Catalysis Communications 37 (2013) 80–84

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Hybrid peroxotungstophosphate organized catalysts highly active and selective in alkene epoxidation

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ARTICLE INFO

Article history:
Received 7 January 2013
Received in revised form 12 March 2013
Accepted 25 March 2013
Available online 6 April 2013

Keywords:
Organic–inorganic hybrid composites
self-assembly
polyoxometalates
heterogeneous catalysis
epoxidation

ABSTRACT

Heterogenization of homogeneous catalysts is still a challenge but can improve drastically the processability of these compounds. Hybridization of polyoxometalates offers an efficient heterogenization route of homogeneous epoxidation catalysts. The Keggin $[PW_{12}O_{40}]^{3-}$ and the Ventruello $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species were inserted by electrostatic interactions in a poly(ampholytic) polymeric matrix in order to prevent the leaching of these species. The presence of the polymeric matrix allows to tune the catalyst performance in cyclooctene epoxidation and to improve the selectivity to epoxide. Indeed, the hydrophobicity of the matrix induces a quick desorption of hydrophilic epoxide species. Their over-oxidation and the catalyst species deactivation by over-adsorption of epoxide are then avoided.

1. Introduction

Hybrid materials that allow to combine complementary characteristics of individual constituents are becoming currently more and more attractive [1–3]. The association of organic and inorganic components at the nanosize level offers many benefits in countless applications. On the one hand, the infinity of inorganic compounds with magnetic, dielectric, mechanic, and catalytic properties allows to use such hybrid materials in various fields such as medicine [4], optics [5], electronics [6] and catalysis [7–9]. On the other hand, the organic part brings additional convenient processing and electronic or photoconductivity properties. Furthermore, the use of a self-assembled organic matrix could induce specific molecular arrangements in the hybrid that leads to a fine control of its structural properties [10].

In catalysis, the main goal of hybridization usually consists in solid catalyst synthesis through active species heterogenization. In the present case, hybridization targets more valuable effects. First, the organization of the organic part is assumed to confer new specificity properties. This could for example occur via the organization of a polymeric partner around the active sites to mimic the enzyme protein arms function. This organization would impose geometrical constraints to control the reaction of the catalytic inorganic partner. Second, the use of an organic environment is expected to induce specific adsorption properties of the reagents. Such a specificity is expected to be induced through the structuring of hydrophilic/phobic environment around the active species.

This tuned behavior of catalytic and physicochemical properties could lead to highly selective heterogeneous catalysts. A self-assembled amphiphilic poly(ampholytic) copolymer was selected here as an efficient matrix to structure the space around an inorganic compound and to form an organized hybrid with improved adsorption performance in catalysis [11].

The inorganic compounds selected here are polyoxometalates (POMs). POMs are inorganic early transition metal oxide clusters. Their composition, structure, size, redox chemistry, charge versatility and solubility in various media are the numerous reasons that boost the POMs chemistry at the forefront of fundamental research today such as catalysis [12], materials [13,14] and medicine [15]. Moreover, in comparison to enzymes and organometallic complexes, POMs are thermally and oxidatively stable [16]. In catalysis, POMs display simultaneously high Brønsted acidity and efficient redox behavior allowing fast transformations under soft conditions. POMs are active in esterification, hydrolysis, and alkylation but also in alcohol or sulfide oxidation and alkene epoxidation [17,18].

Hybridization of POMs was already performed but only very few applications are reported in catalysis [8,9,19]. Different possibilities are allowed for the hybridization. A simple physical blending seems not efficient enough to avoid leaching of catalytic species. Covalent bonding of POMs with organic compounds was already achieved but is limited to a few kinds of POMs [20,21]. Moreover covalent bonding can change the POM structure and composition and induce changes in the catalytic properties. Hybridization was thus achieved here by taking advantage of electrostatic interactions between negatively charged POMs and a poly(ampholytic) copolymer positively charged. The copolymer consists of substituted diallylamines alternated with maleic acid monomers. The amine monomer brings the positive charge and bears side alkyl chains

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http://dx.doi.org/10.1016/j.catcom.2013.03.036

with eighteen carbon atoms (hereafter named C18). Hydrophobic interactions between these alkyl side chains confer to the polymer a self-assembled lamellar arrangement (Scheme 1). The periodic dimension of this comb-like structure is controlled by the length of these chains [11].

Herein, to probe the catalytic performance of hybrids, the epoxidation of cyclooctene with Keggin $H_3PW_{12}O_{40}$ species (hereafter named PW12) and trianionic diperoxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (hereafter named PW4) were selected. This cluster, the so-called Venturello complex, results from the activation of the Keggin-type compound $H_3PW_{12}O_{40}$ with hydrogen peroxide and H_3PO_4. PW4 clusters have been largely recognized for a long time as highly active species in catalytic oxidation [22,23].

2. Experiment

2.1. Matrix synthesis

C18 matrix was synthesized by a copolymerization of equimolar amounts of *N*,*N*-diallyl-*N*-octadecylamine and maleic acid in a water/ethanol (90:10 v/v) mixture as described elsewhere [11], and isolated analogously by precipitation four times into cold acetone. The crude copolymer was dialyzed first in a mixture of ethanol/CH_2Cl_2/37 wt.% HCl (60:39:1 v/v/v) for ten days, then in an ethanol/CH_2Cl_2 (70:30 v/v) mixture for five days, changing the solvent every two days. After removing the solvent, the copolymer was dissolved in ethanol; an equimolar amount of OH^--loaded strong basic exchange resin was added, and the mixture was stirred for 2 h. The collected precipitate was dried at 60 °C in vacuum and gave the pure copolymer in the form of a white, hygroscopic powder.

2.2. Hybrid synthesis

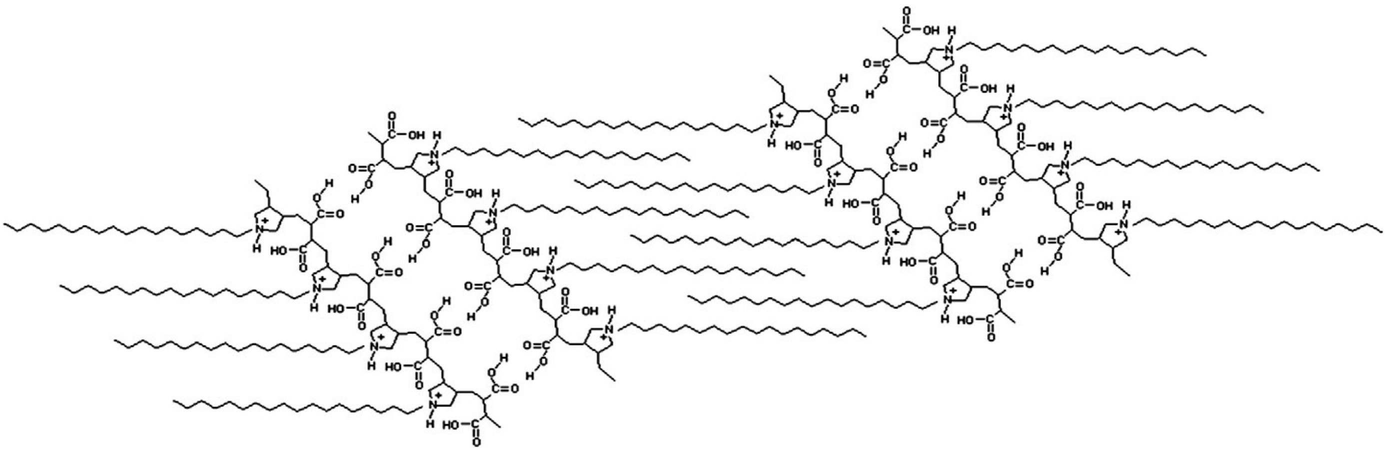
The polyoxometalates used in this work were $H_3PW_{12}O_{40}$ (PW12) supplied by Aldrich. The two hybrids were synthesized by a two-phase ion-exchange process. For the PW12 hybrids, a water solution of PW12 (2 g, 0.67×10^{-3} mol) was mixed with a chloroform solution containing the organic matrix (0.94 g, 2.01×10^{-3} mol of repeated unit). For PW4 hybrids, the peroxotungstophosphate species (PW4) were synthesized according to a protocol adapted from the literature [24]. Its corresponding hybrid was made as follows: after 1 h of agitation, 250 ml H_2O_2 (30%) containing 5 g (1.67×10^{-3} mol) of $H_3PW_{12}O_{40}$ and 0.229 ml (3.35×10^{-3} mol) of H_3PO_4 (85%) were mixed with a chloroformic solution containing the organic matrix (7.01 g, 15.03×10^{-3} mol of repeated unit). The both biphasic mixtures are then magnetically vigorously stirred during 2 h. The solids are recovered by filtration, washed three times with distilled water and dried overnight in vacuum at room temperature. The two hybrids were hereafter denoted PW12–C18 and PW4–C18 respectively.

2.3. Characterizations of the samples

The weight percentages of W and P were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation. X-ray diffraction (XRD) measurements were performed with a Siemens D5000 diffractometer using the Kα radiation of Cu ($\lambda = 1.5418$ Å). The small 2θ range (1°–10°) was scanned at a rate of $0.002° s^{-1}$. The high 2θ range (10°–60°) was scanned at a rate of $0.01° s^{-1}$. Fourier transformed infrared spectroscopy was performed with transparent discs of the samples prepared after diluting them in KBr (>99%, Janssens Chimica) by a weight factor of 100. The spectra were obtained by recording 100 scans between 400 and 4000 cm^{-1} with a 4 cm^{-1} resolution. The IFS55 Equinox spectrometer (Bruker) used in the transmission mode was equipped with a DTGS detector. Raman spectroscopy was performed on a Bruker RFS 100/S apparatus equipped with a coherent Nd-YAG laser ($\lambda = 1064$ nm, 100 mW). The resolution was 4 cm^{-1} and the signal was recorded in the 3500–100 cm^{-1} range. For each reported spectrum 50 scans were recorded and averaged.

2.4. Catalytic experiments

The monophasic catalytic reaction was performed in a 5 ml round-bottomed flask equipped with an oil bath, a magnetic stirring rod and a septum. In a typical experiment, the catalyst (mass adjusted to always have 0.03 mmol of W in the reactor), cyclooctene (0.5 mmol), acetonitrile (5 ml) and hydrogen peroxide (30% in water) (2.5 mmol) were added in the flask. For homogeneous catalytic tests, namely with PW12 and PW4 alone, the addition order of the reaction mixture components is inverted. In these cases, a pre-activation with H_2O_2 is achieved during 1 h followed by the addition of CH_3CN and the alkene. These tests were made with 0.0025 mmol of $H_3PW_{12}O_{40}$ (named PW_{12}-H_2O_2) and 0.005 mmol of H_3PO_4 (85%) (named PW_{12}-H_3PO_4-H_2O_2) to form the corresponding $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species. The reaction was performed at 50 °C and was monitored by GC analysis with the internal standard method (dibutyl ether). Assignments of products were made by comparison with authentic samples and by GC-MS. The catalyst was recovered by centrifugation after reaction, washed with CH_3CN three times, dried overnight in vacuum at room temperature and reused.



Scheme 1. Scheme of the supramolecular organization of the self-assembled amphiphilic poly(ampholytic) copolymer (inspired from [13]).

3. Results and discussion

PW12 and PW4 hybrids were synthesized by a two-phase ion exchange process of water and chloroform. Quantities were based on an equivalent molar charge ratio between three times negatively charged $[PW_{12}O_{40}]^{3-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$ units and one time positively charged polymer repeated unit. The solid hybrids are recovered by filtration and then dried. Thermogravimetric analysis (TGA) under air and ICP-AES analyses revealed that 51.9 wt.% of PW12 and 28.8 wt.% of PW4 were effectively hybridized in the matrix. The obtained molar ratio POM/polymer repeated unit is 0.52/3 and 0.49/3 respectively.

Vibrational spectroscopies (IR and Raman) confirm the hybridization of the Keggin PW12 and PW4 species. In IR, as presented in Fig. 1, the classical bands of Keggin structure at 1080 cm^{-1}, 984 cm^{-1}, 891 cm^{-1} and 810 cm^{-1} are observed and can be assigned to v(P–O), v(W = O) and the asymmetric vibration of v(W–O–W) (corner and edge-sharing respectively) [25]. Small shifts are observed and attributed to electrostatic interactions between POM species and positive charges along the matrix framework [26]. The peroxo species bonds are observed at 1030 cm^{-1}, 966 cm^{-1}, 884 cm^{-1}, 836 cm^{-1} and 560 cm^{-1} for v(P–O), v(W = O), v(W–O–W), v(O–O) and $v(W(O_2))$ respectively [27]. Raman confirms the hybridization of peroxotungstophosphate anions and shows the characteristic bands at 958 cm^{-1}, 853 cm^{-1} and 561 cm^{-1} assigned to v(W = O), v(O–O) and $v(W(O_2))$ [28]. It should be pointed out that the presence of other smaller peroxo species cannot be totally excluded by the IR and Raman results.

X-ray diffraction at small angle reveals the nanoscale organization of the pure C18 matrix and the hybrids (Fig. 2). The self-assembled lamellar organization of the polymer induces two diffraction peaks at 2.80° and 5.61°, which correspond to the first and the second order reflection peaks of the matrix [11]. The hybridization of PW12 and PW4 species leads to two different behaviors. In the first case, the matrix organization is lost as the hybrid is formed. The broad large peak obtained reveals an amorphous reorganization of the polymer chains around the PW12 species likely randomly distributed in the matrix. In the second case, the addition of PW4 species does not perturb the matrix supramolecular organization. Besides, it causes a shift of the main peak to lower diffraction angle (2.49°). According to the Bragg law, the characteristic inter-reticular distance of the resulting structure increases from 3.15 nm to 3.55 nm. This phenomenon is assumed to be due to the regular insertion of the PW4 species inside the matrix. The opposite behavior of the PW12 and PW4 species could be attributed to the difference of size between the two POM species. The 1 nm of diameter of the Keggin PW12 structure appears too big to be inserted in the matrix hydrophilic region without reorganization. The smaller size of PW4 species sounds more favorable for an organized insertion [29].

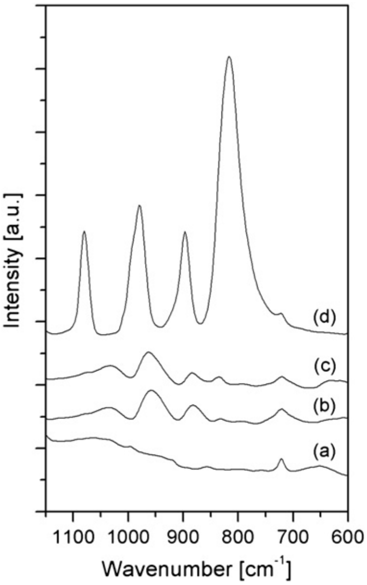


Fig. 1. IR spectra of hybrid materials in the low frequency region of polyoxometalate species: (a) the pure C18 copolymer matrix, (b) the PW4–C18 hybrid, (c) the PW4–C18 hybrid recovered after four catalytic tests and (d) the PW12–C18 hybrid.

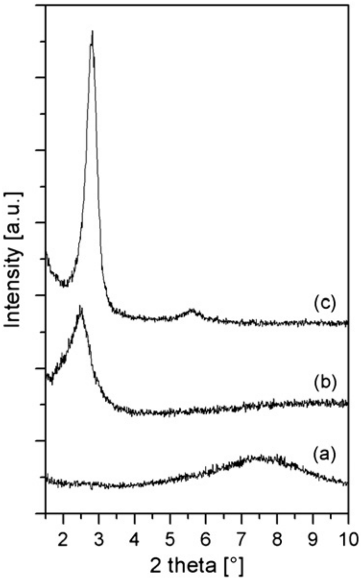


Fig. 2. XRD patterns at small angle of (a) the PW12–C18 hybrid, (b) the PW4–C18 hybrid and (c) the pure C18 copolymer matrix.

The absence of crystalline peak at large angle (results not presented) argues in favor of the absence of "pure" POM crystallized species, and thus of a good dispersion of the polyoxometalates species through the matrix.

Cyclooctene epoxidation managed in acetonitrile was selected to measure the hybrid catalytic performance. Hydrogen peroxide was used as oxidizing agent. Results are presented in Table 1 and Fig. 3. In order to highlight the impact of hybridization, homogeneous catalytic tests were also achieved. The PW12 species appear to be inactive in the reaction but need a pre-activation by H_2O_2 before a test. This pre-activation can be managed by changing the order of addition of reaction mixture components as exposed in Table 1 [28]. After 1 h of reaction with hydrogen peroxide, PW12 forms the active $\{PO_4[WO(O_2)_2]_4\}^{3-}$ Venturello species and dianionic $\{[WO(O_2)_2(H_2O)]_2O\}^{2-}$ species [17]. In that case, a 95% conversion is achieved after 3 h. The conversion is faster when H_3PO_4 is added to perfect the stoichiometric reaction of $[PW_{12}O_{40}]^{3-}$ to form the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species. This result confirms the better activity of Venturello clusters than the peroxotungstate species [17,30].

To be active it appears that the PW12 species must be previously chemically modified by H_2O_2 to form the active species PW4. Then, the effect of the addition order of reaction mixture components will only have an impact if PW12 species are used directly as catalysts. In the case of the PW4–C18 hybrid the reaction order will not have an influence on the catalytic performance (because PW4 are the already active species) and was thus not tested. Results on the effect of reactants introduction order are exposed in Table 1 for the PW12–C18. As suspected, no activity is observed for the C18–PW12 hybrid catalyst even if reaction with H_2O_2 during 1 h is performed. The hybridization of PW12 species does not allow the polyoxometalates transformation into active peroxo species. This may likely be explained by the facts that (i) polyoxometalates are known to be more stable when hybridized [31] and (ii) H_2O_2 has hindered access to PW12 because of the high hydrophobicity of the C18 matrix.

Table 1
Catalytic performance in cyclooctene epoxidation.[a]

Catalyst	Addition order of reaction mixture components	Reaction time	Conversion [%]	Yield [%]	Selectivity [%]	TOF[b] [mol/h mol$_W$]
PW12	CH_3CN/cyclooctene/H_2O_2	5	4	–	–	0.20
PW12	H_2O_2/CH_3CN/cyclooctene	3	95	81	85	10.20
PW12 + H_3PO_4	H_2O_2 + H_3PO_4/CH_3CN/cyclooctene	1.5	98	72	74	32.47
PW12–C18	CH_3CN/cyclooctene/H_2O_2	5	4	–	–	0.15
PW12–C18	H_2O_2/CH_3CN/cyclooctene	5	8	–	–	0.14
PW4–C18	CH_3CN/cyclooctene/H_2O_2	5	96	95	99	6.83

[a] Reaction conditions: catalyst (0.03 mmol of W), hydrogen peroxide (30% in water) (2.5 mmol), cyclooctene (0.5 mmol) and acetonitrile (5 ml), 50 °C.

[b] TOF = (moles of substrate consumed) × (moles of W)$^{-1}$ × time^{-1}; determined by GC from the initial rates of cyclooctene oxidation.

Although slightly less active than the homogeneous activated species, hybridized PW4 is efficient to epoxidize cyclooctene (Fig. 3). The smaller activity may be linked to a lower accessibility of PW4 species either by H_2O_2 or by the alkene molecule due to the hybridization.

Interestingly, the selectivities of the homogeneous and the PW4 hybrid catalysts are quite different. Remarkably, a constant >99% epoxide selectivity is obtained with the hybrid. At the opposite, traces of allylic oxidation products and 1,2-cyclooctanediol were detected for the homogeneous catalysts which leads to diminish epoxy selectivity (80%) (Fig. 3). These catalysts bring acidity induced by the activation of $H_3PW_{12}O_{40}$ by H_2O_2. This leads to the ring-opening of the epoxide and likely explains the obtained lower selectivity. Our experiments reveal that the hybridization prevents the acid-sensitive epoxide from ring-opening. Moreover, despite a large excess of hydrogen peroxide (olefin/H_2O_2 = 1/5 mol/mol), the hybrid catalyst also prevents the over-oxidation process. This interesting property may be related to the hybrid catalyst hydrophobicity. Indeed, some authors pointed out the impact of the catalyst's hydrophobicity on epoxide hydrolysis or over-oxidation [9]. It has been reported that epoxide is not stable in a hydrophilic environment and that allylic oxidation is not significant in hydrophobic environments [32]. Moreover the hydrophobicity could induce a better olefin adsorption. Inversely, the hydrophilicity of the epoxide could reduce the contact time between the epoxide and the hydrophobic hybrid catalyst, preventing its non-desired over-oxidation [33]. The combination of these two aspects brings about the improved epoxide selectivity [34]. Such a combination of high conversion and high selectivity with large excess of H_2O_2 is a quite remarkable phenomenon in olefin epoxidation [9,35]. Finally a test with an olefin/H_2O_2 ratio of 1/0.5 mol/mol was used to evaluate the H_2O_2 decomposition during the reaction. A conversion higher than 49% of the olefin was reached while under these conditions a maximum of 50% could be obtained (owing to the defect of H_2O_2), indicating the excellent H_2O_2 efficiency.

Being an essential aspect of liquid phase heterogeneous catalysis, the occurrence of leaching of hybridized PW4 species was also investigated. The recyclability was only evaluated for the active PW4 hybrid catalyst. The evolution of the conversion of a reaction medium was monitored after catalyst removal by centrifugation at 40% conversion (Fig. 4). It appears that no further conversion was observed in the collected medium. The absence of leaching was confirmed through recycling tests, namely using several times successively a given batch of the hybrid catalyst in fresh reaction media. The corresponding results are presented in Table 2. The latter has been tested four times. Considering 5 h of reaction, the conversion along these consecutive tests is the same, suggesting that no leaching occurs. It appears clearly that electrostatic interactions are strong enough to avoid leaching of catalytic species. According to these observations, the hybrid catalyst used in this work can be assimilated to a heterogeneous catalyst without any ambiguity. The absence of catalyst deactivation is also remarkable. Indeed homogeneous PW4 species are usually deactivated by diols and epoxide (via their over-adsorption) and are thus almost not reusable [24,32]. It comes out that the PW4 immobilization inside the hydrophobic matrix induces an additional and highly interesting protection effect of the PW4 species, namely it favors the quick desorption of deactivating hydrophilic products.

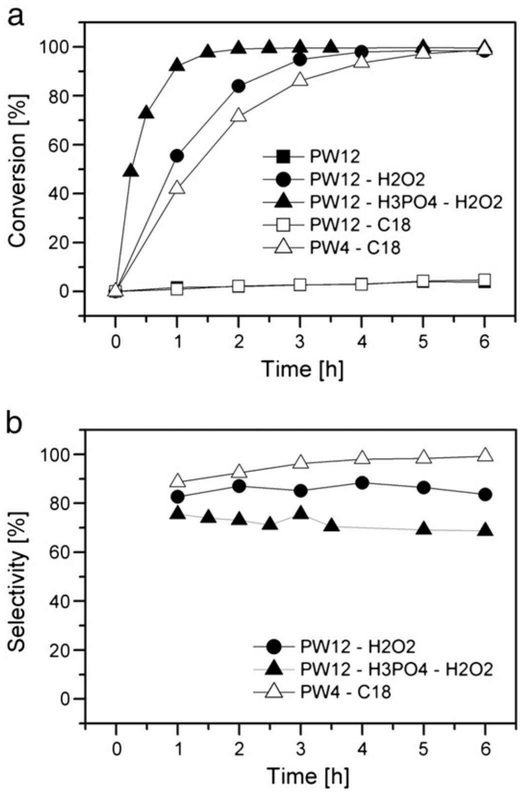


Fig. 3. Catalytic performance of homogeneous and hybrid catalysts for cyclooctene epoxidation in CH_3CN. A better conversion is obtained for homogeneous catalysts (a) but PW4 hybrid catalyst presents a higher selectivity in epoxycyclooctane (b).

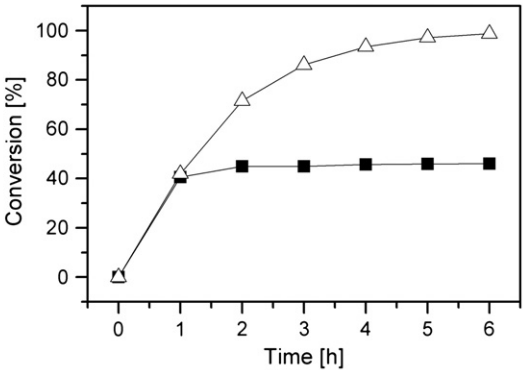


Fig. 4. Hot catalyst filtration experiment on hybrid for cyclooctene epoxidation. (△) Conversion without recovery and (■) test with catalyst recovery after 1 h by centrifugation and filtration.

Table 2
Catalytic performance of the hybrid catalyst recycling in cyclooctene epoxidation after 5 h of reaction.[a]

	Conversion [%]	Yield [%]	Selectivity [%]
Test 1	96	95	99
Test 2	97	97	>99
Test 3	98	98	>99
Test 4	99	99	>99

[a] Reaction conditions: catalyst (0.03 mmol of W), hydrogen peroxide (30% in water) (2.5 mmol), cyclooctene (0.5 mmol) and acetonitrile (5 ml), 50 °C, 5 h.

Post-test characterization hybrid catalyst PW4–C18 was performed by IR after the first and the fourth catalytic tests (Fig. 1). No modifications of the matrix are observed. Only small shifts of the catalytic species were noted for the $\nu(W=O)$ bands. Also, the intensity of the $\nu(O–O)$ bands at 836 cm^{-1} increases for the tested hybrids, confirming the accessibility of these species to the oxidizing agent H_2O_2. Hybrid catalysts are thus not affected during the reaction.

4. Conclusions

In this study, the epoxidation of cyclooctene with homogeneous and hybridized tungstophosphate species was achieved. It appears that homogeneous $[PW_{12}O_{40}]^{3-}$ species need a pre-activation step before a catalytic test in monophasic H_2O_2/CH_3CN conditions. Their direct hybridization as catalyst is then not efficient. Inversely hybrid catalyst with $\{PO_4[WO(O_2)_2]_4\}^{3-}$ shows to be remarkably efficient in various points of view. First, hybridization by electrostatic interaction is sufficient to stabilize heterogenized active species that undergo no leaching under epoxidation conditions. Second, protection against deactivation of PW4 species is brought by their immobilization inside the hydrophobic matrix. Finally, the organic matrix allows to control the olefin and epoxide adsorption so as to avoid epoxide ring-opening or overoxidation processes, giving rise to high selectivities to the desired epoxide. Organized hybrid catalysts seem thus an appropriate route to form highly selective and stable heterogeneous catalysts. Catalytic tests of hybrids with different hydrophobicity are in progress to study the impact of matrix polarity on activity and selectivity on different alkenes.

Acknowledgement

C.S. thanks FRIA for his PhD student position. The Belgian laboratories are partners of the “Inanomat” IUAP network and are indebted to the ‘communauté française de Belgique’ for financial support through the ARC program (08/13-009).

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