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ScienceDirect
Journal of Catalysis 249 (2007) 1–14
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Recyclable solid catalysts for epoxidation of alkenes: Amino- and oniumsilica-immobilized $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ anion

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Received 3 January 2007; revised 15 March 2007; accepted 16 March 2007

Abstract

We designed solid catalysts for liquid-phase epoxidation based on functionalized silica $\equiv Si(CH_2)_3Q^+$ [Q: $-NH_3$, $-NEt_3$, $-NC_5H_5$, $-PPh_3$] and $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$. The approach that we adopted allowed us to avoid the use of chlorocarbon solvent and enabled catalyst recycling. By using supports with 4 different linking chains between the anion and silica and different surface lipophilicities, we followed their influence on catalyst activity in the epoxidation of cyclooctene and (R)-limonene by H_2O_2 in *t*-BuOH. All solids were active in cyclooctene epoxidation (conversion up to 100%; epoxide selectivity 100%; TOF 2–4 h^{-1} $anion^{-1}$). The degree of surface coverage by organic functions was crucial for recycling performance. Catalysts with low densities of organic functions and hydrophilic surfaces were easily deactivated. End-capping improved their stability but decreased their activity. Catalysts with dense coverage of onium groups and the active site in a hydrophobic chloropropyl environment demonstrated high activity and excellent recycling stability. Less promising results were obtained in the epoxidation of (R)-limonene.

Keywords: HPA; Immobilized; Anion exchanger; Silica; Epoxidation; Peroxocomplex; H_2O_2; Cyclooctene; Limonene; ^{31}P NMR

1. Introduction

The epoxidation of alkenes is widely used for the production of oxiranes, valuable industrial products providing an access to various fine chemicals. This reaction is catalyzed by a number of transition metal compounds, titanium silicalites, and titanium-containing molecular sieves [1–4] and is performed in homogeneous or liquid biphasic media, with the latter affording easy product separation [5]. Among the most efficient catalysts suggested for alkene epoxidation are anionic Re-, Mo-, and W-containing compounds [6–13], covered in a review by Kozhevnikov up to 1998 [9]. The most studied and characterized species are the so-called Venturello complex, $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ [6,7], an analogous molybdenum-containing anion, first reported by Beiles et al. [14], and the binuclear complex $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ [15]. Various other transition-metal-substituted heteropolyoxometalates (HPAs) have been reported to be active oxidation/epoxidation catalysts, including tetrameric trititanium(IV)-substituted Wells–Dawson anion $[(P_2W_{15}Ti_3O_{60.5})_4]^{36-}$ [16] and sandwich-type transition-metal-substituted polyoxometalates $[Na_xM_2Zn_3W_{19}O_{68}]$, M = Ru, Mn, Zn, Pd, Pt, Co, Fe, and Rh [17].

The epoxidation of alkenes in a two-phase system involves an organic solution of substrate (often chlorocarbon) and an aqueous solution of H_2O_2, although some other oxygen-transfer reagents, such as alkylhydroperoxides [18,19], iodosylbenzene [18–20], and the environmentally and economically significant O_2 [21–23], can be used as oxidants. The reaction proceeds in the presence of phase-transfer reagents (PTRs) [24].

The need for sustainable chemistry and clean technologies has stimulated the search for new, environmentally friendly

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doi:10.1016/j.jcat.2007.03.018

epoxidation systems. The conventional epoxidation system can be improved by avoiding harmful chlorocarbon solvents. Water-soluble substrates, such as oleic acid, can be epoxidized in aqueous 35–60% hydrogen peroxide solution under catalysis by $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ without the addition of chlorocarbons [25]. Less water-soluble substrates can be epoxidized by aqueous H_2O_2 in the presence of amphiphilic carbohydrate additives, enhancing their solubility [26].

The difficulty of catalyst recycling has inspired the development of recyclable and suitable fixed-bed heterogeneous catalysts [27,28]. Recently, the number of publications devoted to heterogeneous oxidation catalysts has grown enormously. The replacement of homogeneous oxidation catalysts with heterogeneous oxidation catalysts is not simple. The use of heterogeneous catalysts in liquid-phase oxidation is associated with leaching of metal catalysts from the surface, because highly polar molecules are generated in the course of the reaction [28,29]. Heterogenization of redox-active elements in solid matrices can be achieved via several approaches, such as sol–gel methods, including *framework* substitution of molecular sieves, grafting or tethering to the inner walls of mesoporous molecular sieves, encapsulation by the "ship-in-a-bottle" technique, ion exchange in layered double hydroxides, and others [30–33].

Heterogeneous HPA-catalysts are prepared via four approaches:

1. *Deposition on porous, usually inorganic, supports, such* as silica [30,32,33], silica–titania [34], basic oxides such as alumina, MgO [35], alumina and silica–alumina [36]. Achieved via adsorption from, for example, an organic solution of $(Bu_4N)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$ [33] or impregnation with an aqueous solution of $H_2WO_4/H_2O_2/H_3PO_4$ [31]. No strong chemical interaction is involved when silica is used, making catalyst leaching and activity loss unavoidable, except for basic oxides, which provide electrostatic interaction. Such catalysts, e.g. 10 wt% on silica $K_5[PW_{11}TiO_{40}]$, $K_7[PW_{10}Ti_2O_{40}]$, $K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$, $K_7[PW_{10}Ti_2O_{40}]$ can be used in nonpolar media or in gas-phase oxidations [37].

2. *Incorporation of "HPA precursors," redox cations Mo and W in the walls of microporous and mesoporous molecular sieves or amorphous composite oxides via a sol–gel procedure* in alcoholic [38,39], aqueous [32,33,40], or hydrogen peroxide media [32,33,40,41], with the use of $Si(OEt)_4$ and either alkoxides or inorganic precursors of redox cations. The redox cation dispersion and activity depend on the preparation procedure, and although some groups report good distribution of active species and stable performance, others are less optimistic. Most studies report high activity and selectivity in epoxidation with the use of H_2O_2 or t-BuOOH, but with leaching of the cation and homogeneous reaction. Sol–gel microporous Mo-containing silicas were active, selective and stable in epoxidation with the use of t-BuOOH, if prepared using Mo(V)isopropoxide, contrasting molybdenyl–acetylacetonate [39]. Metallosilicates containing TiO_2, MoO_3 and WO_3 were active in the oxidation of alkenes and alcohols with 30% aqueous H_2O_2 if prepared from the dichlorodialkoxy, but not tetraalkoxy, derivatives, with the best efficiency at low metal loadings [38]. Incorporation of molybdenum into silicalite and vanadium into Y-zeolite was unsuccessful [42]. Isomorphously substituted Cr-MCM-41 has been shown to be an active recyclable catalyst in catalytic epoxidation of aromatic olefins and for the oxidation of aromatics with t-BuOOH in C_6H_6 [43].

3. *Entrapping of HPA-anions in a porous inorganic or hybrid organic–inorganic matrix, via sol–gel technology*. This approach is more promising than the above-described inclusion of redox cations, because it applies strong electrostatic or complexing interactions between the functional group of silica and the HPA. Many successful examples of incorporation of HPAs via the sol–gel technique have been reported [44], with most of the research in this field performed by the groups of Neumann et al. [17–19,38,45–47] and Schroeder et al. [49]. The initial work dealt with the incorporation of $[PO_4\{W_2O_2(\mu\text{-}O_2)_2\text{-}(O_2)_2\}_2]^{4-}$ and $[WZnMn_2(H_2O)_2\text{–}(ZnW_9O_{34})_2]^{12-}$ species into silicate xerogels modified with phenyl and quaternary ammonium groups $\{(EtO)_3Si[CH_2]_3N^+Me_3\}$ and $\{(MeO)_3SiPh\text{-}CH_2N^+Me_2[(CH_2)_nMe]\}$ ($n = 7, 9$) [46]. This catalyst gave efficient oxidation of nonbulky alkenes by 30% H_2O_2 at room temperature in the absence of organic solvents, but decreased with substrate bulkiness. Catalyst performance was improved by the presence of phenyl groups.

Cohen et al. [47] described $[ZnWMn^{II}_2\text{–}(ZnW_9O_{34})_2]^{12-}$-containing silicates combining hydrophilic polyethylene oxide (PEO), hydrophobic poly-propylene oxide (PPO), and cationic quaternary ammonium (Q^+) groups ($SiO_2\text{–}PhCH_2N^+(CH_3)_2\text{-}(CH_2)_7CH_3Cl^-$) prepared via the sol–gel technique. The active species was introduced into silicate at the sol–gel stage and either electrostatically bound to Q^+–PE(P)O–SiO_2 or dissolved in PE(P)O–SiO_2. Anion $[ZnWMn^{II}_2\text{–}(ZnW_9O_{34})_2]^{12-}$, bound by a Q^+ moiety, produced an assembly with excellent recycling properties, active in the epoxidation of alkenes with aqueous 30% H_2O_2. Compared with the electrostatically bound species, adsorption of the anion by complexation of its quaternary ammonium salt to tethers did not result in strong retention.

A "quasi"-covalent heterogenization of lacunary Keggin HPA into a polymeric, siliceous, or hybrid matrix has been proposed by Mayer and Thouvenot, who incorporated the functionalized lacunary anion $\{\gamma\text{-}SiW_{10}O_{36}[HC{=}C(Me)C(O)OPr\text{-}SiO]_2O\}^{4-}$ into the polymeric matrix via copolymerization with ethylmethacrylate [48]. A similar procedure for the incorporation of this species into a siliceous matrix with a good dispersion was used by Schroeder et al. in 2001 [49]. Lacunary γ-decatungstosilicate was reacted in acidic solution with tetraethoxysilane with and without addition of the polyfunctional linking group 1,2-bis(triethoxysilyl)ethane, followed by condensation around polystyrene as a templating agent. Removal of the polystyrene by extraction produced porous hybrid materials with intact HPA clusters molecularly dispersed in the walls. These materials exhibited moderate activity in epoxidation with anhydrous H_2O_2/t-BuOH and were resistant to leaching. A similar technique was applied to the preparation of composite silica-HPA films containing several monovacant Keggin-type anions, $[X^{n+}W_{11}O_{39}]^{(12-n)-}$ (X = Si, Ge, P) [50]. These films were active in the photocatalytic degradation of aqueous formic acid and were claimed to not be subject to leaching.

The heterogenization of an active species via incorporation in hybrid materials is a very good choice for catalyst preparation. High degrees of functionalization, strong bonding, and activity can be obtained for the hybrid materials. However, achieving good distribution and accessibility of active sites often requires strict control of the synthetic procedure at all stages.

4. *Chemical immobilization of HPA via ion exchange or coordinative bonding to functional polymers and functionalized silicas* was shown to have considerable potential. Heterogenization of the $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ on Amberlyst A26, with high porosity and moderate surface area ($30\ m^2\ g^{-1}$), via ion exchange was studied by Brégeault et al. [31]. Epoxidation of (R)-limonene in a three-phase system, comprising catalyst and an aqueous solution of H_2O_2 and CH_2Cl_2, afforded high conversion and selectivity (epoxide yield, 68–94%) at room temperature. Diols and diepoxides were formed as byproducts. The reaction was nearly 3 times slower than the corresponding reaction in solution using Arquad 2HT-$[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$; this was considered evidence of catalysis occurring on the surface, not in the solution. Performance of the recycled catalyst and the extent of leaching were not discussed.

Vassilev et al. [51] described epoxidation of styrene with hydrogen peroxide using quaternary ammonium salts of peroxo W(VI) complexes grafted on polymers: poly(2-*N*,*N*-dimethylaminoethyl)methacrylate and a mixed network of poly(oxyethylene) and poly(4-vinylpyridine). The catalytic system comprised a water-immiscible solvent, aqueous H_2O_2, and Na_2WO_4/H_3PO_4. The activity of the polymeric ammonium salts depended on the support, the length of the hydrocarbon radicals, and the nature of the anion. Increased reaction selectivity was observed with the use of a heterogeneous catalyst rather than a homogeneous one.

Up to now, the most outstanding catalytic performance of heterogeneous catalysts for the epoxidation of alkenes by hydrogen peroxide was demonstrated previously [52], using tungsten complexes immobilized on organophosphoryl macroligands. Catalysts were prepared via complexation of peroxotungstic acid to phosphorus on organophosphoryl macroligands related to phosphonic, phosphinic, or phosphoric acid amides, $R\text{-}P(O)(NRR)_2$, $RR' > P(O)NR_2$, and $PO(NR_2)_3$, and introduction of these amides in hydrophobic polystyrene and hydrophilic polymethacrylate resins. Whereas the phosphine oxides were shown to bind the metal insufficiently, the phosphamides grafted onto polymethacrylates formed the best catalysts from the standpoint of reactivity, epoxide selectivity, and stability, allowing recycling of the catalyst. The authors claim very good performance ($TOF = 30\text{–}1200\ h^{-1}$), which is better than that obtained with soluble analogues, thus representing a unique example of an immobilized metal complex with significantly higher selectivity and activity than in solution.

In our work we describe the design and performance of new heterogeneous epoxidation catalysts based on functionalized silica and HPA. The approach that we adopted allowed us to avoid the use of chlorocarbon solvent and enabled catalyst recycling, in accordance with the trend toward "green" reagents and processes. For this, we studied the strong immobilization of HPA by electrostatic interaction with grafted silicas, as an extension of earlier preparations of epoxidation catalysts with silica and polymers [44–47,51,53–55]. A binuclear $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ anion (designated as "PW_2" in what follows) with a well-documented activity in homogeneous media was chosen as the active species [15,33].

Catalysts were tested in the epoxidation of cyclooctene and (R)-limonene by H_2O_2 in *t*-BuOH solution. The former reaction allowed us to monitor the overall activity of the catalyst, whereas we used the latter to study the accessibility of the active site, and the correlation between their structure and reaction selectivity. Using various supports (some hydrophobic), we evaluated the influence of the linking chain between the anion and silica [protonation and anion exchange with different onium salts $\equiv Si(CH_2)_3Q^+$ (with Q^+ as $-NEt_3$, $-NC_5H_5$, or $-PPh_3$)], as well as the degree of surface lipophilicity (i.e., surface proportions of silanol, chloropropyl, and trimethylsilyl groups), on catalyst performance.

2. Experimental

2.1. Characterization techniques

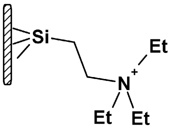
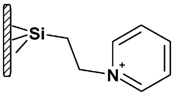
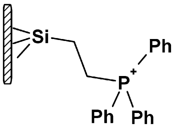
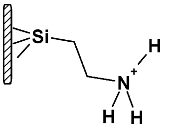
Tungsten concentrations in as-prepared samples and spent samples were determined by X-ray fluorescence measurements. The solids were dried at 100 °C for 1 h (10 wt%) and mixed with boronic acid (90 wt%). W concentrations were determined using a standard calibration set.

DRIFTS spectra with in situ thermal treatment were recorded on a Bruker Vector 22 spectrometer equipped with a Harrick diffuse reflectance cell and a DTGS detector, using KBr as background. Samples were ground and diluted with KBr (1:10). The in situ thermal treatment was performed by heating at 60 °C under vacuum for 1 h; to avoid catalyst decomposition, higher temperatures were not used.) The spectrum of the precursor salt $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ was recorded as nontreated.

^{31}P single-pulse excitation (SPE) magic-angle spinning (MAS) NMR measurements were made at 202.46 MHz on a Bruker ASX 500 NMR spectrometer, operating in a static field of 11.7 Teslas at room temperature. The air-dried sample was placed in a 4-mm double-bearing zirconia rotor and spun at 7–10 kHz for all measurements. Chemical shifts, including the cited literature data, were referenced with respect to external 85% H_3PO_4. The recycle delay was 30 s for all measurements, in accordance with the ^{31}P spin-lattice relaxation times. The number of accumulations (NS) is given on the figures. The relative intensities of the peaks were estimated by decomposition of the spectra with mixed Gauss–Lorentz functions using WIN-NMR software.

Temperature-programmed desorption (TPD) analysis was performed by heating the sample in high vacuum ($P < 10^{-3}$ Pa) and a rate of 0.150 °C/s. Evolving products were analyzed by mass spectroscopy (MS) on a Selmi MX 7304 A instrument. Before TPD-MS measurements, samples were activated by pre-evacuation at 10^{-3} Pa for 20 min.

Table 1
Characteristics of supports and catalysts. Functional (onium or aminopropyl groups) and hydrophobic (chloropropyl or trimethylsilyl) group concentrations, C_L, μmol g^{-1}; specific surface area, S_{BET}, m^2 g^{-1}; pore volume V_{BJH}, cm^3 g^{-1}; pore diameter D_{BJH}, Å, C(PW$_2$), concentration of active anions, as immobilized; and C'(PW$_2$) after last catalysis run

Support	Abbreviation	C_L, μmol g^{-1} (function)	S_{BET}; V_{BJH}; D_{BJH}	Catalyst	C(PW$_2$), μmol g^{-1}	C'(PW$_2$), μmol g^{-1}
Propyltriethyl ammonium 	**EA-1**	77 (EA), 143 (chloropropyl)	267.2; 0.66; 72	**EA-1-PW$_2$**	60	55
	EA-1H	77 (EA), 110 (–SiMe$_3$)	267.2; 0.66; 72	**EA-1H-PW$_2$**	55	50
	EA-2	155 (EA), 535 (chloropropyl)	272.0; 0.64; 69	**EA-2-PW$_2$**	85	85
Propylpyridinium 	**Py-1**	253 (Py), 112 (chloropropyl)	272.4; 0.69; 77	**Py-1-PW$_2$**	145	130
	Py-2	480 (Py), 450 (chloropropyl)	275.6; 0.61; 72	**Py-2-PW$_2$**	280	285
Alkyltriphenyl phosphonium 	**PP-1**	115 (PP), 25 (chloroethyl)	297.2; 0.58; 56.5	**PP-1-PW$_2$**	55	60
	PP-1H	115 (PP), 750 (–SiMe$_3$)	282.0; 0.52; 54.3	**PP-1H-PW$_2$**	50	–
	PP-2H	100 (PP); 900 (–SiMe$_3$)	215.8; 0.50; 62	**PP-2H-PW$_2$**	40	–
Propylammonium 	**Am-1**	580 (amine)	240; nonporous	**Am-1-PW$_2$** (method 1)	255	245
	Am-2H	350 (amine) /820 (–SiMe$_3$)	276; 0.54; 52.0	**Am-2H-PW$_2$** (method 2)	335	–

2.2. Catalyst preparation

2.2.1. Choice of the supports

Functionalized silica supports (Table 1) were described previously [56]. We tested as supports two aminopropylsilica: hydrophilic **Am-1** and hydrophobic end-capped **Am-2H**. We tested two sets of anion-exchanging supports: *hydrophilic* **EA-1** and **PP-1** (prepared starting from chloroalkylsilicas and containing residual silanols and small amounts of chloroalkyl groups) and *hydrophobic* **EA-1H** and **PP-1H** (prepared by end-capping of the two previous silicas), and *supports with improved hydrophobicity*, **EA-2**, **Py-1**, and **Py-2**, which, along with a target onium salt, contain significant amounts of chloroalkyl groups to increase the lipophilicity of the environment of the active site. **Py-2** was prepared to favor formation of a polymerized bonded layer.

2.2.2. Preparation of active anion

An aqueous solution of $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (≈0.5 M) was prepared from WO_3, H_2O_2, and H_3PO_4 as described previously [12]. Tungstic acid (H_2WO_4) (2.5 g, 10 mmol) was added to 30% H_2O_2 (7 ml, 69 mmol). After 1 h stirring at 60 °C, followed by centrifugation to remove the unreacted H_2WO_4, 6 M H_3PO_4 (0.85 ml, 5.1 mmol) was added to the supernatant liquid. The resulting mixture was stirred for 30 min at ambient temperature to produce $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$. This acid was used as prepared for immobilization on aminopropylsilicas.

Solid $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ was synthesized as described previously [33] from $(NBu_4)[HSO_4]$ and an aqueous solution of $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, prepared as follows. A mixture of H_2WO_4 (2.5 g, 10 mmol) and aqueous hydrogen peroxide 30 wt% (7 ml, 69 mmol) was reacted at 60 °C for 40 min. The unreacted WO_3 was removed from solution by centrifugation. Na_2HPO_4 (0.71 g, 5 mmol), dissolved in H_2O (2 ml), was added to the resulting solution to form $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$. To this solution, $(NBu_4)[HSO_4]$ (6.78 g, 20 mmol) dissolved in water (10 ml) was slowly added under magnetic stirring. After 10 min of stirring, the white precipitate was filtered off, washed with 10 ml of H_2O and Et_2O, and air dried.

2.2.3. Immobilization of active anion on supports surface

For immobilization of PW_2 on onium-modified silicas, $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ was dissolved in MeCN (reagent grade) to give a ca. 5×10^{-2} M solution, purified by centrifugation. To 10 ml of this solution (0.5 mmol of active compound) was added an onium-modified silica (1 g, activated in air at 120–140 °C before the experiment) and the resulting suspension was stirred for 6 h at 25 °C. The solid was recovered by filtration, and the anion-exchange procedure was repeated three times with fresh portions of the solution of $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$. Finally, the solid was thoroughly washed with MeCN to completely remove the physically adsorbed salt, then air-dried at ca. 60 °C.

Immobilization of PW_2 on aminopropylsilicas was done through one of two methods. In method 1, a suspension of aminopropylsilica (1 g, activated under vacuum at 140 °C before the experiment) in 10 ml of an aqueous 0.5 M solution of $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, (a 5- to 6-fold excess) was stirred for 24 h at 25 °C. The solid material was filtered off and washed with *t*-BuOH or *i*-PrOH or water to remove unreacted acid (until the elute was neutral in pH), and the solid was dried at 25 °C. In method 2, a suspension of aminopropylsilica (1 g, activated under vacuum at 140 °C before the experiment) in an aqueous solution of $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (molar ratio, 1:1) was stirred for 24 h at 25 °C. The solvent was removed from the reaction mixture at 25 °C.

Only the freshly prepared solids were used in catalysis (kept from several days to two weeks). Before use, the catalysts were kept in closed vials in a refrigerator, whereas no special care was taken to avoid contact with air. The catalysts are identified using the abbreviations for the supports (Table 1) and PW_2 to designate the anion. Sample compositions are given in Table 1.

2.3. *Catalysis testing*

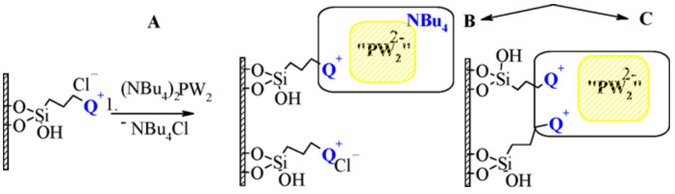
Epoxidation was performed with an anhydrous solution of hydrogen peroxide in *t*-BuOH, prepared by drying a mixture of 150 ml of *t*-BuOH and 45 ml of 30 wt% H_2O_2 with $MgSO_4$ (≈30 g) for 24 h [12]. To a mixture of oxidant solution (5 ml or ca. 12 mmol of H_2O_2) and a catalyst (generally 0.3 g), placed in a Schlenk vessel, was added 0.5 ml of *cis*-cyclooctene (3.73 mmol) or 0.3 ml of (R)-limonene (2.8 mmol). The suspension was stirred at 25 or 60 °C in the tightly closed Schlenk vessel for 24 h (or as indicated in the table). Conversion versus reaction time was followed by gas chromatographic analysis of the organic phase. These experiments were performed using a Delsi 30 gas chromatograph equipped with a 0.25-mm × 50-m OV 1707 capillary column and a flame ionization detector, linked to a Delsi Enica 10 electronic integrator using the following parameters: injector temperature, 180 °C; detector temperature, 200 °C; oven temperature, 70–200 °C; and a linear temperature gradient. For the reuse studies, the spent catalysts were recovered by centrifugation, washed several times with warm *t*-BuOH (ca. 15–20 ml), and dried in air at 60 °C.

3. Results and discussion

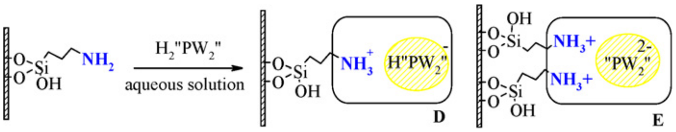
3.1. *Composition of catalysts based on elemental analysis*

3.1.1. *PW_2 anion, immobilised on onium silicas*

Immobilization of the PW_2 anion by treatment of onium silicas with MeCN solution of $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, designated salt **A**, affords a mixture of two types of species, designated salt **B** [(≡SiR–Q–(PW_2)–(NBu_4)] and salt **C** [((≡SiR–Q)$_2$(PW_2)] (Scheme 1). The ratio of the concentration of the onium cation (C_L) to that of the immobilized oxoperoxopolyanions [C(**PW_2**)] for all samples is in the range 1.5:1–2:1 on the basis of the elemental analysis (wt% of C, H, N, Cl, P, and W), suggesting the prevalence of species **C**. The probability of the formation of these species is high for silica supports with dense coverage (samples **EA-2**, **Py-1,** and **Py-2**). For example, sample **Py-2-PW_2** consists of the species propyl chloride $\equiv SiC_3H_6Cl$ (480 µmol g^{-1}), $\equiv Si–C_3H_6Py–[PW_2]\text{-}NBu_4$ (**B**, 110 µmol g^{-1}), and $(\equiv SiC_3H_6Py)_2[PW_2]$ (**C**, 170 µmol g^{-1}). For samples with a low density of grafted groups (**EA-1, EA-1H**, and **PP-1, PP-1H**), formation of a 2:1 species is doubtful. In this case, the 2:1 cation:anion ratio suggests that under the experimental conditions, some of the grafted onium groups were not involved in ion exchange.



Scheme 1. Preparation of catalysts via anion exchange: treatment of oniumsilicas with MeCN solution of $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$.



Scheme 2. Preparation of catalysts via protonation: treatment of amino-silicas with aqueous solution of $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$.

3.1.2. *PW_2 anion, immobilised on amino silicas*

Immobilization of HPA is best performed in organic solvents, because the high polarity of water favors its leaching and hydrolysis. Because the acid $H_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, designated as $H_2[PW_2]$, is available in aqueous solution only, a freshly prepared concentrated solution was used for immobilization to reduce the risk of its decomposition. Catalyst **Am-1-PW_2** was prepared following the equilibrium adsorption method (1) from a solution containing an excess of the $H_2[PW_2]$ reagent. According to the concentrations of the $[PW_2]$ anion (2.55×10^{-4} mol g^{-1}) and of aminopropyl groups (5.80×10^{-4} mol g^{-1}), this sample consists of mainly neutral salt, designated type **E** (Scheme 2). Catalyst **Am-2H-PW_2** was prepared via impregnation with the calculated amount of acid solution (method 2) to produce an acid salt, designated **D** (ca. 1:1 ratio of $H_2[PW_2]$ to amino groups; 3.35×10^{-4} mol g^{-1} of anion). Washing the prepared solids with *t*-BuOH afforded active catalysts; thus, we followed this approach to create catalyst samples and reactivate spent samples. Washing as-prepared catalysts (samples **Am-1-PW_2** and **Am-2H-PW_2**) with water resulted in poisoning of the active sites and absence of catalytic activity.

3.2. *Catalyst structure based on DRIFTS study*

According to previously published work [15,33], the precursor $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ is characterized by the following IR bands at (in cm^{-1}): 1018 and 995 (ν PO_4); 962 (ν W=O); 883, 852–854, and 843–847 cm^{-1} (ν O–O of

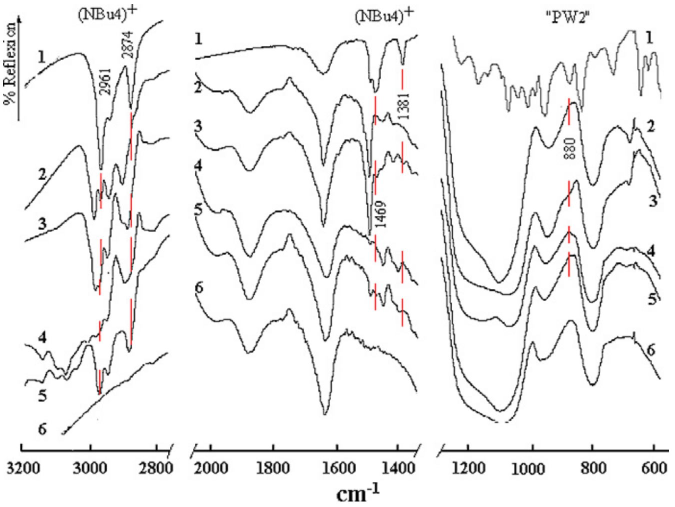


Fig. 1. IR spectra of $[n\text{-}(C_4H_9)_4N]_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (1); precursor silica support Py-2 $[\equiv Si(CH_2)_3N^+C_5H_5$ (2); catalyst Py-2-PW$_2$ $[\equiv Si(CH_2)_3N^+C_5H_5\text{–}PW_2]$ (3); precursor silica support EA-2 $[\equiv Si(CH_2)_3\text{-}N^+Et_3]$ (4); catalyst EA-2–PW$_2$ $[\equiv Si(CH_2)_3N^+Et_3\text{–}PW_2]$ (5); starting silica (6).

the peroxo ligands); 616(w) (ν W_2–O)s, 569 [or 573(m) and 562(m)] (ν_{as} $W(O_2)$), and 517 (ν_{sym} $W(O)_2$). The IR spectrum reported in this work (Fig. 1) confirms the precursor structure [1021(s), 996(m), 964(s), 883(m), 853(m), 844(s), 575(s), and 519(s) cm^{-1}]. As reported previously for solid $(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, the spectrum also contains bands at 1085(s), 1053(m), 975(w), 800(w), 739(m), 648(s), 624(w), 549(w), 488(w), and 457(w) cm^{-1}, which may be indicative of the parallel formation of a PW$_4$ anion [15].

The DRIFTS spectra of samples with immobilized PW$_2$ species are similar to those of the supports (Fig. 1). They give little information in the region of W–O vibrations, because of the relatively small concentration of PW$_2$ and a strong absorption of the silica lattice (Fig. 1, spectra 3, 5). In the spectrum of the **Py-2-PW$_2$** with the greatest amount of grafted anions (Fig. 1, spectrum 3), a shoulder appears at around 880 cm^{-1} that can be easily assigned to the O–O vibration of the peroxo ligand.

In the spectra of all oniumsilica-based catalysts, new C–H absorption bands (2961, 2935, 2874, 1469, and 1381 cm^{-1} [Fig. 1, compare spectra 3 and 1, and 5 and 4]) are observed. These bands correspond to the C–H vibration mode for the $(NBu_4)^+$ cation (Fig. 1, compare spectrum 1 with 3 and 5), providing evidence for the presence of $(NBu_4)^+$ on the surface. Because no physically adsorbed salt can be present as a result of the preparation procedure applied, this cation is included in the structure of the $\equiv$SiR-Q-(PW$_2$)–(NBu$_4$) species (active site of type **B**; Scheme 1).

3.3. Thermal stability by TPD-MS

The thermal stability of one sample, **Py-2-PW$_2$**, was monitored by MS (Fig. 2). Decomposition of the catalyst proceeds in four main stages, accompanied by the evolution of the following fragments: HCl (m/z 36, 38, and Cl with m/z 35, 37), CO (m/z 28), H$_2$O (m/z 18), pyridine (m/z 79, 80), aziridine (m/z 43), butene (m/z 56), propene (m/z 42, 41), ethylene (m/z 28, accompanied by a peak with m/z 27).

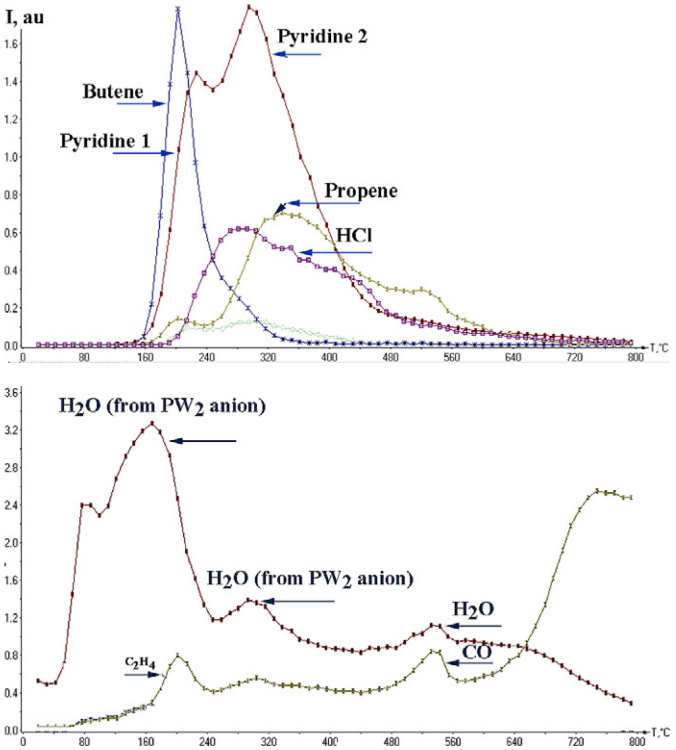
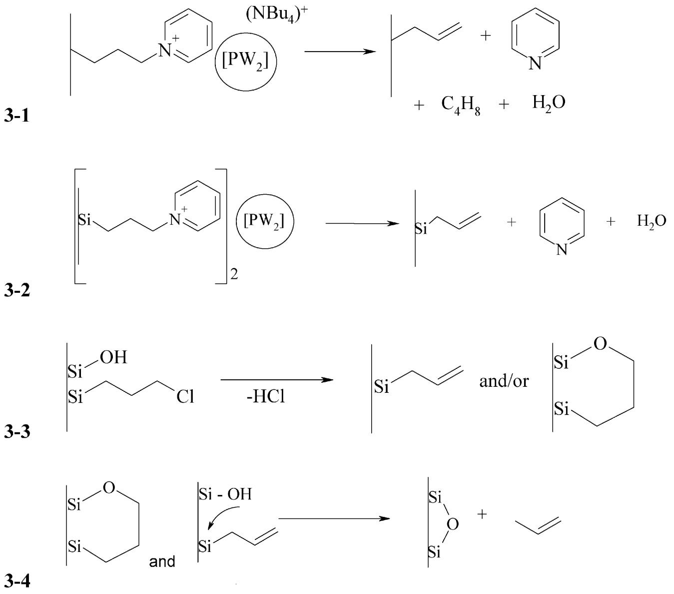


Fig. 2. Thermal decomposition of catalyst Py-2-PW$_2$, followed by mass spectrometry (I–peak intensity, arbitrary units).



Scheme 3. Scheme of thermal decomposition of Py-2-PW$_2$.

In stage 1 (160–240 °C, a maximum around 200 °C), simultaneous evolution of peaks of pyridine (m/z 79), aziridine (m/z 43), butene (m/z 56, accompanied by a peak of propene fragment with m/z 42), H$_2$O (m/z 18) provides evidence for the decomposition of $\equiv$Si–C$_3$H$_6$Py–PW$_2$–NBu$_4$ (**B** species) (Scheme 3-1).

In stage 2 (200–320 °C), two processes can be distinguished: decomposition of species **C**, $(\equiv SiC_3H_6Py)_2PW_2$ (evidenced by the simultaneous evolution of the peaks of water, which is a part of PW_2 anion [m/z 18] and pyridine [m/z 79]), and decomposition of propyl chloride (supported by the evolution of the peak of HCl [m/z 35]) (Scheme 3-2 and 3-3). The pyridine peak (maximum at ca. 300 °C) appears somewhat earlier than that of propene (maximum at 360 °C; the very first peak of propene is a fragment of butene), indicating that species **C** and **B** can first transform into silica-bonded fragments, $\equiv Si–C_3H_5$, which subsequently decompose. HCl is evolved in two steps (maxima at 280 and 440 °C), and these two maxima precede those of propene (340 and 540 °C). Therefore, we assume that the propyl chloride is first transformed into $\equiv Si–C_3H_5$.

In stage 3 (280–400 °C, maximum at 340 °C) and stage 4 (480–600 °C, maximum at 540 °C), decomposition of $\equiv Si–C_3H_5$ fragments occurs, accompanied by evolution of propene (a peak with m/z 42) (Scheme 3-4). The need for ≡Si–OH to react with $\equiv Si–C_3H_5$ affording ≡Si–O–Si≡ explains why some of the $\equiv Si–C_3H_5$ groups decompose at higher temperatures, when silanol migration is favored.

At around 520 °C, peaks of CO (m/z 28) and H_2O (m/z 18) also appear (Fig. 2). These peaks correspond to the in-depth decomposition of an organic residue, with the participation of WO_3 formed from the immobilized anion and to water evolution due to silanol condensation. Therefore, the TPD-MS study shows evidence of both of the structures proposed for the onium-grafted salts, $\equiv Si–C_3H_6Py–PW_2–NBu_4$ and $(\equiv SiC_3H_6Py)_2PW_2$. The thermal stability of these salts is sufficiently high to allow their use in epoxidation reactions; decomposition starts at about 160 °C in the former and at around 300 °C in the latter. Obviously, a disturbance of the structure of the anion and loss of peroxoligands, occurring at lower temperature, would not be detected by this technique.

3.4. Structure of the anion in immobilised catalysts: 31P MAS NMR results

It is well established that several oxoperoxoanions with the general formula [PW_x], ($x = 1$–4) are formed in aqueous peroxide solutions of $H_3PW_{12}O_{40}$, used as a homogeneous epoxidation catalyst. In the presence of PTRs, the organic phase contains a solution of the resultant onium salts. The ^{31}P NMR chemical shifts of these salts are affected by solvent, ion pairing, the degree of protonation, and the nature of the cation. Consequently, the values reported by different authors can vary to some extent. For the isolated salt with the Venturello anion (PW_4), the following chemical shifts have been reported: 3.16 ppm (Arquad 1 cation, solution in $CDCl_3$), 4.13 (tetra-n-hexylammonium cation, solution in $CDCl_3$), and 3.8 ppm (the same cation, solution in CD_3CN) [57]. For the isolated salt with the PW_2 anion, the following chemical shifts were found: 0.9 ppm (tetra-n-hexylammonium salt in solid state) [33], 0.5 ppm (Arquad-1 salt in the solid state) [15] and 2.95 ppm ($[n\text{-}(C_4H_9)_4N]$ cation, solution in $MeCN/CDCl_3$ [15]. For a solution containing a mixture of anions and the $[(nC_{10}H_{21})_4N]^+$ cation in CD_3CN, Duncan et al. [57] reported 1.50 ppm (PW_2), 3.04 ppm (PW_3), and 6.15 ppm (PW_4). A $CDCl_3$ solution used in epoxidation and containing the oxoperoxophosphatotungstic system showed several peaks in the ^{31}P NMR spectrum; two of these, at 0.5 and 3.5 ppm, were assigned to PW_2 and PW_4, respectively [24].

The chemical shifts are also affected by immobilization on solid supports, and the assignment becomes more complex. ^{31}P SPE-MAS NMR spectra recorded for some of the catalysts prepared in this work are shown in Figs. 3 and 4.

3.4.1. Am-1-PW_2

The corresponding ^{31}P SPE-MAS NMR spectrum contains two broad peaks at ca. 6 and −8 ppm (Fig. 3a). The peak at ca. 6 ppm ($\Delta\nu_{1/2}$ 600 Hz, 64% of the total intensity) can be tentatively assigned to the PW_2 anions, taking into account the fact that the solution contains mainly PW_2 species. Comparison of our data with the values reported for the PW_2 anion (2.95 ppm in MeCN-$CDCl_3$ solution [15], 0.9 ppm in the solid state [33], and 0 ppm adsorbed on SiO_2 [33]) indicates an upfield shift of ca. 3 ppm. This shift probably results from the strong chemical interactions of the anion with the support surface. This conclusion is not definite, however. Such a deviation from the reported data also can suggest the formation of a more stable PW_4 species on the support surface as a result of the immobilization procedure. For the latter, the reported values are scattered between 3.1 to 6.15 ppm.

In addition, the main peak contains a shoulder at around 2 ppm (600 Hz, 11% of the whole intensity), which can originate from other polynuclear oxoperoxo species (PW_2 or PW_1) produced in the course of immobilization. A second peak at around −8 ppm, ($\Delta\nu_{1/2}$ 1700 Hz, 25% of the whole intensity) (Fig. 3a) is too upfield and thus cannot be assigned to any of the peroxoligand-containing complexes. This peak indicates formation of other polynuclear oxotungstophosphate complexes with a greater number of tungsten atoms (Keggin-derived lacunary oxotunstophosphate complexes, PW_x, $x > 4$), and no peroxoligands. The ^{31}P SPE-MAS NMR spectrum of sample **Am-2H-PW$_2$** (not shown here) is similar to that of **Am-1-PW$_2$**. The observed line width may be indicative of a "pseudoliquid phase" behavior of the immobilized anion, as suggested for the adsorbed species in [33]. The mobility of HPA-anion is favored by the hydrophilic surface of the support.

The spectrum of Am-1-PW_2 thoroughly washed with water (Fig. 3b) shows two peaks. The first peak, due to the grafted PW_2 or PW_4 oxoperoxo species, is observed at ≈6 ppm ($\Delta\nu_{1/2}$ 900 Hz). Its relative intensity is reduced to 44% after an aqueous wash (Fig. 3b), compared with 64% in the spectrum of the unwashed sample (Fig. 3a). The second peak is observed at around −2 ppm ($\Delta\nu_{1/2}$ 2600 Hz, 56%, overlapped with the peak at ≈6 ppm). As in the spectrum of initial **Am-1-PW$_2$**, this peak arises mainly from the Keggin-derived lacunary complexes (PW_x), which do not bear peroxo ligands. Its relative intensity increases from 25% in the initial **Am-1-PW$_2$** to 56% in the same sample thoroughly washed with water. If irreversible, such a loss of peroxoligands could be at the origin of the lack of catalytic activity of the latter sample.

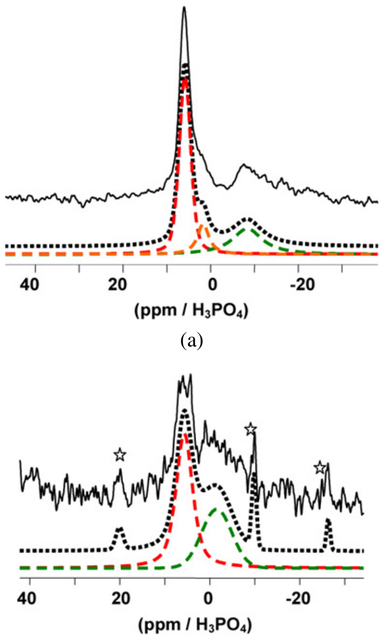


Fig. 3. ^{31}P SPE-MAS NMR spectra of (a) **Am-1-PW$_2$**, "as-prepared" *NS* = 304; (b) **Am-1-PW$_2$**, thoroughly washed with water, *NS* = 16 (at 4000 Hz); asterisks denote spinning side-bands. Experimental spectrum (—), fitted peaks (- - -), sum of the fitted lines (· · ·).

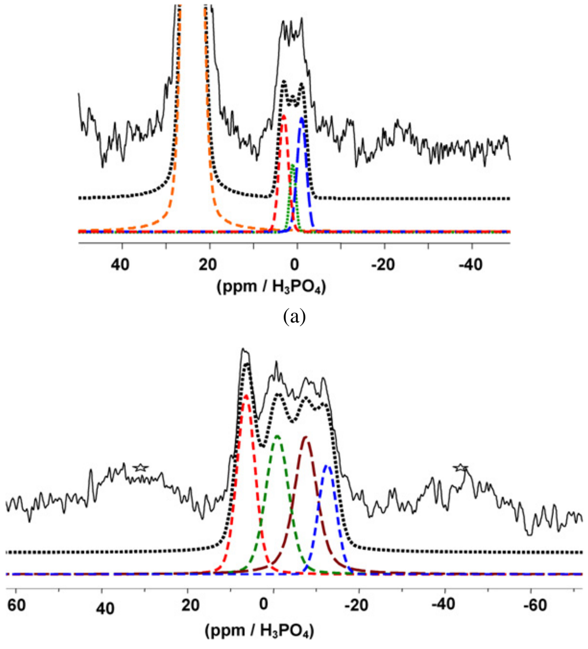


Fig. 4. ^{31}P SPE-MAS NMR spectra of oniumsilica with immobilized $[n\text{-}(C_4H_9)_4N]_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$: (a) **PP-1-PW$_2$**, *NS* = 3200; (b) **Py-1-PW$_2$**, *NS* = 64. Experimental spectrum (—), fitted peaks (- - -), sum of the fitted lines (· · ·).

3.4.2. *Py-1-PW$_2$*

The corresponding ^{31}P SPE-MAS spectrum (Fig. 4b) presents a broad peak and, in contrast to the previously discussed spectra (Fig. 3a), intense spinning side bands. Decomposition of the central line allowed us to distinguish four distinct components (Fig. 4b) of quasi-equal intensities at 6, −0.9, −8, and −13 ppm ($\Delta\nu_{1/2}$ 1000–1300 Hz). These are assigned to oxoperoxoditungstophosphate anions PW$_2$, phosphate groups PO$_4$, and other tungstophosphate anions (PW$_x$, $x > 4$), respectively. These lines are somewhat broader than those observed in the spectra of aminopropylsilica-immobilized species, suggesting a stronger fixation of these species on the surface and/or relatively lower symmetry of the grafted complexes with PW$_2$ anions.

3.4.3. *PP-1-PW$_2$*

The corresponding ^{31}P SPE-MAS spectrum (Fig. 4a) presents a strong peak at 25 ppm arising from the grafted alkyltriphenylphosphonium cations; and a broad peak of low intensity. The latter was perfectly fitted with three components (Fig. 4a), attributed to different immobilized tungstophosphates species: PW$_2$, PO$_4$, and PW$_x$. These are located at 3, 1, and −1 ppm and have relative intensities of 40, 20, and 40%, respectively.

3.4.4. *Influence of the immobilisation on the structure of immobilised PW2-species*

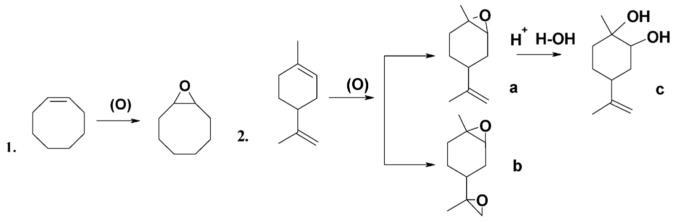
To understand the reason for the large number of peaks observed in the ^{31}P SPE-MAS NMR spectra of immobilized catalysts and their different chemical shifts, several factors, including the different degree of protonation and the number of peroxo bridges, should be considered. However, we consider the main reason to be the formation from the initial PW$_2$ anion in solution of various polynuclear species PW$_x$ ($x = 1, 3, 4$, and higher) and their subsequent immobilization. For the system studied here, ^{31}P MAS NMR spectra suggest that immobilization by means of both precursors, either an aqueous solution of $H_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ or an acetonitrile solution of $[n\text{-}(C_4H_9)_4N]_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, yields a mixture of grafted PW$_x$ species ($x = 1$–4).

For aminopropylsilica-based catalysts, these species are mostly the target PW$_2$/PW$_4$ (their attribution cannot be definitive), whereas for oniumsilica, there is a mixture of equal proportions of the target anions PW$_2$/PW$_4$ together with other anionic species, including phosphate ions and PW$_x$ (x = 1, 3). Important parts of these species (peaks at −8 ppm for the aminopropylsilica-based catalyst and −13 ppm for the oniumsilica-based catalyst) are attributed to the Keggin-derived lacunary oxotungstophosphate complexes with fewer peroxo ligands or without such ligands. These results are not surprising if one considers the equilibrium existing between PW$_x$ anions in aqueous peroxide solution [57]. On contact with the support, the equilibrium can be changed in favor of the polynuclear complexes with a greater number of tungsten atoms and larger size, because of the stronger interaction between these anions with "soft" onium cations. As a result, these anions may be preferred for adsorption by the support.

One previously reported experiment of immobilization of oxoperoxo anions on siliceous supports gave results consistent with those reported herein. Hoegarts et al. attached the PW$_x$ anion (presumably a PW$_2$ species) to the surface of MCM-41 with grafted amino groups by reaction with WO_4^{2-}/H_3PO_4 solution and, as supposed by the author, formation of a phosphoramide linkage. The resulting catalyst sample displayed three ^{31}P NMR peaks, at 6, 0, and −10 ppm [53]. These values are very close to those observed in the present work. In contrast to these and our results, $[n\text{-}(C_4H_9)_4N]_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, physically adsorbed on silica, displayed a single peak at 0 ppm, which could be indicative of adsorption of phosphate anion [33]. Even more dissimilar results were obtained when heterogenization of PW_2 anions was performed by sol–gel insertion of its precursor into MCM-41. Such immobilization resulted in the formation of at least three species with chemical shifts of ca. 0, −10, and −20 ppm [33]. We assume that in this case, immobilization resulted in a mixture containing not only PW_x (PW_2 or PW_4) species, but also several polynuclear oxotungstophosphates without peroxo ligands.

4. Catalysis results and discussion

Epoxidation of cyclooctene and (R)-limonene is described in Scheme 4. Epoxidation of *cis*-cyclooctene to 1,2-epoxycyclooctene (Scheme 4.1) is a model reaction that reflects the general activity of the catalysts. Epoxidation of a bulkier substrate, (R)-limonene (Scheme 4.2), allowed us to test the accessibility of the active sites. The selectivity of the latter reaction is very sensitive to the Brønsted acidity of catalysts. Indeed, in acidic media epoxide, **a** is hydrolyzed to a mixture of diastereomeric diols **c**; moreover, in the case of overoxidation, diepoxides **b** can be obtained. For this substrate, the two immobilization routes [adsorption of H_2PW_2 and ion exchange with $(NBu_4)_2PW_2$] gave very different results in terms of activity and selectivity.



Scheme 4. Epoxidation of cyclooctene (1); epoxidation of (R)-limonene (2).

4.1. Epoxidation of cyclooctene

4.1.1. Activity of PW_2 catalysts immobilized on oniumsilica

Results of cyclooctene epoxidation with the use of the oniumsilica-based catalysts are presented in Table 2. To compare the samples, average turnover frequencies (TOFs) and turnover numbers (TONs) were calculated as the number of moles of substrate converted per mole of PW_2 anion per hour (TOF) and per total reaction time (TON).

In the first run, most of the immobilized catalysts exhibited high activity and selectivity toward epoxidation of cyclooctene with $H_2O_2/t\text{-BuOH}$. Complete (100%) conversion was achieved with **EA-1-PW$_2$** and **Py-2-PW$_2$**. High conversion was obtained with **EA-2-PW$_2$** (50%) and **Py-1-PW$_2$** (66%). Other catalysts turned out to be less active. To make experimental conditions regular, we used equal catalyst weights; however, this resulted in unequal PW_2/substrate ratios (0.5–2.5%), because the solid catalysts have different concentrations of PW_2 anion per gram of catalyst). Therefore, we compare them on the basis of average TOF, per anion per hour.

Table 2
Catalytic activity of oniumsilica-based catalysts in epoxidation of cyclooctene. Catalysis conditions: 60 °C, 3.73 mmol of cyclooctene, 12 mmol of H_2O_2/in *t*-BuOH, 0.3 g of catalyst (substrate/“PW_2” ratio varied depending on the catalyst, 50–250), reaction time 24 h. In all cases, selectivity was around 100%

N	$C(PW_2)$, ±5	$C'(PW_2)$, ±5	Run	Y, %	TOF, h^{-1}	TON, ac^{-1}
EA-1-PW$_2$	60	55	1	100 (6 h)[a]	35	175
			2	34	3.0	72
			3	7	0.6	16
EA-1H-PW$_2$	55	50	1	12	1.2	27
			2	19	1.8	43
EA-2-PW$_2$	85	85	1	49	2.6	74
			2	50	3.2	76
Py-1-PW$_2$	145	130	1	66	2.6	63
			2	78	3.1	75
			3	75	2.7	65
Py-2-PW$_2$	280	285	1	100 (5 h)[a]	8.8	44
			2	100 (14 h)[a]	4.4	44
PP-1-PW$_2$	55	60	1	60	5.6	135
			2	34	3.2	77
			3	23	2.2	52
PP-1H-PW$_2$	50	–	1	37	3.8	92
			2	25	2.6	62
PP-2H-PW$_2$	40	–	1	12	1.5	37
			2	17	2.2	54

Note. *N*, catalyst reference; $C(PW_2)$, initial concentration of anions, $\mu mol\,g^{-1}$; $C'(PW_2)$, concentration in spent sample after last run, $\mu mol\,g^{-1}$; Y, yield of epoxycyclooctane in 24 h; TOF, average turnover frequency per hour per anion; TON, turnover number (total yield) per immobilized anion.

[a] Time of complete conversion when the reaction is over before 24 h.

Table 3
Catalytic activity of **Am-1-PW$_2$** in epoxidation of cyclooctene. Catalysis conditions: Tests were made with 3.73 mmol of cyclooctene and 12 mmol of H_2O_2. The weight of catalyst varied from 0.15 to 0.095 g, giving substrate/PW$_2$ ratios (run): 89 (first), 155 (second), 190 (third)

Run	Substrate/“PW$_2$” ratio	t, h	T, °C	Y, %	TOF, h^{-1}	TON
1	89	24	22	59.5	2.3	57
2	155	24	22	24.0	1.9	40
2[a]	155	5	60	51.0	9.0	40 + 45
3	190	5	60	22.0	8.2	41

Y, yield of cycloepoxyoctane; TOF, turnover frequency; TON, turnover number. In all cases, the selectivity was close to 100%.

[a] Run 2 is continuation of Run 2 after the temperature was increased.

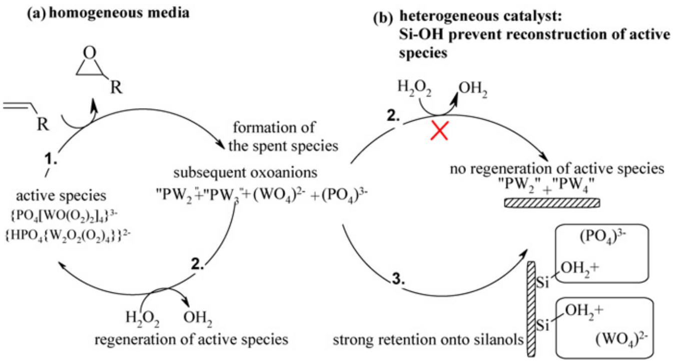
Comparison of the oniumsilica-based catalysts with the same cation but prepared by different silanization procedures (e.g., series **EA-1-PW$_2$**, **EA-1H-PW$_2$**, **EA-2-PW$_2$**; series **PP-1-PW$_2$**, **PP-1H-PW$_2$**, **PP-2H-PW$_2$**; and series **Py-1-PW$_2$**, **Py-2-PW$_2$**), and with different onium salts but made via a similar silanization route (e.g., series **EA-1-PW$_2$**, **PP-1-PW$_2$** and series **EA-2-PW$_2$**, **Py-1-PW$_2$**), suggests the following conclusions:

(a) The structure of the onium salt does not determine catalyst activity (expressed as TOF value of the immobilized PW$_2$ anion). Most of the catalysts (**EA-1H-PW$_2$**, **EA-2-PW$_2$**, **Py-1-PW$_2$**, **PP-1-PW$_2$**, **PP-1H-PW$_2$**, **PP-2H-PW$_2$**) exhibit consistent TOF (1.5–5.6 h^{-1}), especially in the second and third runs (2.2–3.3 h^{-1}), with the exception of much greater values for **EA-1-PW$_2$**, **Py-2-PW$_2$** (35 and 8.8 h^{-1}; Table 3).

(b) The method of preparation of the siliceous support and the composition of the grafted layer (presence of hydrophilic silanols and hydrophobic –SiMe$_3$ and propylchloride groups; see Table 1) has a considerable effect on the catalytic activity (Table 2). In particular, the performance of the recycled catalysts differs significantly. Supports **EA-1** and **PP-1** have a small concentration of grafted onium cations and a hydrophilic support surface [56]. The corresponding catalysts **EA-1-PW$_2$**, **PP-1-PW$_2$** are rapidly deactivated. It must be emphasized that **EA-1-PW$_2$** displays very high TOF (35 h^{-1}) in the first run, but is quickly deactivated (TOF 3.0 and 0.6 h^{-1} in subsequent runs). These supports, when end-capped, were used for preparation of samples **EA-1H-PW$_2$**, **PP-1H-PW$_2$**, and **PP-2H-PW$_2$**. End-capping gave catalysts that were less active but relatively more stable in the consecutive runs. Supports **EA-2** and **Py-1** (obtained by direct silanization with a mixture of target onium-silane with chloropropyltriethoxysilane) had a higher degree of surface coverage and a large proportion of chloropropyl groups. Catalysts **EA-2-PW$_2$**, and **Py-1-PW$_2$** based on these supports are quite stable in two or three consecutive runs (TOF 2.6–3.1 h^{-1} for **Py-1-PW$_2$** and 2.6–3.2 h^{-1} for **EA-2-PW$_2$**).

4.1.2. Recycling performance. Influence of structure of catalyst supports

As follows from the IR study, absorption bands due to the grafted organic moieties of catalysts are not altered for the spent samples (after 3 catalysis cycles). This demonstrates sufficient stability of the bonded organic layer toward the oxidant solution. Analysis of the W concentration for the catalysts before and after catalysis run (last run, Table 2) suggests that the marked reduction of the activity (observed for catalysts **EA-1-PW$_2$** and **PP-1-PW$_2$**) should be attributed to some other factor than the simple leaching of active species, even though a slight decrease in tungsten concentration occurred.



Scheme 5. Suggested pathways for deactivation and regeneration of active species in homogeneous and heterogeneous reactions.

Several groups have studied the Venturello–Ishii system, but little is known about the mechanism. Study of the kinetics of epoxidation by a PW$_4$ complex by Hill et al. [57] revealed that the reaction is first-order in both alkene and $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$. The reaction follows the rate equation $\nu_0 = k\,[[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}]$ [alkene].

Epoxidation, starting from the Ishii precursor, $(PW_{12}O_{40})^{3-}$, begins with the generation of $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$, which transfers oxygen to alkene, and is followed by the formation of subsequent peroxo PW$_x$ species (predominantly PW$_4$ and PW$_3$ complexes) rapidly regenerated into $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ by the reaction with H_2O_2 [9]. Species $[PO_4\text{-}\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ is proposed as the kinetically most significant epoxidizing agent.

In a homogeneous system and in the presence of an oxidant solution, this process is reversible, with transformation between PW$_x$ complexes and reconstruction of the active species proceeding readily (Scheme 5). In contrast to what occurs in a homogeneous system, the surface of the catalyst support can entrap the subsequent PW$_x$ species and also inactivate $(PO_4)^{2-}$ and $(WO_4)^{2-}$ anions via adsorption on silanols. Strong retention by polar silanols can prevent reconstruction of the active species by reaction with H_2O_2 and result in a loss of activity.

Fast deactivation of active species in the Venturello–Ishii system is one of its major drawbacks. Hill et al. [57] pointed out the unavoidable drop in catalytic activity of PW$_x$-based complexes in the Venturello–Ischii system. ^{31}P NMR spectroscopy revealed that the catalyst is irreversibly inactivated by the epoxide produced. A maximum TON of 500 was found for the $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ anion, whereas the reaction rate decreased even before the catalytic activity disappeared.

We believe that particularly in the case of heterogeneous catalysts, the degree of such poisoning can be influenced by the hydrophilic/hydrophobic nature of the silica and the structure of the interfacial layer. High surface polarity may favor

Table 4
Catalytic activity of oniumsilica- and aminopropylsilica-based catalysts in epoxidation of limonene. Catalysis conditions: Tests were made at 22 or 60 °C using 2.8 mmol of limonene and 12 mmol of H_2O_2; the substrate/W_2 ratio was 113 (**EA-2-PW$_2$**), 33 (**Py-2-PW$_2$**), 29 (**Am-2H-PW$_2$**)

Catalyst	Run	T, °C	C, %	t, h	S, %	TOF, h^{-1}	TON, ac^{-1}
EA-2-PW$_2$	1	22	0	24	–	0	0
	1	60	33	48	88	1.8	60
	2	60	9	24	78	0.5	12
Py-2-PW$_2$	1	22	86	22	81 (100 in 1 h)	1.3	29
	2	22	50	25	93	0.66	17
	3	22	12	24	94	0.2	4
Am-2H-PW$_2$	1[a]	22	36	0.3	4	40	–
	2[a]	22	31	0.6	32	14	–

Note. Run, number of catalysis run; t, time of reaction; C, conversion of limonene; S, selectivity to epoxide; Y, yield of epoxide; TOF, average turnover frequency; TON, turnover number.

[a] Reaction was monitored over a short period of time, so TON was not calculated.

stronger retention of polar epoxides near the active sites and lead to faster catalyst deactivation.

Because the hydrophilic surface of **PP-1-PW$_2$** and **EA-1-PW$_2$** can contribute to the poisoning by adsorption of epoxides and deactivated species, reducing the concentration of silanols should result in greater stability of PW_2 anions toward poisoning. Indeed, **EA-1H-PW$_2$** and **PP-1H-PW$_2$**, prepared from end-capped **EA-1** and **PP-1** and **PP-2H-PW$_2$**, displayed more similar TOF values in two runs, though the activity of the active site is lowered by the end-capping [**EA-1H-PW$_2$** (TOFs, 1.2 h^{-1} in run 1 and 1.8 h^{-1} in run 2), **PP-1H-PW$_2$** (TOFs, 3.8 h^{-1} in run 1 and 2.6 h^{-1} in run 2), and **PP-2H-PW$_2$** (TOFs, 1.5 h^{-1} in run 1 and 2.2 h^{-1} in run 2). Possibly, end-capping $-SiMe_3$ fragments on the catalyst surface reduce the accessibility of the active sites to some degree.

Very stable performance, together with high activity, was displayed by the catalysts **EA-2-PW$_2$**, (TOF 2.6–3.2 h^{-1}) and **Py-1-PW$_2$** (TOF 2.6–3.1 h^{-1}), with high grafted layer densities, prepared by one-step silylation with a mixture of two silanes. The higher density and the increased lipophilicity of the grafted layer, due to the grafted propylchloride, may be responsible for the stabilization of the catalyst performance. Consequently, the variations in the performance of the immobilized catalysts with different grafted layer structures can be ascribed to inherent deactivation of active species, which hinders their regeneration due to silanols, and to poisoning and different resistance toward poisoning with epoxide.

4.1.3. Activity of PW_2-aminopropylsilica catalysts

The results obtained with PW_2-aminopropylsilica catalysts are presented in Table 3. At 22 °C, **Am-1-PW$_2$** exhibited high selectivity (100%) and a TOF, similar to the oniumsilica-based catalysts (1.9–2.3 h^{-1}). Its activity was stable in the two subsequent runs with TOF 2.3 h^{-1} (run 1) and 1.9 h^{-1} (run 2). Increasing the temperature to 60 °C using the reaction mixture of the second run increased the TOF to 9 h^{-1}, and this value was not significantly changed in the subsequent run (run 3) using spent catalyst. The concentration of PW_2 anions in the as-prepared sample was 2.6–2.8 × 10^{-4} mol g^{-1}; after the fourth run, the catalyst contained 2.4–2.6 × 10^{-4} mol g^{-1} of PW_2 anion, according to the X-ray fluorescence analysis. This result indicates slight leaching of the immobilized anion.

4.2. Epoxidation of (R)-limonene with PW_2-aminopropylsilica and PW_2-oniumsilica

To test epoxidation of a more sterically demanding substrate, (R)-limonene, two most active onium-based catalysts, **Py-2-PW$_2$** and **EA-2-PW$_2$**, were chosen. Use of these catalysts for epoxidation of the limonene gave low activity (Table 4). **Py-2-PW$_2$** at room temperature resulted in 86, 50, and 12% conversion in 3 consecutive runs, with 80–90% selectivity. Catalyst **EA-2-PW$_2$** was not active at room temperature, although it catalyzed the reaction at 60 °C. The conversion reached 33% in 24 h. The selectivity to epoxides fell from 88% (after 1 h) to 76% (after 24 h). A subsequent test done with the spent catalyst gave only 9% conversion. Thus, the activity of both catalysts decreased considerably when they were reused (TOF fell from around 1.8 to around 0.5 and from around 1.3 to around 0.2 h^{-1}).

In both cases of (R)-limonene oxidation, selectivity to epoxide was 78–94%, and highly reactive nucleophilic diols were formed as side products. This suggests that strong deactivation of catalyst can result from diol adsorption on the catalyst surface. Marked catalyst poisoning by diols is in contrast to what was observed with cyclooctene as substrate. Moreover, the polar diols can induce transfer of the active species from the surface to the solution. According to elemental analysis, leaching of active species, not observed in cyclooctene epoxidation, was around 15%.

Catalyst **Am-2H-PW$_2$** (prepared by method 2 to obtain acid salt, 1:1 amine-to-acid ratio) was active at room temperature: (Table 4; 36% conversion in 0.3 h, TOF 40 h^{-1}); however, the selectivity to epoxide was poor (4%). The relatively high activity (approaching homogeneous conditions) and low selectivity of this sample can be explained by the high residual acidity of the supported anion and its strong leaching into the solution. Apparently, the reaction is homogeneous in the first run. In the second run, **Am-2H-PW$_2$** gave lower activity (Table 4; 31% limonene conversion in 0.6 h, TOF 14 h^{-1}) but better selectivity (32%). Its activity was close to that obtained in the epoxidation of cyclooctene (sample **Am-1-PW$_2$**). **Am-1-PW$_2$** and **Am-2H-PW$_2$**, thoroughly washed with water (to remove the leaching species and reduce catalyst acidity), exhibited no catalytic activity. According to their ^{31}P NMR spectra, these catalysts retained immobilized PW$_x$ anions; however, these anions were mostly the non-peroxo ligand-containing species (^{31}P NMR peak at −4 ppm). This finding could be at the origin of the lack of activity of the washed catalysts.

Thus, in contrast to the epoxidation of cyclooctene, the catalysts based on grafted silicas were found to be inappropriate for the epoxidation of the sterically demanding and acid-sensitive substrate. The aminopropylsilica-based catalysts were active but gave insufficient selectivity in this reaction, due to their high acidity, and favored formation of diols as side products. The nonacidic onium-based catalysts were selective and prevented formation of diols, but turned out to be relatively weakly active as well as insufficiently stable.

4.3. Comparison of catalytic activity with published results

Comparison of our results with those reported for homogeneous systems—namely epoxidation under phase transfer conditions (PTC), using $Q_2[\mathrm{HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}}]$, where $Q = $ Arquad $2HT = (\mathrm{C_{18}H_{37}})_2$ 75% + $(\mathrm{C_{16}H_{33}})_2$ 25%] $\mathrm{N(CH_3)_2Cl}$, (21 °C, 10% H_2O_2, $CHCl_3$)—shows much greater activity of the catalyst in the latter case (TOF 100 $\mathrm{h^{-1}}$) [12]. This is not surprising, because immobilization of active HPA anions has been previously reported to cause reduced activity [31]. For instance, a ca. 3-fold rate reduction, compared with the corresponding reaction in solution, was reported for Amberlyst-supported $[\mathrm{HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}}]$ catalyst (used in a triphase system, comprising catalyst, aqueous H_2O_2, and CH_2Cl_2, at room temperature). In this system, moderate to high selectivities (epoxide yields 68–94%) were obtained for (R)-limonene epoxidation at 70–95% conversion, which is close to those observed with the Py-2-PW$_2$ catalyst in our study (81–94%) [31].

The activity of catalysts prepared in much the same way as our immobilization approach was described by Hoegaerts et al. Three types of catalysts were studied: mononuclear and binuclear tungsten oxoperoxo anions on organic resins, Venturello anions on triethylpropylammonium-MCM-41, and a tungsten complex with phosphoramide-MCM-41. Resin-immobilized mononuclear and binuclear anions had very low activity, whereas tetranuclear anions exhibited high activity (TOF 5.3 $\mathrm{h^{-1}}$ per W site), selectivity, and efficiency in terms of H_2O_2 consumption, along with no leaching (epoxidation in MeCN with aqueous H_2O_2 [35%] at 50 °C). The tetranuclear anion $\{\mathrm{PO_4[WO(O_2)_2]_4}\}^{3-}$ on tetraalkylammonium-MCM-41, immobilized from a solution of $\mathrm{H_3\{PO_4[WO(O_2)_2]_4\}}$, was less active (TOF 1.5 $\mathrm{h^{-1}}$ per W site). Interestingly, we found similar TOF values (1–2 $\mathrm{h^{-1}}$ per W site) with different precursors, silica supports, and epoxidation conditions [53]. Hoegaerts et al. reported the formation of diols as a result of the residual acidity of the immobilized oxoperoxo anion, which we avoided in our work by using a nonacidic precursor, $(n\text{-}\mathrm{Bu_4N})[\mathrm{HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}}]$ salt. The third type, phosphamide-linked PW$_2$ catalyst (on aminopropylated MCM-41), led to the epoxidation of cyclooctene with much greater TOF (around 84 $\mathrm{h^{-1}}$). In our work, we also found greater TOF for aminopropylsilica-based catalysts than for oniumsilica-based ones. Moreover, for the acid-sensitive epoxides, Hoegaerts et al. reported diol formation, which we also noted in our study.

Another related approach to heterogeneous epoxidation catalysts is based on the use of $\{\mathrm{PO_4[WO(O_2)_2]_4}\}^{3-}$ and $[\mathrm{WZnMn_2(H_2O)_2\text{–}(ZnW_9O_{34})_2}]^{12-}$ anions immobilized in composite silica containing phenyl and quaternary ammonium groups [46]. The oxidation of cyclooctene with aqueous H_2O_2 proceeds with a TOF of around 1–5 $\mathrm{h^{-1}}$ per tungsten atom, which is again consistent with our results. The previously reported $\equiv\mathrm{Si\text{–}Ph\text{–}CH_2N^+Me_2(C_8H_{17})}$-and-$[\mathrm{ZnWMn_2^{II}\text{–}(ZnW_9O_{34})_2}]$12-based catalyst displayed the highest activity, which was significantly improved by the presence of hydrophobic phenyl groups in silica–gel. Epoxidation of alkenes with bulky substituents was much less successful [47], similar to our results on (R)-limonene. Further investigation by the same research group showed very high activities and excellent recycling properties of a catalyst consisting of $[\mathrm{WZnMn_2(H_2O)_2\text{–}(ZnW_9O_{34})_2}]^{12-}$ (compared with $\{\mathrm{PO_4[WO(O_2)_2]_4}\}^{3-}$) and silica–gel containing polyethylene, polypropylene, and quaternary ammonium groups.

This analysis led us to the conclusion that the catalytic performance of the heterogeneous catalysts reported here is comparable to that of previously reported related solids. We have shown that the degree of surface coverage by organic functions is a crucial factor in determining catalyst stability and recycling behavior. We confirm the importance of hydrophobization of the catalyst surface on its dispersion in reaction media as well as its catalytic activity.

5. Conclusion

The protonation of aminopropylsilica with $\mathrm{H_2[HPO_4\{W_2O_2\text{-}(\mu\text{-}O_2)_2(O_2)_2\}]}$ and anion exchange on the onium-modified silica with $\mathrm{(NBu_4)_2[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]}$ allows us to strongly immobilize peroxoophosphoditungstate PW$_2$ anions and prepare heterogeneous catalysts for liquid-phase epoxidation. Our ^{31}P SPE-MAS NMR study revealed that the immobilized species in fact consists of several PW$_x$ anions, including mainly the starting PW$_2$ and PW$_4$ anions as well as some others containing more than four tungsten atoms and a reduced number of peroxo ligands.

The catalysts were active in epoxidation using H_2O_2/t-BuOH oxidant solution in the absence of chlorocarbon solvent. In the case of cyclooctene, high conversion (up to 100%) and selectivity to epoxide (100%) were achieved. The oniumsilica-based catalysts perform similarly to the previously reported related heterogeneous catalysts based on HPA, with TOF values per anion of 2–4 $\mathrm{h^{-1}}$. Aminopropylsilica-based catalysts are somewhat more active (TOF values per anion of around 8 $\mathrm{h^{-1}}$) but less stable toward leaching.

The nature of the grafted onium cations (triethylammoniopropyl, pyridiniopropyl, and triphenylphosphonioalkyl) was not important for the catalytic activity. The degree of surface coverage by organic functions (onium cation, chloropropyl, or –SiMe$_3$ groups) and thus the hydrophobicity of the environment of the catalytic site are the crucial factors in determining catalyst stability and recycling behavior. The performance of onium-based catalysts depends greatly on the procedure used for grafting the onium cation on the surface.

Catalysts with a low coverage by organic functions and a hydrophilic surface gave rather poor results in terms of recycling. Because no or very little leaching was detected, we assume that this effect is due in part to the poisoning of active sites with the epoxide. Silanols may promote this effect either by strong retention of polar epoxides or by retention of deactivated (decomposed) species, preventing the regeneration of active species by reaction with H_2O_2. The stability of these catalysts is somewhat increased by silica end-capping, but at the same time their activity is decreased.

Catalysts based on oniumsilicas **EA-2** and **Py-1** (grafted tetralkylammonium and alkylpyridinium cations) prepared by one-step silanization, with a high density of the grafted layer, also containing hydrophobic chloropropyl groups, demonstrated high activity and selectivity in epoxidation of cyclooctene as well as excellent recycling stability. Less promising results were obtained in the epoxidation of (R)-limonene. The use of onium-grafted catalysts resulted in (R)-limonene epoxidation with adequate selectivity but low activity and fast deactivation. Immobilization of HPA on aminopropylsilicas via their protonation produced active catalysts. However, their residual acidity induced undesirable hydrolysis of acid-sensitive epoxides to diols, which poisoned the active sites.

Acknowledgments

This work was supported in part by NATO (grant RiG 98155 to T.K.). The authors thank L. Salles for help with HPA preparation, the epoxidation tests, and discussion of the results.

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