectroscopy (δ 4.4 ppm in $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ solution).

Immobilization of PW_x on MIL-101. Adsorption/desorption measurements were carried out using UV–vis spectroscopy as described previously.⁸⁹ The composite $\text{PW}_{12}/\text{MIL-101}$ was synthesized by dissolving $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (5 mg, 0.002 mmol) in water (1.5 mL, pH 2.05), adding MIL-101 (100 mg), stirring for 3 h at room temperature, filtering off, thorough washing with water and acetone, and drying at room temperature. Additional drying at 150°C for 4 h led to about 5% of weight loss.

$\text{PW}_4/\text{MIL-101}$ was prepared by adding MIL-101 (100 mg) to 0.005 M PW_4 solution (1 mL) obtained by decomposition of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with excess of H_2O_2 (vide supra), stirring at room temperature for 3 h, filtering off, washing with water and acetone, and drying at room temperature.

The POM loading was determined by elemental analysis. The catalysts were also characterized by N_2 adsorption, FT-IR, Raman, and ^{31}P NMR MAS spectroscopy.

Treatment of the $\text{PW}_{12}/\text{MIL-101}$ (150 mg) with 1 M solution of Bu_4NClO_4 in MeCN (3 mL) was carried out at room temperature under vigorous stirring for 1 h followed by filtration and drying at room temperature.

Catalytic Oxidations. Catalytic experiments were carried out in thermostatted glass vessels under vigorous stirring (900 rpm) at 50°C . Alkene oxidations over $\text{PW}_x/\text{MIL-101}$ were carried out following three different modes designated as methods A, B, and C.

Method A. Reaction was started by adding H_2O_2 (0.1–0.2 mmol) to a mixture containing alkene (0.1 mmol), $\text{PW}_x/\text{MIL-101}$ catalyst (28 mg; $5.8 \cdot 10^{-3}$ mmol W in $\text{PW}_{12}/\text{MIL-101}$ or $4.9 \cdot 10^{-3}$ mmol W in $\text{PW}_4/\text{MIL-101}$) prepared as described above, an internal standard (biphenyl), and acetonitrile (1 mL).

Method B (with Catalyst Pre-Treatment). A mixture containing $\text{PW}_{12}/\text{MIL}$ (28 mg, $4.7 \cdot 10^{-4}$ mmol $[\text{PW}_{12}\text{O}_{40}]^{3-}$), H_2O_2 (0.2 mmol, 510 equiv with respect to PW_{12}), internal standard (biphenyl), and acetonitrile (1 mL) was stirred for 1 h at 50°C . Then the oxidation reaction was started by the addition of cyclohexene (0.1 mmol).

Method C (One-Pot Catalyst Preparation and Catalytic Oxidation). To a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (1.4 mg, $4.7 \cdot 10^{-4}$ mmol) in MeCN (1 mL) was added MIL-101 (28 mg) under vigorous stirring. After stirring the solution at 25°C for 30 min, the oxidation reaction was started by adding cyclohexene (0.1 mmol) and H_2O_2 (0.2 mmol) followed by heating the reaction mixture to 50°C .

Aliquots of the reaction mixture were withdrawn periodically during the reaction course by a syringe through a septum. Each experiment was reproduced at least 2–3 times. After the reactions, catalysts were filtered off, washed with acetonitrile, methanol, dried in air at room temperature overnight, and then reused.

Instrumentation and Methods. The reaction products were identified by GC-MS and quantified by GC using an internal standard. GC analyses were performed using a gas chromatograph “Tsvet-500” equipped with a flame ionization detector and a quartz capillary column (30 m \times 0.25 mm) Agilent DB-5MS. GC-MS analyses were carried out using a gas chromatograph Agilent 6890 (quartz capillary column 30 m \times 0.25 mm/HP-5 ms) equipped with a quadrupole mass-selective detector Agilent MSD 5973.

Nitrogen adsorption at 77 K was studied using an ASAP-2020 instrument within the partial pressure range 10^{-6} –1.0. Before measurements, samples were degassed at 150°C under vacuum during 48 h. The specific surface area and pore volume were measured by the comparative method.⁹⁶ XRD measurements were performed on a high-precision X-ray diffractometer Philips APD1700 using cupric radiation ($\text{CuK}_{\alpha 1,2}$ 1.54060; 1.54439). FT-IR spectra were recorded using pellets containing 2 mg of a sample and 500 mg of KBr (for PW_{12} -containing samples) and as Nujol mull between CsI windows (for PW_4 -containing samples) on a BOMEM-MB-102 spectrometer in the 250 – $4000\ \text{cm}^{-1}$ range. The Raman spectra were recorded at room temperature in the range of 100 – $3600\ \text{cm}^{-1}$ using FT-Raman spectrometer RFS 100/S BRUKER. The excitation source was the 1064 nm line of the Nd:YAG laser operating at power level of 100 mW. UV–vis spectra were recorded using an Agilent 8453 spectrophotometer ($\lambda = 250$ – $255\ \text{nm}$, $l = 10\ \text{mm}$). ^{31}P NMR MAS spectra were recorded on a Bruker Avance-400 spectrometer. The spectrum frequency was 161.97 MHz, and the rotation speed of a 7 mm rotor was 6.5 kHz. The duration of the $\pi/2$ pulse was 7 μs , and the delay for spectrum acquisition was 20 s. Spectra were referenced to 85% H_3PO_4 as external standard. Elemental analyses were performed using atomic emission spectroscopy.

Results and Discussion

Catalysts Preparation and Characterization. Férey et al. estimated that about five $[\text{PW}_{11}\text{O}_{39}]^{7-}$ polyanions can be incorporated within a large cage of MIL-101.⁸⁸ Recently, we have shown that only one Keggin anion per nanocage (this corresponds to 7–10 wt % of POM in the material) is irreversibly adsorbed from acetonitrile solution by MIL-101.⁸⁹ An electrostatic character of POM binding to the MIL surface has been suggested based on ion exchange experiments.

In this work, we prepared $\text{PW}_{12}/\text{MIL-101}$ hybrid materials following a similar methodology, but adsorption

(96) Fenelonov, V. B.; Romannikov, V. N.; Derevyankin, A. Yu. *Micro-porous Mesoporous Mater.* **1999**, 28, 57–72.

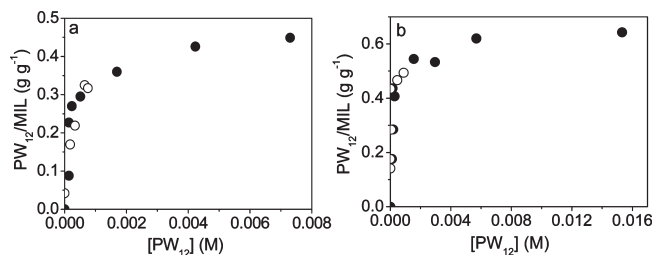


Figure 1. Adsorption/desorption isotherms (MeCN, 25 °C) for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (adsorption and desorption curves are marked by \bullet and \circ , respectively) on (a) MIL-101 and (b) MIL-101-B.

of heteropolyacid PW_{12} was carried out from an aqueous solution. The Venturillo complex, PW_4 , was generated in situ from PW_{12} , H_3PO_4 , and an excess of H_2O_2 , following a standard procedure described by several research groups^{26,64,94} and immobilized on MIL-101 directly from the $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ solution. The complete transformation of PW_{12} ($\delta -15.0$ ppm) to PW_4 ($\delta +4.4$ ppm) was confirmed by ^{31}P NMR spectroscopy. The adsorption/desorption process was monitored by UV-vis spectroscopy. The amount of irreversibly adsorbed PW_{12} and PW_4 typically achieved 4–5 wt % (the adsorption/desorption curves are shown in Figure 1a).

The elemental analysis data for the prepared $\text{PW}_x/\text{MIL-101}$ samples along with the P/W/Cr values calculated for POM loadings acquired from the adsorption measurements are given in Table 1. The results of the adsorption study are in good agreement with the elemental analysis data.

Textural properties of the initial MIL-101 and hybrid $\text{PW}_x/\text{MIL-101}$ materials assessed from N_2 adsorption isotherms are also presented in Table 1. One can observe some decrease (ca. 20 %) in both specific surface area (A) and pore volume (V_p) after POM insertion. A similar trend was observed earlier for immobilization of PW_{11}M on MIL-101.⁸⁹ XRD patterns of MIL-101 and $\text{PW}_x/\text{MIL-101}$ materials are shown in Figure 2. The XRD data confirmed the preservation of the MIL-101 structure after the immobilization of the POMs.

Recently, Férey and co-workers reported a few methods for MIL-101 purification which allowed enlarging significantly its surface area and pore volume.^{90,94} We have also found a significant increase of the surface area (from 2200 to 3900 $\text{m}^2 \text{g}^{-1}$, see Table 1) after treating MIL-101 with hot EtOH. In turn, this led to a significant augmentation of the maximal amount of POM accommodated within MIL-101 and allowed us to introduce irreversibly up to 14 wt % of PW_{12} into MIL-101 (see Figure 1b and Table 1).

FT-IR and Raman spectroscopic studies were performed to check whether the POM and MIL-101 structures are preserved in the hybrid materials. As one can judge from the FT-IR spectra of MIL-101 and $\text{PW}_x/\text{MIL-101}$ presented in Figure 3a (the most intensive peaks belong to MIL-101), the matrix structure certainly retained upon POM immobilization. Figure 3b shows FT-IR spectra of the bulk and MIL-supported PW_{12} after subtraction of the spectrum of MIL-101. The IR spectra of the $\text{PW}_{12}/\text{MIL}$ composite exhibit principal bands of the PW_{12} Keggin unit: 1081 $\nu_{\text{as}}(\text{PO}_4)$, 985 $\nu_{\text{as}}(\text{W}=\text{O})$, 895 and 820 cm^{-1} $\nu_{\text{as}}(\text{W}-\text{O}-\text{W})$, which is a definite

indication of the maintenance of the POM structure after immobilization.

Since FT-IR bands of the MIL-supported PW_4 were rather weak because of the low POM loading, we used Raman spectroscopy to characterize this material. The Raman spectra of the aqueous solution of PW_4 and MIL-supported PW_4 are shown in Figure 4. They exhibit principal bands of the peroxotungstate: 965 $\nu(\text{W}=\text{O})$, 853 $\nu(\text{O}-\text{O})$, and 563 $\nu(\text{W}(\text{O}_2))$, thus indicating preservation of the PW_4 structure after immobilization.

^{31}P NMR MAS technique is a useful tool to probe the state of a POM after immobilization.^{29–32,43,50} Figure 5 shows ^{31}P NMR MAS spectra of $\text{PW}_{12}/\text{MIL-101}$ samples after different treatments. The ^{31}P NMR MAS spectrum of the initial $\text{PW}_{12}/\text{MIL-101}$ exhibits three main peaks at -16.4 (form I), -14.9 (form II), and -11.7 ppm (form III). Since the FT-IR spectra indicated no noticeable change in the POM structure after deposition of PW_{12} onto MIL-101 (see Figure 3), the presence of several peaks in the ^{31}P NMR MAS spectrum might imply different modes of interaction between PW_{12} and the MIL-101 surface.

Earlier, deposition of PW_{12} onto silica^{29–32,35,42,43,46} and carbon⁵⁰ was found to result in a signal shift, line-broadening and splitting in the ^{31}P NMR MAS spectra, indicating a distortion of the PW_{12} structure compared with the bulk PW_{12} . Different peaks were associated with different types of interaction between the Keggin anion and surface. According to Lefebvre,³² the signal at about -15 ppm is due to PW_{12} having no interaction with silica surface, while the peak at -14.6 ppm can be related to a polyanion which undergoes a slight electrostatic interaction with a support via the formation of $(\equiv\text{Si}-\text{OH}_2)^+(\text{H}_2\text{PW}_{12}\text{O}_{40})^-$ species. It was also supposed that a low field shift in the ^{31}P NMR MAS signal can be due to partial dehydration of the heteropolyacid during the impregnation process.^{35,43} Indeed, for dehydrated bulk $\text{H}_3\text{PW}_{12}\text{O}_{40}$ a sharp ^{31}P NMR MAS peak was observed at -11.0 ppm, while $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ showed a peak at -15.6 ppm.⁹⁷ Additionally, ^{31}P NMR spectra of $\text{Cs}_x\text{H}_{3-x}$ salts of PW_{12} were found to display four resonances which have been assigned to the polyanions associated with 0, 1, 2, and 3 protons, respectively.⁹⁸ Hence, a ^{31}P NMR MAS signal drift could arise also from a different protonation state of the POM. Kozhevnikov et al. assumed that a ^{31}P NMR MAS signal shift and splitting might be due to partial decomposition of PW_{12} producing lacunary species, like PW_{11} or P_2W_{17} , during the preparation of supported catalysts.³¹

We have found that the ratio of forms I–III changed after drying the $\text{PW}_{12}/\text{MIL-101}$ sample at 150 °C (Figure 5B). This implies that, in effect, the forms could be related to different hydration states of the POM. Previously, electrostatic binding between POM and MIL-101 surface has been hypothesized based on the ion exchange experiments.⁸⁹ We performed three consecutive treatments of the sample 5% $\text{PW}_{12}/\text{MIL-101}$ with

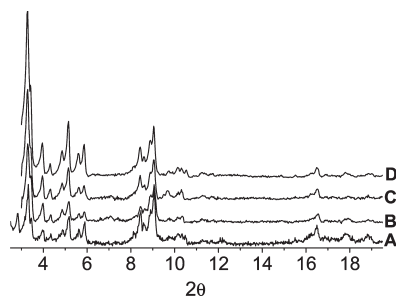
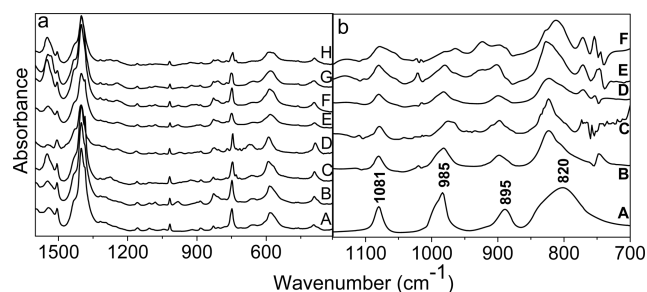
(97) Uchida, S.; Inumaru, K.; Misono, M. *J. Phys. Chem B* **2000**, *104*, 8108–8115.

(98) Okuhara, T.; Nishimura, T.; Watanabe, H.; Misono, M. *J. Mol. Catal.* **1992**, *74*, 247–256.

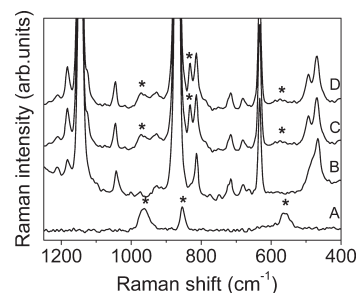
Table 1. Physicochemical Properties of Hybrid PW_x/MIL-101 Catalysts

sample	P/W/Cr ^a (wt %)	P/W/Cr ^b (wt %)	<i>A</i> ^c (m ² g ⁻¹)	<i>V</i> _p ^d (cm ³ g ⁻¹)
MIL-101		—/—/13	2200	1.1
MIL-101-B ^e			3900	2.1
5% PW ₁₂ /MIL-101	0.04/3.1/13	0.05/3.0/12	1700	0.8
		0.05/3.0/12 ^f	1700 ^f	0.8 ^f
		0.05/3.2/13 ^g	600 ^g	0.4 ^g
5% PW ₄ /MIL-101	0.1/2.6/13	0.1/2.8/14	1800	0.8
		0.1/2.7/14 ^h	500 ^h	0.3 ^h
14% PW ₁₂ /MIL-101-B ^e	0.15/10.7/12	0.13/9.4/12	2900	1.2

^a Evaluated from the adsorption data. ^b Based on the elemental analysis data. ^c Specific surface area. ^d Mesopore volume. ^e After treatment with hot EtOH (see Experimental Section). ^f After one cycle of cyclohexene oxidation; reaction conditions as in Table 2. ^g After five cycles of cyclohexene oxidation. ^h After four cycles of cyclohexene oxidation.

**Figure 2.** XRD patterns for (A) MIL-101, (B) PW₁₂/MIL-101, (C) PW₄/MIL-101, and (D) PW₁₂/MIL-101 dried at 150 °C for 4 h.**Figure 3.** (a) FT-IR spectra of (A) MIL-101, (B) PW₁₂/MIL-101, (C) PW₄/MIL-101, (D) PW₁₂/MIL-101 after treatment with 0.2 M H₂O₂ for 1 h at 50 °C, (E)–(G) PW₁₂/MIL-101 after 1, 3, and 5 cycles of cyclohexene oxidation, and (H) PW₄/MIL-101 after 4 cycles of cyclohexene oxidation. (b) FT-IR spectra of (A) PW₁₂, (B) PW₁₂/MIL-101, (C) PW₁₂/MIL-101 after treatment with 0.2 M H₂O₂ for 1 h at 50 °C, and (D)–(F) PW₁₂/MIL-101 after 1, 3, and 5 cycles of cyclohexene oxidation; in (B)–(F) the spectra of MIL-101-supported PW₁₂ are given after subtraction of the spectrum of MIL-101. For reaction conditions, see Experimental Section, method A.

1 M solution of Bu₄NClO₄ in MeCN. The corresponding ³¹P NMR MAS spectra are presented in Figure 5 C–E. One can see that after the first treatment the ³¹P NMR MAS peak at −16.3 ppm decreased markedly (Figure 5C), while after the second treatment it disappeared completely along with the signal at −15.0 ppm (Figure 5D). According to the elemental analysis data, about one-third of the immobilized PW₁₂ was transferred into solution after the first treatment with Bu₄NClO₄. The ³¹P NMR measurements confirmed that the wash-out solution contained only intact Keggin PW₁₂ (Figure 6A). After the third treatment, the ³¹P NMR MAS spectrum (Figure 5E) was similar to that run after the second treatment, indicating the presence of solely form III. Elemental analysis indicated that about one-fifth of the

**Figure 4.** Raman spectra of (A) PW₄ (0.05 M solution in H₂O–H₂O₂), (B) MIL-101, (C) PW₄/MIL-101, and (D) PW₄/MIL-101 after 4 cycles of cyclohexene oxidation.

immobilized PW₁₂ (ca. 1 wt %) remained after three consecutive treatments with Bu₄NClO₄. Hence, forms I and II can be removed using Bu₄NClO₄, thus pointing to the electrostatic character of binding between these forms and positively charged surface of the MIL-101 nanocage.

It should be mentioned that the ratios of forms I–III in the samples 5% PW₁₂/MIL-101 and 14% PW₁₂/MIL-101-B were different (compare Figure 5 A and G). While in the former sample form I predominated (ca. 50%), the latter was enriched with form III (56%). At the moment, the nature of form III is not understood completely. Most likely, it derives from a stronger interaction of dehydrated PW₁₂ and the MIL surface. It seems reasonable that purification of MIL and increasing surface area would enhance this interaction. Yet, the formation of lacunary POM species can not be ruled out completely.³¹ The minor broad signal in the ³¹P NMR MAS spectrum at about −7.1 ppm could be tentatively assigned to such species.

Catalytic Oxidation. The catalytic performance of the PW₄/MIL-101 and PW₁₂/MIL-101 hybrid materials was first assessed in cyclohexene oxidation with aqueous H₂O₂ in acetonitrile medium. The results of the catalytic runs along with blank experiments and experiments performed in the presence of the corresponding homogeneous POMs are presented in Table 2. Both PW₄ and PW₁₂ incorporated within the MIL-101 matrix showed fairly good catalytic activity, while the matrix alone was quite inert. The catalytic activities of 5% PW₁₂/MIL-101 and 5% PW₄/MIL-101 referred to one W atom were similar (compare entries 4 and 6 in Table 2). It is worth noting that the activities of PW_x/MIL expressed in TOF values were just slightly lower than the activity of homogeneous PW_x (0.36 vs 0.34 min⁻¹ for PW₄ and 0.41 vs 0.39 min⁻¹ for PW₁₂). This implies that immobilization of

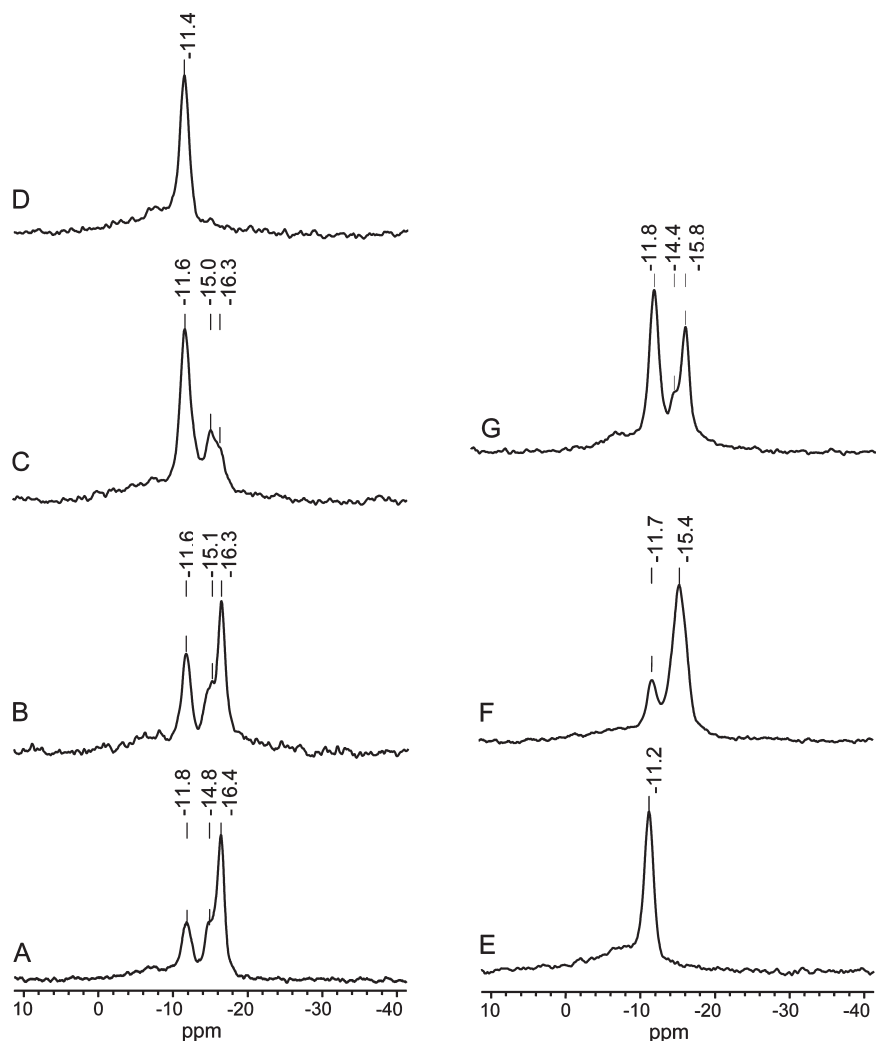


Figure 5. ^{31}P NMR MAS spectra of 5% $\text{PW}_{12}/\text{MIL-101}$: (A) initial, (B) dried at 150 °C for 4 h, (C)–(E) after 1–3 consecutive treatments with 1 M Bu_4NClO_4 in MeCN, and (F) after 5 cycles of cyclohexene oxidation; (G) ^{31}P NMR MAS spectrum of 14% $\text{PW}_{12}/\text{MIL-101-B}$.

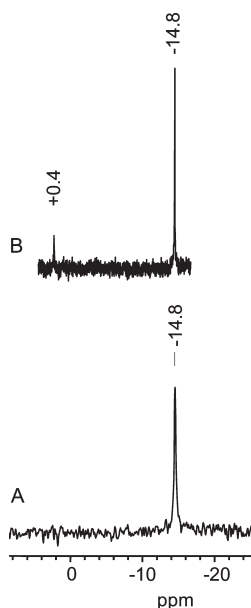


Figure 6. ^{31}P NMR spectra of: (A) washout solution after treatment of $\text{PW}_{12}/\text{MIL}$ with 1 M Bu_4NClO_4 in MeCN and (B) PW_{12} after homogeneous cyclohexene oxidation.

POM on MIL-101 causes no deactivation and allows to keep the catalytic activity, at least, at the same level.

With 2 equiv of H_2O_2 , cyclohexene was converted mainly to its epoxide over 5% $\text{PW}_x/\text{MIL-101}$. The allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (totally ca. 10%) were identified as the main byproduct, while the product of epoxide ring-opening, 1,2-*trans*-cyclohexane diol, was not found in the reaction mixture. This contrasts with the homogeneously catalyzed oxidation in the presence of PW_x where the diol was the main byproduct. The reaction over $\text{PW}_4/\text{MIL-101}$ gave epoxide with 74% selectivity at 76% substrate conversion after 3 h; a similar result was acquired over $\text{PW}_{12}/\text{MIL-101}$ (entry 6, Table 2). For comparison, cyclohexene (3 mmol) oxidation with H_2O_2 (3 mmol) over PW_4 –Amberlite (0.016 mmol PW_4) at 32 °C gave epoxide with only 57% selectivity at a similar conversion after 24 h.⁷⁰ In turn, 5% $\text{PW}_{12}/\text{NH}_2$ –SBA-15 produced mainly *trans*-cyclohexane diol under the same reaction conditions (entry 13, Table 2).

It has been established by several research groups that the catalytic activity of the $\text{PW}_{12}/\text{H}_2\text{O}_2$ system in alkene epoxidation is caused by in situ formation of

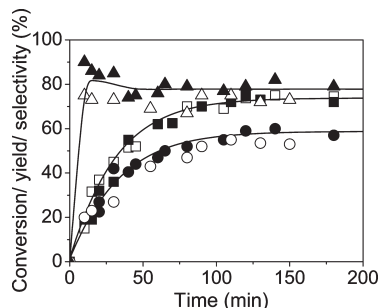
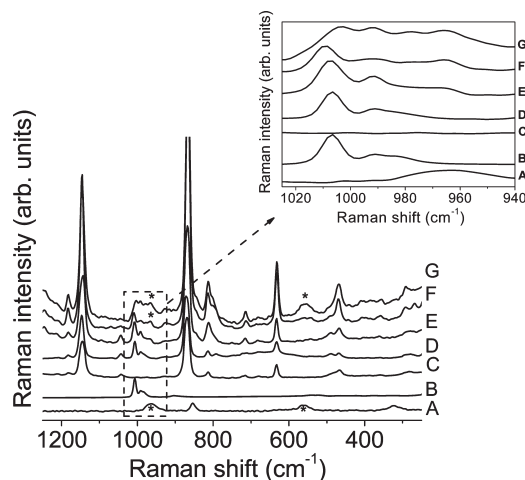
Table 2. Cyclohexene Oxidation with H₂O₂ in the Presence of PW_x/MIL-101 Catalysts^a

entry	catalyst	cyclohexene conversion (%)	TOF ^b (min ⁻¹)	epoxide selectivity ^c (%)
1	— ^d	12		67
2	MIL-101 ^e	11		64
3	PW ₄ ^f	90	0.36	77
4	5% PW ₄ /MIL-101	76	0.34	74
5	PW ₁₂ ^f	72	0.41	78
6	5% PW ₁₂ /MIL-101	72	0.39	76
7	5% PW ₁₂ /MIL-101 ^g	71	0.39	77
8	5% PW ₁₂ /MIL-101 ^h	75	0.41	77
9	5% PW ₁₂ /MIL-101 ⁱ	84	0.40	80
10	1% PW ₁₂ /MIL-101 ^j	68	0.32	81
11	5% PW ₁₂ /MIL-101 ^k	67	0.32	83
12	14% PW ₁₂ /MIL-101-B ^l	78	0.42	36
13	5% PW ₁₂ /NH ₂ -SBA-15 ^m	48	0.19	17

^a 0.1 M cyclohexene, 0.2 M H₂O₂, 28 mg of catalyst (5.8×10^{-3} and 4.9×10^{-3} mmol W in PW₁₂/MIL-101 and PW₄/MIL-101, respectively), method A, 1 mL of MeCN, 50 °C, 3 h. ^b TOF = (moles of substrate consumed) · (moles of W)⁻¹ · time⁻¹; determined by GC from the initial rates of cyclohexene oxidation. ^c GC yield based on the substrate consumed. ^d No catalyst was present. ^e MIL-101 matrix without POM. ^f Homogeneous catalyst (5.8×10^{-3} mmol W for PW₁₂ or 4.9×10^{-3} mmol W for PW₄). ^g Method B. ^h Method C. ⁱ 60 mg of the catalyst (1.2×10^{-2} mmol W). ^j 99 mg of PW₁₂/MIL-101 (4.1×10^{-3} mmol W) after 3 consecutive treatments with 1 M Bu₄NClO₄ in MeCN. ^k PW₁₂/MIL-101 dried at 150 °C for 4 h. ^l 14 mg of the catalyst (8.2×10^{-3} mmol W). Allylic oxidation products, cyclohexenol/-one (ca. 5%), along with *trans*-cyclohexane diol (24%), 2-hydroxycyclohexanone, and adipic aldehyde were also found. ^m *trans*-Cyclohexane diol (67%) and cyclohexenol/-one (15%) were also found.

lower nuclearity peroxotungstates, such as PW₄ and PW₂.^{99–104} In water, PW₁₂ completely transforms to PW₄ and other peroxotungstates after 1 h treatment with 50 equiv of H₂O₂ at room temperature.¹⁰⁰ However, the use of organic medium (acetophenone, DMF) enables increasing POM stability with respect to solvolytic destruction in the presence of aqueous H₂O₂, which leads to incomplete and reversible PW₁₂ transformations under the conditions of H₂O₂ excess (400 equiv, 2 h, 90 °C).¹⁰² Indeed, we found no PW₄ and only 3% of PW₂ (small signal with δ 0.4 ppm in the ³¹P NMR spectrum shown in Figure 5B)¹⁰⁵ in the acetonitrile solution of PW₁₂ after homogeneous cyclohexene oxidation under turnover conditions (500 equiv of H₂O₂). We had a thought that immobilization on MIL-101 could additionally increase stability of the polyanion structure.

Indeed, we performed cyclohexene oxidation over PW₁₂/MIL-101 after a preliminary treatment of the catalyst with a 500-fold excess of 30% H₂O₂ (see the Experimental Section, method B) but found no changes in both activity and selectivity (compare entries 6 and 7 in Table 2). Additionally, the curves of cyclohexene

**Figure 7.** Cyclohexene conversion (■, □), epoxide yield (●, ○) and selectivity (▲, △) versus time in the oxidation with H₂O₂ over PW₁₂/MIL-101 (method A — ■, ●, ▲ and method B — □, ○, △). Reaction conditions as in Table 2.**Figure 8.** Raman spectra of (A) PW₄ (0.05 M solution in H₂O–H₂O₂), (B) solid PW₁₂, (C) MIL-101, (D) PW₁₂/MIL-101, (E)–(G) PW₁₂/MIL-101 after 1, 3, and 5 cycles of cyclohexene oxidation, respectively. Reaction conditions as in Table 2 (method A).

conversion and epoxide yield versus time showed no induction period, and the initial rate areas coincided in methods A and B (Figure 7). In turn, the ³¹P NMR MAS spectrum of 5% PW₁₂/MIL-101 remained practically unchanged after five cycles of cyclohexene oxidation (see Figure 5A and F). Hence, we may conclude that if the transformation of the MIL-immobilized PW₁₂ to the lower nuclearity species occurs in the course of the catalytic oxidation under the conditions employed, such transformation is apparently reversible. Yet, one can not exclude that the active species responsible for catalysis is present in minor amounts, not detectable by ³¹P NMR MAS.

According to the FT-IR and Raman spectra (Figures 3b and 8, respectively), MIL-101 supported PW₁₂ does not lose its Keggin structure after 3 cycles of cyclohexene oxidation with H₂O₂, but begins to transform to the peroxotungstate species PW₄ after five reuses (i.e., after about 770 TON). The FT-IR band at 1081 cm⁻¹ broadens after several cycles of cyclohexene oxidation because of anion symmetry lowering (Figure 3b). As was mentioned above, homogeneous PW₁₂ partially transformed to PW₂ peroxotungstate already after the first cycle of cyclohexene oxidation (155 TON) under the conditions employed. Thus, we may conclude that immobilization onto MIL-101 does increase stability of PW₁₂ toward destruction in the presence of H₂O₂.

(99) Aubry, C.; Chottard, G.; Platzer, N.; Brégaud, J.-M.; Thouvenot, R.; Chauveau, F.; Huet, C.; Ledon, H. *Inorg. Chem.* **1991**, *30*, 4409–4415.

(100) Duncan, D. C.; Chambers, R. C.; Hecht, E.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 681–691.

(101) Bailey, A. J.; Griffith, W. P.; Parkin, B. C. *J. Chem. Soc., Dalton Trans.* **1995**, 1833–1837.

(102) Zhang, S.; Zhao, G.; Gao, S.; Xi, Z.; Xu, J. *J. Mol. Catal. A: Chem.* **2008**, *289*, 22–27.

(103) Neumann, R. *Prog. Inorg. Chem.* **1998**, *47*, 317–370.

(104) Brégaud, J.-M. *Dalton Trans.* **2003**, 3289–3302.

(105) Salles, L.; Aubry, C.; Thouvenot, R.; Robert, F.; Doremieux-Morin, C.; Chottard, G.; Ledon, H.; Jeannin, Y.; Brégaud, J.-M. *Inorg. Chem.* **1994**, *33*, 871–878.

We also examined a “one-pot” procedure which combined the preparation of the $\text{PW}_{12}/\text{MIL-101}$ catalyst and cyclohexene oxidation (see the Experimental Section, method C). Importantly, following such a simple protocol we managed to obtain cyclohexene epoxide with the yield even superior to that found using conventional method A (compare entries 6 and 8 in Table 2).

One can see from the data shown in Table 2 and Figure 7 that cyclohexene conversion was incomplete over $\text{PW}_x/\text{MIL-101}$ catalysts despite a 2-fold excess of H_2O_2 was employed. This could be due to partial unproductive decomposition of the oxidant on MIL-101. Previously, we revealed that MIL-101 does possess some activity in H_2O_2 dismutation at 50 °C.⁸⁹ Indeed, the presence of some amount of cyclohexene allylic oxidation products supports the involvement of radical species in the oxidation process. Meanwhile, we found that about 25% of the oxidant was still present in the reaction mixture at the end of the catalytic reaction. So, we believe that another reason of the incomplete cyclohexene conversion could be blockage of active sites by the reaction products. Indeed, by increase of the catalyst amount (entry 9, Table 2) we managed to achieve higher cyclohexene conversion (84%) and epoxide yield (66%).

The catalyst prepared using MIL-101 with enlarged surface area and pore volume (14% $\text{PW}_{12}/\text{MIL-101-B}$) also revealed a higher conversion of cyclohexene (entry 12, Table 2). However, the selectivity to epoxide was lower for this catalyst compared to 5% $\text{PW}_{12}/\text{MIL-101}$ because of subsequent transformations of the epoxide to *trans*-1,2-cyclohexanediol, 2-hydroxycyclohexanone, and adipic aldehyde. Hence, we may conclude that 5 wt % is an optimal PW_{12} loading required for the selective alkene epoxidation, and higher loadings should be avoided.

To clarify the catalytic behavior of forms **I–III** which are present in $\text{PW}_{12}/\text{MIL-101}$ catalysts, we compared the performance of the parent 5% $\text{PW}_{12}/\text{MIL-101}$ sample (entry 6, Table 2) with the performances of the sample dried at 150 °C (entry 11, Table 2) and the sample obtained after three consecutive treatments with 1 M Bu_4NClO_4 (entry 10, Table 2) in cyclohexene oxidation with H_2O_2 . The latter two materials contained mostly form **III** and were found to be less active (TOF 0.32 min^{-1}) but more selective (81–83%) toward epoxide formation compared to the initial 5% $\text{PW}_{12}/\text{MIL}$ which included mainly form **I**. The higher selectivity of form **III** in the epoxidation reaction corroborated its assignment to dehydrated PW_{12} . Interestingly, form **III** also predominated in 14% $\text{PW}_{12}/\text{MIL-101}$ according to its ^{31}P NMR MAS spectrum (Figure 5G), but as we mentioned above, the selectivity over this sample was rather low because high POM loading favors epoxide ring-opening and/or overoxidation processes.

To assess the scope and limitations of the $\text{PW}_x/\text{MIL-101}$ catalysts, the activity of the optimal sample, 5% $\text{PW}_{12}/\text{MIL-101}$, was tested in the oxidation of alkenes with different steric and electronic structures, including natural terpenes (α -pinene, 3-carene, and limonene), cyclooctene, octene-1, styrene, and *cis*-/ *trans*-stilbenes. The results are presented in Table 3. The rank of the catalytic activity expressed in TOF values was typical for an electrophilic oxygen transfer process: $\text{R}_2\text{C}=\text{CHR}$ (3-carene) > $\text{RCH}=\text{CHR}$ (cyclooctene) > $\text{RCH}=\text{CH}_2$

(octene-1). Both homogeneous PW_{12} and heterogeneous $\text{PW}_{12}/\text{MIL-101}$ revealed a very similar range of the maximal (3-carene) and minimal (octene-1) TOF values, which may indicate the absence of diffusive limitations in the alkene epoxidation over $\text{PW}_{12}/\text{MIL-101}$. It is worth noting that activity of $\text{PW}_{12}/\text{MIL}$ expressed in TOF values is significantly higher than the activity of previously reported PW_4 –Amberlite catalyst at the same reaction conditions. For example, TOF for limonene epoxidation over PW_4 –Amberlite calculated on the basis of reported data is equal to 0.01 min^{-1} .⁷¹

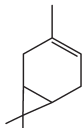
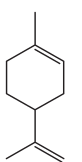
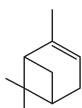

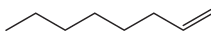
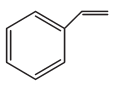
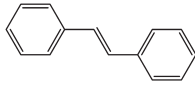
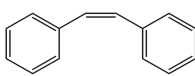
Importantly, $\text{PW}_{12}/\text{MIL-101}$ is able to catalyze selectively epoxidation of acid sensitive terpenes, and 70–96% selectivities can be achieved depending on the specific alkene structure and reaction conditions. Oxidation of styrene and stilbenes proceeded less efficiently than oxidation of electron-rich alkenes, but note that substrate conversions and epoxide selectivities were higher with $\text{PW}_{12}/\text{MIL-101}$ than with homogeneous PW_{12} . Thus oxidation of styrene with 1 equiv of H_2O_2 over $\text{PW}_{12}/\text{MIL-101}$ gave 24% substrate conversion and 54% epoxide selectivity after 3 h at 50 °C, while the corresponding parameters for homogeneous PW_{12} were 20 and 40% (see Table 3). This effect can be rationalized if we take into account the affinity of the MIL-101 framework for benzene-like molecules.⁸⁶

It is worth noting that for the majority of alkene substrates an increase of H_2O_2 /alkene molar ratio led to both higher substrate conversions and epoxide selectivities (Table 3). With 2 equiv of H_2O_2 the selectivity of epoxidation attained 96, 89, and 99% for 3-carene, limonene and cyclooctene, respectively. These values exceed the selectivities acquired using homogeneous PW_{12} . The same tendency was observed earlier for caryophyllene epoxidation with H_2O_2 over Ti-POM/MIL-101.⁸⁹ Note that maintenance of selectivity with growing conversion under excess of H_2O_2 is a quite unusual phenomenon for alkene epoxidation,⁶⁹ for which an excess of olefin is usually employed to achieve a high selectivity.²³ The epoxide selectivity typically tends to decrease with conversion because of consecutive epoxide ring-opening and overoxidation processes. This is exactly what happens in the presence of homogeneous PW_{12} (see examples in Table 3). We suppose that the non-typical behavior that we revealed for the hybrid $\text{PW}_{12}/\text{MIL-101}$ catalysts might originate from an ability of MIL-101 to adsorb preferably H_2O_2 and alkene substrate and not to adsorb water because of hydrophobicity of the organic linker. This agrees with the recently published data on the water sorption on MIL-101, which showed that H_2O uptake starts at rather high partial pressures ($p/p_0 = 0.4$).¹⁰⁶ On the basis of these results, one might expect that MIL-101 surface would behave as a hydrophobic one at rather low water concentration in an organic solvent.

Catalyst Stability and Recycling. While studying liquid phase processes over solid catalysts it is extremely important to address the issues of stability of the active component with respect to leaching and maintenance of the catalyst porous structure under the reaction conditions. The nature of catalysis and recycling behavior are crucial points as well. Following the methodology suggested

(106) Küsgens, P.; Rose, M.; Senkovska, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel, S. *Microporous Mesoporous Mater.* **2009**, *120*, 325–330.

Table 3. Alkene Oxidation with H₂O₂: Homogeneous PW₁₂ versus 5% PW₁₂/MIL-101^a

Substrate	Catalyst	[H ₂ O ₂] (M)	Substrate conversion (%)	TOF ^b (min ⁻¹)	Epoxide selectivity ^c (%)
3-Carene	PW ₁₂	0.1	61	0.57	90
	PW ₁₂	0.2	66	0.62	78
	PW ₁₂ /MIL-101	0.1	60	0.52	90
	PW ₁₂ /MIL-101	0.2	72	0.59	96
Limonene	PW ₁₂	0.1	53	0.41	79 ^d
	PW ₁₂	0.2	59	0.46	65 ^d
	PW ₁₂ /MIL-101	0.1	46	0.35	70 ^d
	PW ₁₂ /MIL-101	0.2	55	0.43	89 ^d
α-Pinene	PW ₁₂	0.1	62	0.43	76
	PW ₁₂ /MIL-101	0.1	53	0.38	74
	PW ₁₂ /MIL-101	0.2	65	0.47	71
Cyclooctene	PW ₁₂	0.2	78	0.40	95
	PW ₁₂ /MIL-101	0.2	76	0.38	99
Octene-1 ^e	PW ₁₂	0.2	56	0.13	56
	PW ₁₂ /MIL-101	0.2	50	0.11	61
Styrene	PW ₁₂	0.1	20	0.09	40
	PW ₁₂ /MIL-101	0.1	24	0.10	54
	PW ₁₂ /MIL-101	0.2	30	0.11	73
trans-Stilbene	PW ₁₂	0.1	28	0.10	65 ^f
	PW ₁₂ /MIL-101	0.1	35	0.11	69 ^f
cis-Stilbene	PW ₁₂	0.1	15	0.09	47 ^{f,g}
	PW ₁₂ /MIL-101	0.1	22	0.12	68 ^{f,g}

^a Reaction condition: 0.1 M substrate, 28 mg of catalyst 5% PW₁₂/MIL-101 or 1.4 mg of PW₁₂ (5.8×10^{-3} mmol W), method A, 1 mL of MeCN, 50 °C, 3 h. ^b TOF = (moles of substrate consumed) · (moles of W)⁻¹ · time⁻¹; determined by GC from the initial rates. ^c GC yield based on the substrate consumed. ^d Limonene 1,2-epoxide. ^e 5 h. ^f Benzaldehyde was also formed. ^g cis-Stilbene epoxide.

by Sheldon and co-workers,⁶⁸ we performed fast hot catalyst filtration tests and found no further substrate conversion in the filtrate after the removal of both PW₁₂/MIL-101 and PW₄/MIL-101 (Figure 9). This proves the true heterogeneous nature of the oxidation catalysis over the PW_x/MIL-101 catalysts. Additionally, elemental analysis data (see Table 1) confirmed that no evident tungsten or chromium leaching occurred under the conditions employed.

The recycling behavior of the PW_x/MIL-101 catalysts is shown in Figure 10. One can see that the performance of PW₄/MIL-101 was quite stable during four consecutive runs, but the epoxide yield slightly decreased after the third run (Figure 9a). In turn, PW₁₂/MIL-101 kept its

activity and selectivity during four catalytic cycles (600 TON) and then the activity decreased (Figure 10b).

The Raman spectrum of PW₄/MIL-101 run after four cycles of cyclohexene oxidation (Figure 4D) revealed the principal bands of the peroxotungstate structure. Hence, we may suppose that PW₄ supported on MIL-101 kept its structure during four cycles of cyclohexene oxidation (250 TON). Hill and co-workers have reported that deactivation of homogeneous PW₄ is caused mainly by the reaction product, epoxide.^{100,107} The PW₄-Amberlite

(107) Hill C. L. In *Comprehensive Coordination Chemistry II*; Wedd, G. A., Ed.; Elsevier Science: New York, 2004; Vol. 4, p 679–759.

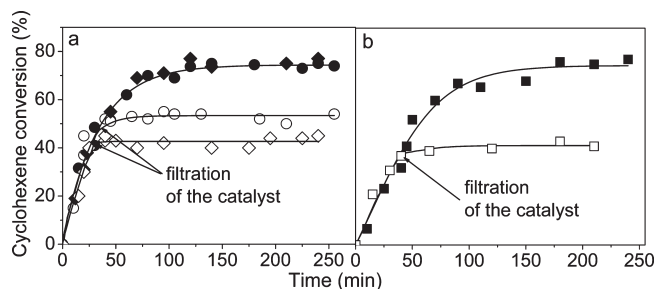


Figure 9. Hot catalyst filtration experiments for cyclohexene oxidation with 0.2 M H_2O_2 over (a) $\text{PW}_{12}/\text{MIL-101}$ (methods A—● and C—◆) and (b) $\text{PW}_4/\text{MIL-101}$.

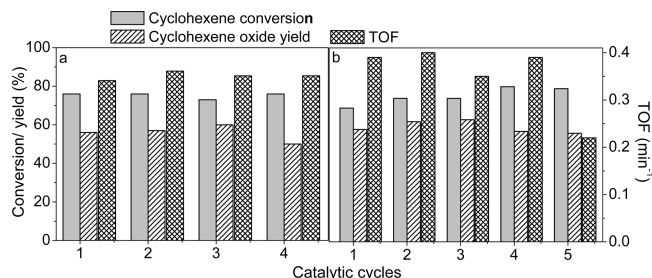


Figure 10. Catalyst recycling in cyclohexene oxidation with 0.2 M H_2O_2 : (a) $\text{PW}_4/\text{MIL-101}$ and (b) $\text{PW}_{12}/\text{MIL-101}$ (method A). Reaction conditions as in Table 2 (method A).

catalyst was also reported to be poisoned by the epoxide product.⁷¹ We believe that some deactivation of $\text{PW}_x/\text{MIL-101}$ might be caused by destruction of the MIL-101 matrix and/or filling pores by the reaction products. Indeed, both specific surface area and pore volume decreased after 4–5 cycles of cyclohexene oxidation over $\text{PW}_x/\text{MIL-101}$ (see Table 1). In turn, the XRD technique showed some amorphization of the MIL-101 structure because of its partial decomposition.

Conclusions. Polyoxotungstates $[\text{PW}_4\text{O}_{24}]^{3-}$ and $[\text{PW}_{12}\text{O}_{40}]^{3-}$ have been electrostatically attached to the

surface of the mesoporous zeotype coordination polymer MIL-101 with retention of both POM and MOF structures. The hybrid $\text{PW}_4/\text{MIL-101}$ and $\text{PW}_{12}/\text{MIL-101}$ materials demonstrate similar catalytic activities in H_2O_2 -based alkene epoxidation, comparable to the activity of the corresponding homogeneous PW_x and significantly higher than activities of the known supported PW_4 catalysts.⁷¹ In turn, the epoxide selectivities achieved over the $\text{PW}_x/\text{MIL-101}$ catalysts are close^{15,69,72,73} or even superior⁷⁰ to those reported for PW_4 immobilized by other techniques. The selectivity strongly depends on the POM loading, the optimal value of which is about 5 wt %. A simple one-pot procedure which involves both the catalyst preparation and oxidation reaction can be used to achieve high yields of epoxides. In contrast to the homogeneous systems, the use of a higher H_2O_2 /alkene molar ratio allows increasing simultaneously both the alkene conversion and the epoxide selectivity. This unusual behavior, most likely, results from the specific sorption properties of MIL-101. Immobilization within the MIL-101 matrix allows increasing considerably the stability of PW_{12} toward solvolytic destruction in the presence of H_2O_2 .

Both $\text{PW}_4/\text{MIL-101}$ and $\text{PW}_{12}/\text{MIL-101}$ materials behave as true heterogeneous catalysts and can be recycled several times without loss of activity and selectivity with retention of both POM and MIL-101 structures; however, some deterioration of the catalytic properties may occur after several reuses because of partial destruction of the MIL-101 matrix and/or filling pores by the reaction products.

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