Epoxidation with peroxotungstic acid immobilised onto silica-grafted phosphoramides

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Abstract

Epoxidation of alkenes with hydrogen peroxide was catalysed with peroxotungstic acid complexed to immobilised mono- and bisphosphotriamides. Several silica-based materials such as amorphous silica, K10 montmorillonite and hectorite were used as carriers; these were first aminated with methylaminopropyl-trimethoxysilane and phosphorylated to the required phosphotriamides. Styrene, α-methylstyrene, indene, cyclohexene and cyclooctene were used as substrates and repeated uses of catalysts were performed to test the stability of the metal complexes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen peroxide is an efficient epoxidation reagent in neutral medium for non-conjugated olefins and prompted continuous interest of academic and industrial groups due to its high selectivity but some peroxometallic species are involved as catalysts [1,2]. Some metals were successfully used but high turnover frequencies were obtained with tungsten-based compounds [3,4] when organophosphorous ligands such as phosphonic acids and phosphotriamides are used. We previously showed these beneficial effects with homogeneous catalytic species [5] of general formula $>P=O \cdots WO_5$.

For the sake of recycling, a series of polystyrene [6] and polymethacrylate [7] polymeric supports (P)

with macroligands were developed. They contained the same (P)-$\bigwedge\bigwedge\bigwedge$->P=O-grafted structures. Epoxidation carried out with these catalysts showed that indeed phosphotriamides are the best ligands for tungsten in this reaction. But the use of organic polymers may have some practical inconvenience, and therefore their replace with inorganic ones seems to be more attractive. According to a similar approach, the imidazole units in polybenzimidazole polymers were shown to complex molybdenum oxide, MoO_3, and the resulting material was used in several epoxidations with *t*-butylhydroperoxide (TBHP) [8,9]. Polystyrene- and polyacrylate-grafted Mn(II) salens and tartaric acid-derived polyesters complexed with titanium were also used successfully in epoxidation with TBHP [10].

There are several examples in the literature on the use of the clays as carriers for the immobilisation of homogeneous catalysts. Organometallic complexes

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containing rhodium, ruthenium, palladium, cobalt or manganese have been introduced between the sheets through an ion-exchange process when the complexes are in their cationic form. Hydrogenation [11–18], hydroformylation and carbonylation reactions [19–21] were carried out with such complexes. Oxidation and epoxidation with intercalated porphyrins were also reported [22–25].

The use of silica-derived materials may provide supports with high neutrality. A phosphoramidic acid-grafted MCM-41 was already reported for the epoxidation with hydrogen peroxide [26]. Our goal was to compare catalysts resulted from grafting of phosphoramide ligands on pure silica materials with catalysts resulted from grafting of the same ligands on different clays. For such purpose we report in this paper about the use of two kinds of silica supports (bead-shaped Shell silica and a sol–gel prepared amorphous silica) and two clays (K10 montmorillonite and hectorite) with general chemical formula $(SiO_2)_x(Al_2O_3)_y(MgO)(CaO)$ and $(SiO_2)_x(MgO)_y(Na_2O)$, respectively, [27,28]. Further complexation with peroxotungstic acid afforded the catalytic materials. Lipophilisation of the surface was obtained by prealable silylation. This treatment afforded an easy penetration of the solvent, substrate and product inside the solid.

A comparative behaviour of these catalysts in epoxidation of conjugated and non-conjugated olefins was an additional goal.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of the supports

To immobilise the peroxotungstic acid four different kinds of silica containing supports were used: carrier A, bead-shaped Shell silica; carrier B, sol–gel prepared amorphous silica; carrier C, K10 montmorillonite (Fluka); carrier D, hectorite. Carrier B was obtained by a sol–gel procedure in the presence of micellar CTAB (trimethylcetylammonium bromide) and 3-(N-(2-aminoethyl)aminopropyl)trimethoxysilane. According to the preparation procedure tetraethylorthosilicate was dissolved in 100 ml ethylene glycol (TEOS, 73.33 mmol). The formation of the sol was

Table 1
Acid washing of K10 montmorillonite

Sample	K10	1st wash	2nd wash	3rd wash
% Fe	1.78	0.38	0.27	0.09
% Al	7.35	2.83	ND	2.15

initiated with water (333.3 mmol) in the presence of concentrated HCl (1.67 mmol). The mixture was heated at 80 °C for 30 min and allowed to cool. Then CTAB (8.33 mmol) and silane **2** (5 mmol) previously dissolved in ethylene glycol (100 ml) were added under vigorous stirring. The mixture was stirred further for 4 h then poured in a teflon-lined autoclave and heated at 100 °C for 6 days.

Before the grafting of the peroxotungstic acid all the supports were pre-activated. Carriers A and B were activated by heating overnight at 120 °C under vacuum. Carrier C was acid-washed in order to remove the iron. For such purpose 15 g of K10 were refluxed overnight in 60 mL of concentrated HCl (35 wt.%). After cooling, the suspension was filtered. The hot acid washing was repeated two times under the same conditions. The final product was washed with water until neutrality of the filtrate, rinsed with MeOH (2 × 20 mL) and dioxane (2 × 20 mL). The elemental analysis of Fe and Al was performed on carefully rinsed samples. Chemical composition of these samples indicated that some dealumination occurred too (Table 1). The solid was also dried under vacuum at 120 °C. Carrier D in the H$^+$ form was obtained by acidification of Laponite$^®$ RD, which is a synthetic hectorite from Laporte. Fifteen grams of Laponite were stirred in 2 L of a 1/1 water/ethanol mixture, and a solution of 1 N HCl was added from time to time so as to maintain the pH just above 2. After 6 h, the suspension was filtered and the procedure was repeated once again; the solid was finally washed with ethanol until neutrality and allowed to dry at air overnight. The solid was dried under vacuum at 120 °C. The extend of the cation exchange was checked by elemental analysis. The amount of Na and Li in the initial clay was 1.87 and 0.33%, respectively, while after the acid treatment was less than 140 ppm for Na and 0.18% for Li. This corresponded to a capacity of about 1 mequiv. Si–OH/g.

The adsorption–desorption isotherms of N_2 at 77 K were determined with a Micromeritics ASAP-2010

apparatus. They indicated the following surface areas for these supports: (A) S_{BET} of 350 m^2/g; (B) S_{BET} of 450 m^2/g; (C) S_{BET} of 350 m^2/g; and (D) S_{BET} of 700 m^2/g.

XRD patterns were registered on a Bruker D5005 apparatus. They showed that the resulted supports were amorphous.

2.1.2. Preparation of grafting precursors

The grafting precursors were prepared by phosphorylation of aminopropylsilanes. A solution of the silane **1** (10 mmol) and triethylamine (20 mmol) in dry toluene (20 mL) was introduced into a round flask fitted with a magnetic bar, a reflux condenser, a dropping funnel and a CaCl$_2$ moisture trap. Then a solution of tetramethylphosphoramidic chloride (Cl-P(O)(NMe$_2$)$_2$, 10 mmol in 10 mL dry toluene) was added dropwise, with temporary external cooling of the reaction flask. After the addition, the mixture was heated for 6 h at 60 °C. When cooled, the precipitate of ammonium hydrochloride was filtered and the filtrate was rotatory evaporated. After evaporation, toluene (8 mL) was added and some additional ammonium was filtered again. The concentration and distillation of the residual oil afforded the product **3**. The precursors **4** and **5** were obtained in a similar way. A solution of the silane **1** containing 3 equiv. of triethylamine was phosphorylated with 0.5 equiv. of dimethylphosphoramidic dichloride, to give the product **4**. The ligand **5** was obtained in the same way from 3-(N-(2-aminoethyl)aminopropyl)trimethoxysilane **2** and 2 equiv. of triethylamine when phosphorylated with 2.1 equiv. of tetramethylphosphoramidic chloride. These silylated phosphotriamides were obtained in good yields (over 80%). Table 2 contains FT-IR and NMR data confirming the integrity of the structures **3**, **4** and **5**.

Phosphorylation of the pendant 3-methylaminopropyl chains contained in the carrier B was performed similarly as above. A sample containing 5 mequiv. of amino groups was suspended in dry toluene (10 mL) and Cl-P(O)(NMe$_2$)$_2$ (10 mmol) in dry toluene (20 mL) was added by the funnel. The mixture was heated overnight at 80 °C under gentle stirring (to avoid crushing of the material into an unfiltrable powder). The filtered material was Soxhlet-washed with methanol and dried under vacuum at 120 °C.

2.1.3. Grafting of the ligands

Grafting of the ligands was carried out following the next procedure. The carrier (1 g) was allowed to swell with gentle stirring in dry dioxane (15 mL) for 3 h at 60 °C. Then, the ligands **3**–**5** (1 g) were added and the mixture was heated overnight at 110 °C under moisture protection. The product was filtered, carefully washed with dioxane and methyl-t-butylether and dried under vacuum at 100 °C. Phosphoramide-grafted materials **6**–**8** were resulted from this procedure.

2.1.4. Silylation of the grafted materials

Silylation of the grafted materials was made by suspending these in a 1/1 mixture of trimethylchlorosilane and hexamethyldisilazane. The resulted mixture was refluxed under stirring in a flask fitted with a condenser and CaCl$_2$ moisture trap for 24 h [29]. The suspension was filtered when cold, rinsed with acetone, Soxhlet-washed with methanol and dried under vacuum at 80 °C. Physical data of the grafted ligands are reported in Table 3.

2.1.5. Complexation with peroxotungstic acid

The phosphoramide-grafted materials **6**–**8** were suspended in dioxane and a stoichiometric amount of peroxotungstic acid [30] was added (1 mequiv. WO$_5$/1 mequiv. P). The mixture was stirred and heated at 60 °C for 5 h, washed with dioxane and dried overnight under vacuum below 50 °C (peroxo complexes may decompose in the dry state). Analytical and physical data of the catalysts are reported in Table 4.

Table 2
Physical properties of the soluble silylated phosphoramides

Ligand	bp (mm)	ν(P=O) (cm^{-1})	^{13}C NMR (ppm)	^{31}P NMR (ppm)
3	155–165 (0.05)	1195	36.5 (CH$_3$N), 51.6 (CH$_2$N), 5.90 (CH$_2$Si)	+25.6
4	170–175 (0.03)	1195	36.75, 33.72 (CH$_3$N), 51.76 (CH$_2$N), 6.04 (CH$_2$Si)	+25.7
5	220–230 (0.04)	1213	36.4, 36.9 (CH$_3$N), 46.6 (CH$_2$N), 5.97 (CH$_2$Si)	+30.0

Table 3
Spectral data of phosphoramides[a] on silica-based carriers

Material	mequiv. P/g	$\nu(P=O)$ (cm^{-1})	^{13}C (ppm)	^{31}P (ppm)
6A[b]	0.36	1193	35.47.1 (CH$_3$N), 51.2 (CH$_2$N), 8.1 (CH$_2$Si)	37.0
6B[c]	0.6	f	37.1 (CH$_3$N), 52.5 (CH$_2$N), 10.7 (CH$_2$Si)	21.4
6C[d]	0.68	1192	35.4 (CH$_3$N), 51.3 (CH$_2$N), 10.25 (CH$_2$Si)	23.9
6D[e]	0.68	1192	36.4 (CH$_3$N), 50.0 (CH$_2$N), 5.0 (CH$_2$Si)	26.3
7D[e]	0.68	1190	34.4 (CH$_3$N), 51.1 (CH$_2$N), 8.2 (CH$_2$Si)	27.8
8D[e]	1.4	1200	37.3 (CH$_3$N), 53.7 (CH$_2$N), 10.25 (CH$_2$Si)	25.0

[a] Soluble ligands **3**, **4** and **5** afforded **6**, **7** and **8**, respectively.
[b] Amorphous silica from Shell.
[c] Mesoporous silica from sol–gel.
[d] K10 clay.
[e] Synthetic hectorite from Laponite[®] RD.
[f] Broad overlap of the Si–O bands.

Table 4
Silica-grafted tungsten catalysts

Carrier	Catalyst	mequiv. W/g	N/P	FT-IR data
6A	6AW	0.18	3.3	1184 (sh) $\nu(P=O)$, 807 $\nu(W–O–O)$, 755 $\delta(N–P–O)$
6B	6BW	0.31	2.9	1198 (sh) $\nu(P=O)$, 814 $\nu(W–O–O)$, 755 $\delta(N–P–O)$
6D	6DW	0.62	3.3	1193 (sh) $\nu(P=O)$, 867, 848 $\nu(W–O–O)$, 756 $\delta(N–P–O)$
7D	7DW	0.29	2.8	1198 (sh) $\nu(P=O)$, 867, 861 $\nu(W–O–O)$, 755 $\delta(N–P–O)$
8D	8DW	0.28	2.6	1198 (sh) $\nu(P=O)$, 800 $\nu(W–O–O)$
6C	6CW	0.25	2.9	1180 $\nu(P=O)$, 816 $\nu(W–O–O)$, 754 $\delta(N–P–O)$

Spectral and physical data were collected with the following apparatus: Brucker IFS-48 (FT-IR), Brucker AC-200 (^{1}H, ^{13}C and ^{31}P NMR), Brucker DSX-400 (^{13}C and ^{31}P CP-MAS NMR).

2.2. Epoxidation procedure

Epoxidation of cyclohexene and styrene was carried out using an alkene/hydrogen peroxide ratio of 5/1 or 1/1 and a W/H$_2$O$_2$ molar ratio of 0.05. Dioxane or acetonitrile was added to make the alkene–hydrogen peroxide mixture homogeneous [5–7]. The mixture was stirred at 60 °C and samples were withdrawn for analysis. In some catalytic tests, the catalyst was separated and the solution was kept under reaction conditions for another 2 h. The separated catalyst was reused in a new reaction. The analysis of the reaction products was made using an HP chromatograph, model 5890, series II equipped with a Chrompack column or an Erba Science, model Fractovap 2151 equipped with a DB1 column. Reference epoxides were commercially available (epoxycyclohexane and epoxystyrene) or prepared by a stoichiometric epoxidation of the alkene with *m*-chloroperbenzoic acid [5]. Subsequent hydrolysis of epoxide to diol is an undesired reaction.

3. Results and discussion

Both silica and clay-derived catalysts contained neutral tungsten complexes, the ligands being covalently bonded to the surface. The clay-derived catalytic materials were obtained according to a four step procedure: (i) removal of the intercalated cations by acidic exchange of the lamellar material to get free Si–OH; (ii) synthesis of the soluble hexaalkylphosphotriamide (HAPA) ligands by reaction of a chlorophos-
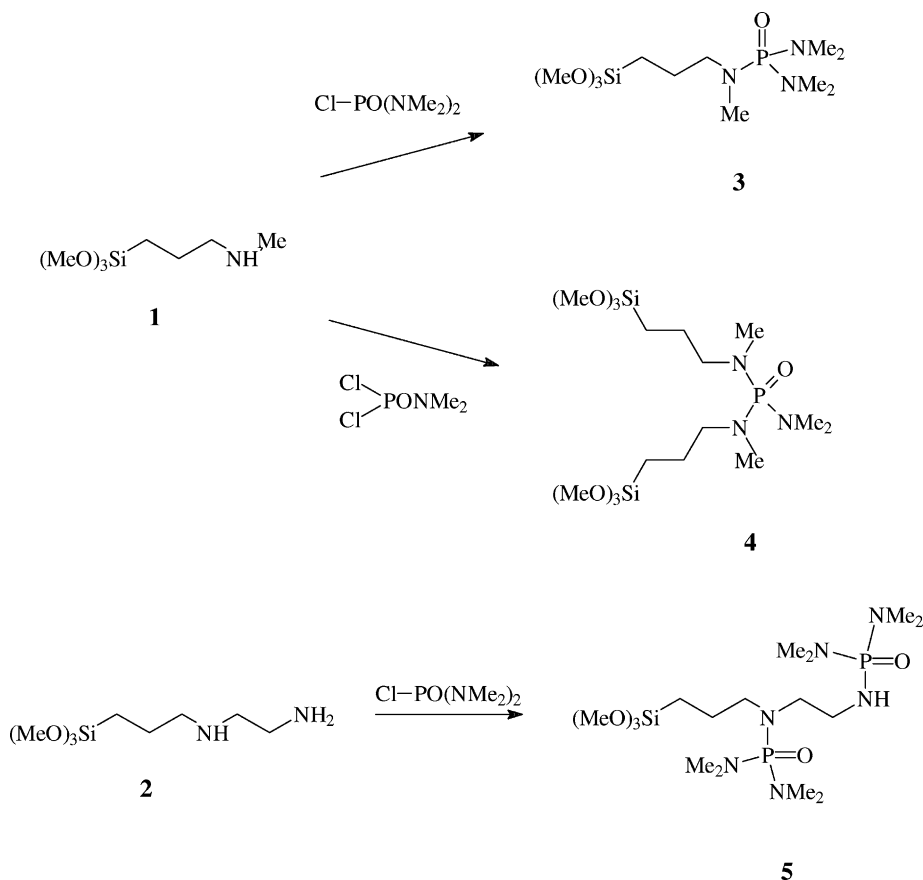
Fig. 1. Preparation of the soluble silylated phosphotriamides.

phoramide with an aminated silane to get derivatives of general formula $(MeO)_3Si-C_3H_6-(HAPA)$. N-Phosphorylation of the aminated trimethoxysilylpropylamino derivatives **1** and **2** with N,N′-tetramethylphosphodiamide chloride or N-dimethylphosphoramide dichloride is presented in Fig. 1; (iii) grafting of the trimethoxysilyl part of the ligand to the surface and end-capping with HMDS (this reaction provided a very lipophilic surface, Fig. 2); (iv) in situ formation of the complexes by soaking in a solution of peroxotungstic acid. Fig. 3 gave a description of the surface of these catalysts.

The structure of the grafted ligands was confirmed by comparison of the spectral data of the phosphoramide units before and after grafting (Tables 3 and 4). For the soluble ligands, the typical FT-IR P=O stretching is located at $1195\,cm^{-1}$ for **3** and **4** and at $1213\,cm^{-1}$ for **5**. In the grafted supports **6**, **7** and **8**, this stretching appeared at 1193, 1190 and $1200\,cm^{-1}$, respectively, which demonstrate a perfect integrity. This integrity also resulted from the NMR measurements. The ^{31}P NMR resonance was in the 25–30 ppm range for the soluble phosphoramides and in the 21–27 ppm range after grafting. The small shift is caused by the bond with the support. As for P, the ^{13}C NMR resonances for CH_3-N, CH_2-N and CH_2-Si bonds were also slightly shifted.

The complexation of tungsten to the materials **6**, **7** and **8** was performed using a dioxane–water solution of peroxotungstic acid, a mixture of HWO_6 and $H_2W_2O_{11}$. The loading of tungsten and the spectral data of the resulted catalysts are given in Table 4. It is worth to note that the structure of the phosphotriamide units was kept essentially intact after this series
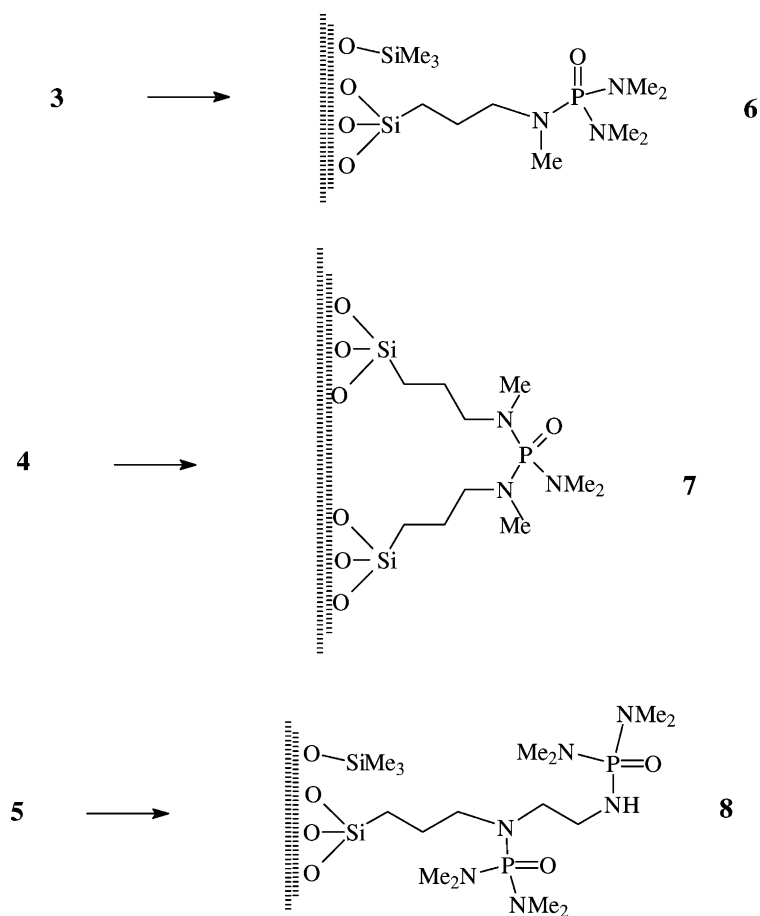
Fig. 2. Grafting of phosphotriamides onto siliceous materials and silylation.

of transformation as shown by the N/P ratios which remained near the value of 3, as chemical analysis has shown.

Before the catalytic tests the catalysts were pre-washed with a hot solution of hydrogen peroxide in dioxane in order to remove most of the weakly bounded peroxotungstic species.

3.1. Epoxidation of aliphatic and aromatic alkenes

The results of catalytic epoxidation are given in Tables 5 and 6. Epoxidation of cyclohexene and cyclooctene occurred with different performances. For cyclohexene, high yields (above 90%) and TOF above 100 were obtained with some catalysts (Table 6).
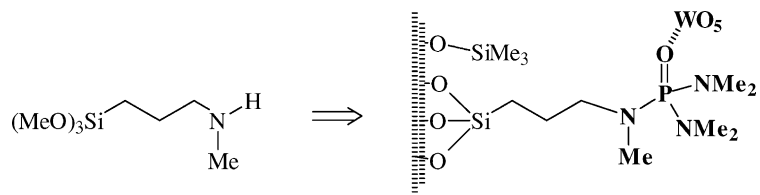

Fig. 3. General scheme.

Table 5
Epoxidation of styrene[a], β-methylstyrene[a] and indene[a]

Catalyst	Substrate	Epoxide[a]	Aldehyde[b]	dec. H$_2$O$_2$	TOF
6CW	Styrene	5.5	3.6	0	ND
6DW	Styrene	<1	<1	25	ND
8DW	Styrene	10.3	3.4	0	3.8
6AW	β-Methylstyrene	21.5	1.2	29	8.0
6CW	β-Methylstyrene	12.4	1.2	15	3.4
8DW	β-Methylstyrene	12.1	0.7	25	3.2
6BW	Indene	71	ND	ND	345
8BW	Indene	11	ND	ND	70

[a] 2 M in dioxane, yields after 6 h.
[b] 5 M in acetonitrile, yields after 8 h.

However, these experiments indicated the differences induced by the carriers and ligands. As a function of the carrier, TOF varied in the order A > C > B > D. Several factors may contribute to this behaviour like the neutrality of the surface and the strength of the bond of the ligand with the carrier. A good concordance between TOF and the frequency of P=O bond may be observed from Tables 4 and 6. This has a direct effect on the bonding of tungsten. In such respect might be indicated the very different frequencies determined for W–O–O in the case of the carrier D, which was the worse in the series (Table 4). Very close results were obtained with the monodentate **3** and bidentate **5** ligands. But again, it is worth to note that the effect of the ligand is in close correlation with that of the

Table 6
Epoxidation of cyclohexene and cyclooctene

Catalyst	Substrate	Epoxide	Diol	dec. H$_2$O$_2$	TOF
Soluble[a]	Cyclohexene	57	28	14	74
6AW	Cyclohexene	96	3	0	140
Reuse	Cyclohexene	50	10	–	50
6BW	Cyclohexene	97	3	0	42
6CW	Cyclohexene	86	14	0	124
6DW	Cyclohexene	25	3	0	27
7DW	Cyclohexene	92	8	0	40
Reuse	Cyclohexene	80	15	–	40
8DW	Cyclohexene	91	9	0	80
Reuse	Cyclohexene	65	10	–	60
6BW	Cyclooctene	88	0	12	210
Reuse	Cyclooctene	88	0	12	210

[a] See Ref. [7].

carrier. Thus for carrier B, the best results were obtained with the ligand **6**, while for D with the ligand **8**.

Cyclooctene was also epoxidised very efficiently with TOF values above 200, though some decomposition of hydrogen peroxide occurred in this case with catalyst 6BW.

These data must be compared with data reported in literature using other catalysts. On titanium-substituted Keggin-type polyoxotungstates cyclohexene epoxidation resulted with a TOF of 1–28, while cyclooctene with a TOF of 25–211 [31]. On Ti–Si xerogels the same substrates were epoxidated with TOF of 79 and 102, respectively, [32], while cyclooctene was epoxidated on mesoporous hexagonal titanium aluminophosphate molecular sieves with a TOF of 9.2 [33], on amberlite-based catalysts with TOF of 0.2–5 [34], on PW-exchanged MCM-41 of 1.2 [35] and on tungsten–phosphoramide-grafted MCM-41 catalysts with 2 [34].

Conjugated aromatic alkenes: styrene, β-methylstyrene and indene, were differently epoxidated. Styrene appeared inert and gave disappointing low conversions with similar amounts of epoxide and benzaldehyde as a cleavage product. β-Methylstyrene was epoxidised with yields in the 12–22% range leading also to cleavage products (Table 5). These low-nucleophilic substrates were very unreactive with the neutral peroxotungstic complexes described here. The low reactivity of these substrates is already known and these results confirmed previous data obtained with the analogous soluble species [5,9].

Indene was found significantly more reactive (TOF 70 and 345). Its epoxidation occurred with good yields and a remarkable high turnover (TOF 345) when using 'anhydrous' hydrogen peroxide (58 wt.%). Under such conditions the results obtained with hectorite (carrier D) and the ligand **5** appeared as promising constructing elements.

These data clearly confirmed the benefits of the immobilisation of these catalysts following the methodology we proposed, both in terms of yields and TOF when compared with the results given, as reference, by the soluble analogues or other categories of catalysts [31–34]. These results are in the same line with those reported using organic polymers carriers when a good stability of epoxycyclohexane versus hydrolysis and a good efficiency of the hydrogen peroxide were also observed [7].

Table 7
Stability of the grafted complexes[a]

	6AW epoxidation	6AW washing	7DW epoxidation	7DW washing	8DW epoxidation	8DW washing
% W	3.36	3.36	6.65	6.65	5.30	5.30
	3.10	2.80	6.10	6.60	–	4.65
	2.95	2.50	5.90	6.10	4.50	4.10
P/W	2.10	2.10	2.10	2.10	1.62	1.62
	2.16	2.30	2.0	1.80	–	0.90
	2.05	2.37	1.90	2.04	0.90	0.94

[a] First line: starting complexes, then first and second run.

3.2. Leaching and recycling tests

To check the stability of the anchored catalysts, recycling experiments were performed successively with catalysts recovered by hot filtration after 6 h reaction and reused immediately. The recovered catalyst 7DW behaved quite similarly in the epoxidation of cyclohexene, whereas 6AW and 8DW exhibited significant loss in yield and reactivity. Interestingly, 6BW was found to be very stable in the epoxidation of indene (Table 6).

Elemental analyses were performed on the recovered materials after the first and/or the second use (Table 7 and Fig. 4). The tungsten content decreased slightly but regularly after each use and the elemental P/W ratio remained near the values of 1 or 2. This indicated the chemical stability of the free and complexed phosphoramide ligands.
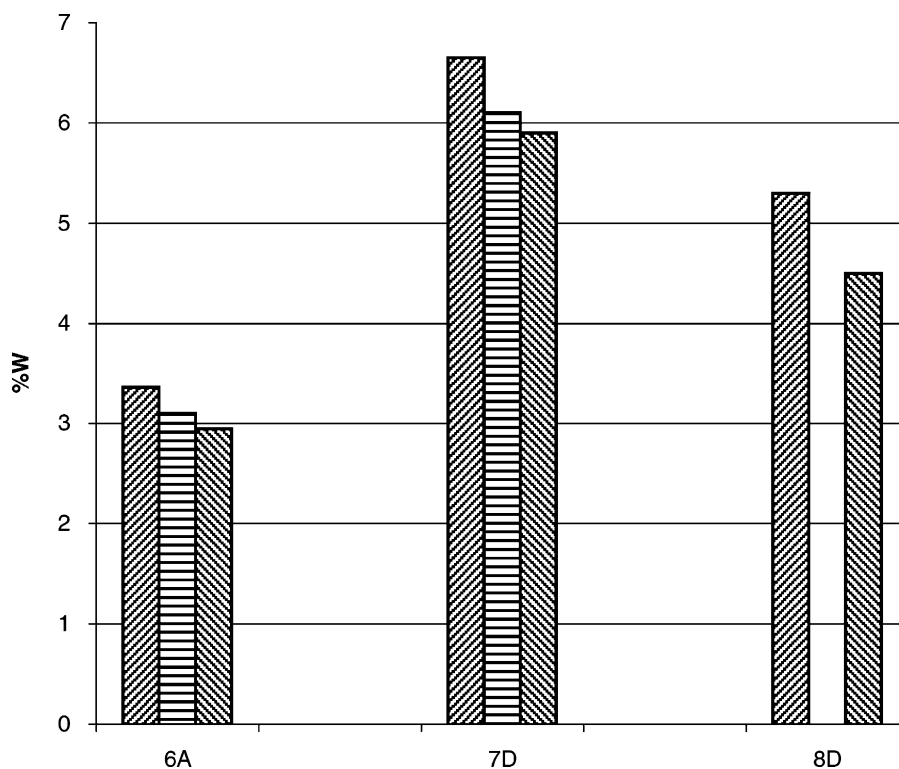

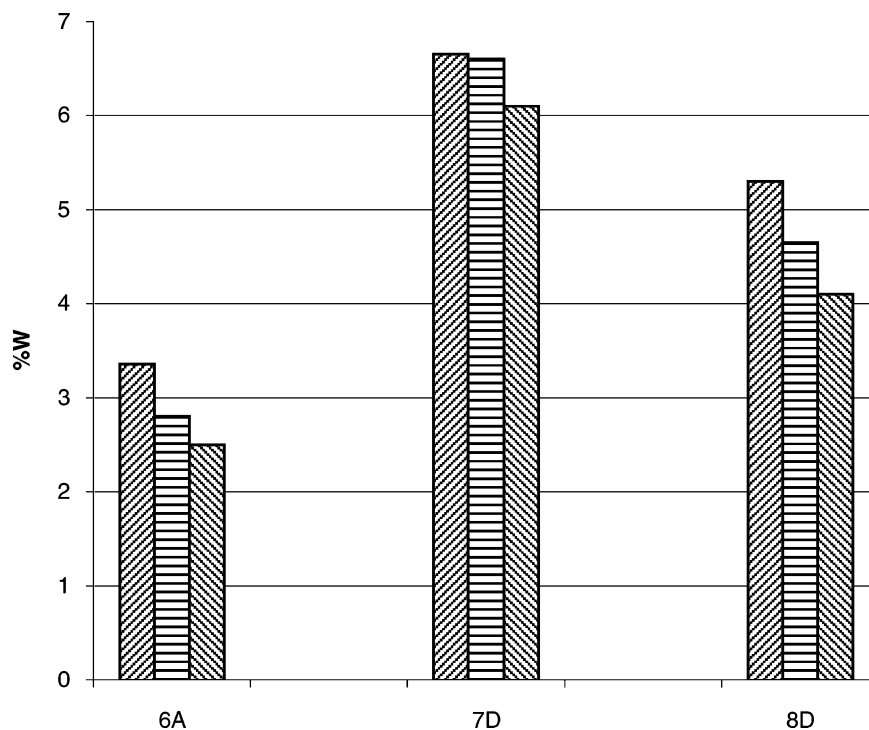Fig. 4. Leaching of tungsten in repeated epoxidations.

Fig. 5. Leaching of tungsten in repeated washings.

More direct experiments on the stability were performed by heating repetitively the catalysts during several hours in a reaction-like medium (hydrogen peroxide in hot dioxane) and chemical analysis of the solids after hot filtration. Very similar results with those resulted after reaction were obtained concerning the residual tungsten and the P/W ratio (Table 7 and Fig. 5).

Considering the two methods, the leaching of tungsten was found in the 3–10% range after each use. Interestingly, the limited amount of free peroxotungstic acid which was in solution seemed not to induce significant hydrolysis of the epoxides to the diols. The most stable catalytic material was 7DW, which exhibited a total leakage below 10% after two uses.

4. Conclusions

In conclusion, the grafting of phosphotriamides on silica-derived carriers provided catalysts with high turnover and selectivity to epoxides. The nature of the silica-derived precursor is a very important factor in this process. On most of the catalysts, the tungsten units were fairly bounded to the carrier and afforded the reuse of these.

References

[1] G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic Publishers, Dordrecht, 1992.
[2] C.W. Jones (Ed.), Applications of Hydrogen Peroxide and Derivatives, RSC, London, 1999.
[3] R. Ugo (Ed.), Metal-catalysed epoxidations of olefins with hydroperoxides, in: Aspects of Homogeneous Catalysis, Vol. 4, Reidel, Dordrecht, 1981.

[4] S. Patai (Ed.), Transition-metal peroxides—synthesis and uses as oxidizing agents, in: The Chemistry of Peroxides, Wiley, New York, 1983.

[5] M. Quenard, V. Bonmarin, G. Gelbard, New J. Chem. 13 (1989) 183.

[6] G. Gelbard, F. Breton, M. Benelmoudeni, M. Quenard, React. Polym. 33 (1997) 117.

[7] G. Gelbard, F. Breton, D.C. Sherrington, M. Quenard, J. Mol. Catal. 153 (2000) 7.

[8] M.M. Miller, D.C. Sherrington, S. Simpson, J. Chem. Soc., Perkin Trans. 2 (1994) 2091.

[9] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 377.

[10] D.C. Sherrington, J.K. Karjalainen, L. Canali, H. Deleuze, O.E.O. Hormi, Macromol. Symp. 156 (2000) 125.

[11] T.J. Pinnavaia, P.K. Welty, J. Am. Chem. Soc. 97 (1975) 3819.

[12] T.J. Pinnavaia, R.R. Raythatha, J.G.S. Lee, L.J. Halloran, J.F. Hoffman, J. Am. Chem. Soc. 101 (1979) 6891.

[13] W.H. Quayle, T.J. Pinnavaia, Inorg. Chem. 18 (1979) 2840.

[14] T.J. Pinnavaia, Science 220 (1983) 365.

[15] R.R. Raythatha, T.J. Pinnavaia, J. Catal. 80 (1983) 47.

[16] M. Mazzei, W. Marconi, M. Riocci, J. Mol. Catal. 9 (1980) 381.

[17] M.M. Taqui-Khan, S.A. Samad, M.H.R. Siddiqui, H.C. Bajaj, G. Ramachandriah, Polyhedron 10 (1991) 2729.

[18] S. Shimazu, T. Chiaki, T. Uematsu, in: L. Guszi (Ed.), New Frontiers in Catalysis, Proceedings of the 10th International Congress on Catalysis, Elsevier, Amsterdam, 1993, p. 2467.

[19] M. Lenarda, R. Ganzerla, S. Enzo, L. Storaro, J. Mol. Catal. 67 (1991) 295.

[20] B.N. Lee, H. Alper, J. Mol. Catal. 111 (1996) L3, 11, 17.

[21] K. Nozaki, M.N. Kantam, T. Horiushi, H. Takaya, J. Mol. Catal. 118 (1997) 247.

[22] G. Gelbard, SHHC-8, Balatonfured, September 1995, Contribution P25; ADHOC-6, Noordwijkerhoout, April 1996, Contribution O27.

[23] B.M. Choudary, V.L.K. Valli, A.D. Prasad, J. Chem. Soc., Chem. Commun. (1990) 1186.

[24] L. Barloy, J.P. Lallier, P. Battioni, D. Mansuy, Y. Piffard, M. Tournoux, J.B. Valmin, W. Jones, Nouv. J. Chim. 16 (1992) 71.

[25] P.S. Dixit, K. Srinivasan, Inorg. Chem. 27 (1988) 4507.

[26] D. Hoegaerts, B.F. Selks, D.E. De Vos, F. Verpoort, P.A. Jacobs, Catal. Today 60 (2000) 209.

[27] J.M. Thomas, in: M.S. Whittingham, A.J. Jacobson (Eds.), Intercalation Chemistry, Academic Press, New York, 1982, p. 55.

[28] R.M. Barrer, Zeolites and Clay Mineral as Sorbents and Molecular Sieves, Academic Press, New York, 1978, p. 107.

[29] T. Yangisawa, K. Kuroda, A. Doi, C. Kato, Clay Sci. 8 (1991) 107.

[30] G. Gelbard, M.T. Charreyre, D. Dong, F. Breton, J. Macromol. Chem. Macromol. Symp. 59 (1992) 353.

[31] T. Yamase, E. Ishikawa, Y. Asai, S. Kanai, J. Mol. Catal. A 114 (1996) 237.

[32] Y. Deng, W.F. Maier, J. Catal. 199 (2001) 115.

[33] M.P. Kapoor, A. Raj, Appl. Catal. A 203 (2000) 311.

[34] D. Hoegaerts, B.F. Sels, D.E. de Vos, F. Verpoort, P.A. Jacobs, Catal. Today 60 (2000) 209.

[35] K. Vassilev, R. Stomenova, C. Tsvetanov, Funct. Polym. 46 (2000) 165.