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Heterogeneous tungsten-based catalysts for the epoxidation of bulky olefins

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Abstract

This paper discusses the design of different W and PW heterogeneous catalysts. The first part focuses on the electrostatic immobilization of those species on organic resins. In the second part, some new silica materials are synthesized as carrier materials for PW species. Both electrostatic immobilization and covalent linking of the species on the modified silica materials are discussed. Besides a thorough spectroscopic study (FT-IR, Raman, NMR, TGA and EPMA), the catalytic properties of the designed catalysts are evaluated for the epoxidation of a variety of bulky olefins. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Tungsten catalysis; Hydrogen peroxide; Epoxidation; MCM-41 materials; Heterogeneous catalysis

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1. Introduction

Olefin epoxidation is a major industrial reaction for the production of a broad variety of chemicals. The oxirane group is highly reactive which makes epoxides an essential group of organic intermediates [1]. Moreover, some of these epoxides play an important role in the context of biological activity and are therefore very valuable as precursors for the development of drugs, agrochemicals and food additives [2]. Consequently, there is a growing interest in the synthesis of fine chemicals via this versatile reaction.

The use of hydrogen peroxide in oxidation chemistry has steadily grown during recent years. There are two important reasons for this. First, with the exception of O_2, H_2O_2 contains the largest amount of active oxygen among the known oxidants and second, water is the only by-product of the epoxidation. This makes H_2O_2 the ideal oxidant from an economic point of view as well as for environmental reasons.

Currently, rhenium and tungsten-based compounds are the best catalysts for epoxidation using aqueous H_2O_2 [3]. In the case of tungsten chemistry, the most significant developments were made in the 1980s by the groups of Venturello et al. [4] and Ishii et al. [5]. They used phosphotungsten-based catalysts in biphasic reaction media for the epoxidation of apolar olefins. The use of chlorinated solvents is however necessary for obtaining high yields and selectivities. Recently, Noyori and coworkers [6] developed a halide-free method for olefin epoxidation with W and H_2O_2. In this case, an acidic reaction medium, addition of an alkylammonium hydrogen sulfate and an (α-aminoalkyl)-phosphonic acid are necessary to achieve high rates.

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Although the Venturello–Ishii and the Noyori catalysts are remarkably efficient, they share a common drawback: separation and reuse of the catalyst are extremely difficult. For that reason, this work aims at developing efficient heterogeneous epoxidation catalysts with tungsten as the transition metal. As supports for the W, both macroreticular resins and siliceous materials are used. Firstly, some typical negatively charged W and PW species are heterogenized via ion exchange. Both commercially available organic materials and a newly synthesized modified silica support are used as ion exchangers. The second part is devoted to the synthesis of a heterogeneous PW catalyst with the transition metal coordinated on covalently immobilized phosphoramide groups. The value of these strategies is eventually tested in catalytic reactions.

2. Experimental

2.1. General techniques

IR spectra were obtained with a Nicolet model 730 FT-IR spectrometer using 2–4% (w/w) KBr pellets. Raman spectra were recorded on a BRUKER FRA106/S spectrometer. All spectra were recorded with a laser power of 100 mW. The laser had a wavelength of 1064 nm. ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker AMX-300. ^{31}P chemical shifts are expressed in ppm relative to an 85% H_3PO_4 solution. The MCM-41 samples were characterized by X-ray powder diffraction using a Siemens D 5000 automatic diffractometer.

Electron probe microanalysis (EPMA) measurements were performed on a JEOL JXA scanning electron microscope. This apparatus was equipped with a Si–Li energy dispersive detector (EDS). The EDS system was connected to a computerized data processing unit (Series II, Tracor Northern). Quantitative chemical analysis was performed for Si, W and P.

Thermogravimetric measurements were made on a SETARAM92 apparatus using a 25/75 atmosphere of O_2/He. The temperature was increased to 800°C using a rate of 5°C/min. Inductively coupled plasma (ICP) measurements were performed on a Perkin-Elmer 3000 apparatus. Organic products were identified by gas chromatography using a Hewlett-Packard 5890 Series II chromatograph. This instrument was equipped with a $50\,\text{m}\times0.32\,\text{mm}$ capillary column (CP-Sil-5 CB, Chrompack) and an FID detector linked to a HP 3396 Series II electronic integrator.

2.2. Materials

All solvents were of commercial origin and were used as received. High purity *cis*-cyclooctene, norbornene, cyclohexene and geraniol were purchased from Aldrich and used without further purification. Hydrogen peroxide (35% (w/w) aqueous solution) was obtained from Acros and used in all experiments. Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) and tungstic acid ($WO_3{\cdot}H_2O$) were supplied by Acros. Phosphorous oxychloride ($POCl_3$) (Aldrich) and 2,4,6-collidine (Acros) were purchased and used as received. The amberlite IRA-900 (anion exchange capacity (AEC)=4.2 meq/g) was obtained from Ventron and Ludox AS-40 (40% (w/w) colloidal silica in water) was supplied by Dupont de Nemours. All synthesized catalysts were dried under a nitrogen flow and stored in inert conditions before use.

2.3. Catalyst synthesis

2.3.1. W and PW species exchanged on organic resins

2.3.1.1. $WO_4{}^{2-}$ *exchanged on amberlite IRA-900.* 8.75 mmol of Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) was dissolved in 10 ml of distilled water. To this solution, 1 g amberlite IRA-900 (in chloride form) was added and the mixture was stirred for 16 h at room temperature. Next, the resin was filtered off and washed consecutively with water, water–acetone (1/1) and acetone.

2.3.1.2. $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ *exchanged on amberlite IRA-900.* $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ ($= W_2O_{11}(H_2O)_2{}^{2-}$) was prepared following the method of Campbell et al. [7]. Five millimoles of $Na_2WO_4{\cdot}2H_2O$ were dissolved in 10 ml of distilled water. To this solution, 60 mmol of H_2O_2 (35% (w/w) aqueous solution) were added. The resulting yellow solution was acidified to a pH of 2.5 with 0.1 N HCl. This resulted in a colorless solution to which 1 g of amberlite was added. The suspension was stirred for 16 h at room temperature. Afterwards, the obtained material was washed consecutively with water, water–acetone (1/1) and acetone and dried under a nitrogen flow.

2.3.1.3. $[PO_4[WO(O_2)_2]_4((n\text{-}Bu)_4N)_3$ *(isolated) exchanged on amberlite IRA-900.* $[PO_4[WO(O_2)_2]_4]((n\text{-}Bu)_4N)_3$ (Venturello's complex=$PW_4O_{24}((n\text{-}Bu)_4N)_3$) was prepared according to literature procedures [8]. To a solution of 0.46 mmol isolated $[PO_4[WO(O_2)_2]_4]((n\text{-}Bu)_4N)_3$ in acetone (3 ml) were added 1 ml of H_2O_2 (35% (w/w) aqueous solution) and 1 g of amberlite, and the mixture was stirred for 16 h at room temperature. After separation of the resin, the material obtained was treated consecutively with water, water–acetone (1/1) and acetone.

2.3.2. MCM-41 based catalysts

Scheme 1 shows the general synthesis strategies followed in this work. Siliceous MCM-41 was prepared according to synthesis procedures similar to those reported by Beck et al. [9].

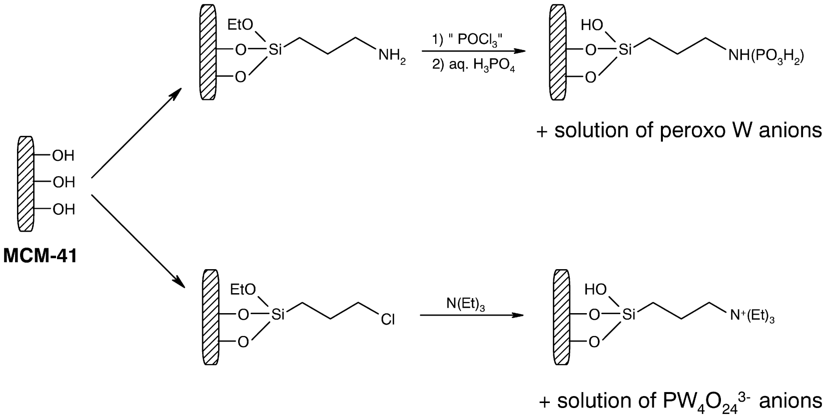
2.3.2.1. Synthesis of an MCM-41 with grafted quaternary ammonium groups (MCM-N^+). Firstly, the freshly prepared MCM-41 material was treated with 3-chloropropyltriethoxysilane. In the second step, ammonium groups were obtained by reaction of the chloropropyl-functionalized MCM-41 (MCM-Cl) with triethylamine.

Before silylation of the MCM-41 surface, the material was dried at 220°C for 16 h under vacuum. Next, 2 g of the vacuum-dried support was reacted with 9 mmol of 3-chloropropyltriethoxysilane in anhydrous toluene (reflux, 3 h). Excess of silylating agent was removed by a lengthy soxhlet extraction using a diethyl ether–dichloromethane mixture (1/1). The resulting material was then dried for 12 h at 60°C.

One gram of MCM-Cl was degassed at 110°C for 16 h under vacuum. After cooling down to ambient temperature, 20 ml of anhydrous toluene was added and the silica was treated with an excess of triethylamine (20 mmol). The mixture was refluxed for 24 h and afterwards, the resulting quaternary ammonium MCM was purified in a soxhlet extraction (Et_2O–CH_2Cl_2 (1/1)).

The preparation of the "active catalyst" was based on the original Venturello procedure [4]. Ten millimoles of tungstic acid ($WO_3{\cdot}H_2O$) and 7 ml of a 35% aqueous H_2O_2 solution were heated for 60 min at 50°C. After cooling down to room temperature, the mixture was centrifugated and 1 ml of H_3PO_4 (85% (w/w) solution), 21.5 ml of distilled H_2O and 8 ml of acetone were added to the supernatant. To 0.75 ml of this solution, 0.1 g of MCM-N^+ and 1 ml of acetone were added. After 16 h of stirring at ambient temperature, the catalyst was filtered off and washed consecutively with water, water–acetone (1/1) and acetone.

2.3.2.2. Synthesis of phosphoramide-based MCM-41 epoxidation catalyst (MCM-$NH(PO_3H_2)$). In the



Scheme 1. Synthesis of MCM-41 based catalyst precursors.

first step, 2 g of MCM-41 was treated with 9 mmol of 3-aminopropyltriethoxysilane (cf. Scheme 1). For the silylation reaction as well as for the consecutive washing, the same conditions were used as for the chloropropyl MCM-41.

Secondly, 30 ml of a $POCl_3$ solution (50 mM in acetonitrile) and 30 ml of a 2,4,6-collidine solution (50 mM in acetonitrile) were consecutively added to 0.5 g of the dried MCM-NH_2 [10]. The mixture was stirred for 24 h at room temperature, after which the resulting solid was firstly washed with water to remove the chloride salts, and secondly in a soxhlet extraction (Et_2O–CH_2Cl_2 (1/1)).

Finally, the phosphoramide-functionalized MCM-41 (MCM-NH(PO_3H_2)) was subjected to an acidic washing with a dilute aqueous acid solution (0.1 N H_3PO_4) in order to have the phosphoramide groups in fully hydrolyzed form.

For the preparation of the "active catalyst" (MCM-NH(PO_3H_2)–W–peroxo), 10 mmol of tungstic acid ($WO_3 \cdot H_2O$) was added to 7 ml of a 35% aqueous H_2O_2 solution. The mixture was heated for 60 min at 50°C. Next, after cooling down to room temperature, the mixture was centrifugated. To 2.5 ml of the supernatant were added 8 ml of acetone, 1 ml of H_2O_2 (35% (w/w) in water) and finally 0.25 g of MCM-NH(PO_3H_2). This mixture was stirred for 24 h at 20°C. The catalyst was then isolated and washed six times with a 1/1 mixture of acetone/H_2O_2 (35% (w/w) in water) and finally three times with acetone.

2.4. Reaction setup

All reactions were carried out in glass vessels of about 7 ml. This recipient was charged with the desired amounts of catalyst, substrate, oxidant and solvent. The reaction mixture was stirred magnetically by the use of a stirring flea. Control of the temperature was achieved in an oil bath using a thermocouple. At regular intervals, the formation of epoxide was followed by removing aliquots with a syringe and analyzing them by gas chromatography or ^{1}H-NMR.

To follow the evolution of the oxidant consumption during reaction, the amount of H_2O_2 in the reaction mixture was determined by cerimetry [11]. 0.2 ml of the reaction mixture was diluted in 3 ml of distilled water and acidified with 0.5 ml of HCl_{conc}. The resulting mixture was then titrated with a 0.1 N $Ce(SO_4)_2$ solution.

To check the heterogeneous character of the used catalysts, filtration experiments were performed. Firstly, a freshly prepared catalyst was used for a new reaction until substrate conversion reached approximately 50%. The catalyst was then separated from the hot reaction mixture (centrifugation, filtration) and reused in a new reaction for an equal reaction time as in the first reaction. Moreover, the reaction filtrate from the first experiment was kept at reaction temperature for another 24 h. Comparison of the conversions of these three reactions gives a reliable idea of the heterogeneity of the catalyst.

3. Results and discussion

3.1. Anion-exchanged catalysts

3.1.1. Epoxidation with W and PW-exchanged amberlites

In this work, different anionic W and PW species were exchanged on a macroreticular styrene–divinylbenzene polymer. This material is commercially known as amberlite IRA-900 and has –$N(CH_3)_3^+$ functional groups. It consists of spherically shaped particles with diameters of about 0.5 mm and is available in the chloride form. The AEC of this ion exchanger is 4.2 meq/g of resin.

3.2. Characterization of catalysts used

3.2.1. Loading of the prepared catalysts

Tungsten loadings of the synthesized amberlite catalysts were determined via an EPMA. As the amount of WO_4^{2-} exchanged on amberlite IRA-900 corresponded to four times the AEC, the chloride was fully displaced by the tungstate. This was checked and proved via an EPMA.

When $W_2O_{11}(H_2O)_2^{2-}$ and $PW_4O_{24}((n\text{-Bu})_4N)_3$ were exchanged on the amberlite material, approximately 50% of the available AEC was used as determined by EPMA. This results in loadings of, respectively, 1.05 mmol of the dinuclear W complex and 0.71 mmol of the tetranuclear complex withheld per gram of amberlite.

Table 1
IR and Raman data of amberlite catalysts and reference data for different (P)–W–peroxo species [7,8,17]

	P=O	W=O	O–O	$W(O_2)_{sym,asym}$	Other bands
$PW_4O_{24}^{3-}$ [8]					
IR (solid)	1086, 1055	972	855, 845	595, 523	730, 650, 575, 550
Raman (in CH_3CN)		981	861	593, 534	750, 653, 577, 229, 299, 257
Raman (in dilute H_2O_2)		962	853	627, 562	326
$HPW_2O_{14}^{2-}$ [17]					
IR (solid)	1018, 995	962	843	569, 517	646
Raman	–	–	–	–	–
$W_2O_{11}^{2-}$ [7]					
IR (solid)		964	850	617, 554	835, 775
Raman (in H_2O)		962	853	619, 556	326
Amberlite/W_2O_{11}					
IR		955	855	610, 548	770
Amberlite/PW_4O_{24}					
IR	1069	931	860	591, 541	
Raman	1050	961	853	627, 563	323
MCM-NH(PO_3H_2)–W–peroxo					
IR			835	622, 544	1233 (phosphoramide)
Raman		956	852	620, 565	795, 323

3.2.2. *IR and Raman spectroscopy*

In order to verify that the active peroxo groups remain intact after ion exchange, vibrational spectra were recorded for amberlites exchanged with $W_2O_{11}^{2-}$ and $PW_4O_{24}^{3-}$. In many cases, IR spectra are sufficient. However, when structural vibrations of the supporting material interfered with the typical peroxo vibrations, Raman spectra were recorded (Table 1).

A comparison between the measured IR vibrations for the $W_2O_{11}(H_2O)_2^{2-}$-exchanged amberlite and the reported spectra of the complex as such shows a satisfactory agreement (Table 1, [7]). The small divergence with literature values is most likely an influence of the polymeric support material.

Furthermore, a good accordance can be noticed when comparing the reported IR absorption bands of isolated $PW_4O_{24}^{3-}$ species and the $PW_4O_{24}^{3-}$-exchanged amberlite (Table 1, [8]). Nevertheless, some displacements of the bands can be observed for the amberlite catalyst probably due to effects of the catalyst support. For that reason, Raman measurements were performed on the amberlite/PW_4O_{24} material (Table 1). The observed peaks can be assigned to P=O (1050 cm^{-1}), W=O (961 cm^{-1}), O–O (853 cm^{-1}), W–O–O_{asym} (628 cm^{-1}), W–O–O_{sym} (563 cm^{-1}) and W–(OH_2) (323 cm^{-1}) vibrations. These wavenumbers are highly similar to literature data for the $PW_4O_{24}^{3-}$ anion measured in dilute H_2O_2 (Table 1, [8]).

All these spectroscopic results reveal that exchange of the different W and PW species in acetone, with addition of some H_2O_2, leads to intact peroxo species on the polymeric support.

3.3. *Catalytic results*

Some typical negatively charged mono- and polynuclear tungsten species were exchanged on amberlite IRA-900 and their catalytic properties were explored for the epoxidation of *cis*-cyclooctene. The most significant results are summarized in Table 2.

When using the mononuclear tungstate anion as the active metal center, only a negligible yield of the epoxide was obtained (entry 1). Moreover, this catalyst did not consume the oxidant in a very efficient way and some leaching was observed.

Dinuclear tungsten species are known to have more active oxidizing moieties than their mononuclear analogues [7]. The catalyst support was exchanged with

Table 2
Epoxidation of *cis*-cyclooctene with amberlite-based catalysts[a]

Entry	Catalyst	t (h)	Conversion (%)	S_{epox} (%)[b]	E_{ox} (%)[c]	Leaching (%)[d]
1	Amberlite/WO_4^{2-}	16	2	>90	55	6
2	Amberlite/$[W_2O_3(O_2)_4(H_2O)_2]^{2-}$	16	19	>90	17	7
3	Amberlite/$\{PO_4[WO(O_2)_2]_4\}^{3-}$	16	85	>95	95	n.d.[e]
4	Blank	24	0	–	–	–

[a] Reaction conditions: 3.15 mmol of cyclooctene in 5 ml acetonitrile, 3.78 mmol H_2O_2 (35% (w/w) in water), 0.0315 mmol W on amberlite IRA-900, 50°C.

[b] Selectivity towards epoxide production; by-product is diol.

[c] E_{ox} is the oxidant efficiency (mole of epoxide produced per mole of H_2O_2 consumed).

[d] Measured with ICP analysis and checked by filtration experiments.

[e] n.d.=no W detected.

the dinuclear anion. This catalyst showed higher activity, but conversions still remained low (entry 2). The consumption of the oxidant was far less efficient than in the previous case and this catalyst also showed some leaching.

In homogeneous catalysis, PW associations are known to be powerful and stable epoxidation catalysts [4]. For that reason, the tetranuclear Venturello complex $[PO_4[WO(O_2)_2]_4]((n\text{-Bu})_4N)_3$ was exchanged on the amberlite support. In comparison to previous cases, this catalyst showed a noteworthily higher activity for the epoxidation of *cis*-cyclooctene (entry 3). Furthermore, the H_2O_2 was consumed in a remarkably efficient way. Another important fact is the heterogeneous character of the used catalyst. Filtration experiments proved that leaching was avoided and that the catalyst could be reused several times without any loss of activity. These results were confirmed by ICP analysis; no traces of tungsten could be detected in the reaction mixture.

The results reveal that the catalytic performances of the PW associations are superior to those of the tungsten alone. The PW catalyst shows a good activity for the epoxidation of *cis*-cyclooctene and also consumes the oxidant in a highly efficient way, even at nearly stoichiometric olefin to peroxide ratios. Moreover, these PW complexes seem to be more stable and easily retained on the anion exchange material in comparison to tungsten species. The interaction between the soft $\{PO_4[WO(O_2)_2]_4\}^{3-}$ anion and the soft N^+ cation of the carrier seems to be strong enough to prevent leaching of the PW species under the applied reaction conditions.

For the above-mentioned reasons, it is evident that the rest of this work is focussed on alternative routes for the immobilization of these catalytically superior PW species.

3.3.1. Epoxidation of cis-cyclooctene by use of a PW-exchanged MCM-41 material

Although the PW-exchanged amberlite material provides good catalytic properties for the epoxidation of *cis*-cyclooctene, it is known that polymeric supports lack sufficient mechanical and thermal stability over longer reaction times [12]. For that reason, attention was focussed on the development of a catalyst similar to the ones mentioned above, but with an inorganic anion exchanger. Inorganic materials show better mechanical and physicochemical stability even when used at relatively high reaction temperatures.

In this work, a mesoporous MCM-41 was used as starting material. This M415 type material has uniform, hexagonally ordered mesopores with tunable dimensions and a large volume in these pores [9]. It is an ideal starting material for the design of new solids with adjustable physicochemical properties. Not surprisingly, the synthesis, characterization and potential uses of these silicates have attracted considerable interest in recent years [13,14].

In order to prepare a positively charged MCM-41, a quaternary ammonium functionality was introduced by reacting the freshly prepared MCM-41 material with 3-chloropropyltriethoxysilane. Thermogravimetric analysis revealed a loading of 2.7 mmol of chloropropyl groups per gram of MCM-41. Treatment of the resulting MCM-Cl material with an excess of triethyl-

Table 3
Epoxidation of *cis*-cyclooctene by use of PW-exchanged MCM-41 materials[a]

Entry	Catalyst	t (h)	Conversion (%)	S_{epox} (%)[c]	E_{ox} (%)[d]
1[b]	$MCM\text{-}N^+/\{PO_4[WO(O_2)_2]_4\}^{3-}$	16	20	>95	90
2	Blank	24	0	–	–

[a] Reaction conditions: 3.15 mmol of cyclooctene in 5 ml acetonitrile, 3.78 mmol H_2O_2 (35% (w/w) in water), ∼0.0315 mmol W on MCM-N$^+$, 50°C.

[b] Leaching was less than 1 ppm W, as measured with ICP analysis and checked by filtration experiments.

[c] Selectivity towards epoxide production; by-product is diol.

[d] E_{ox} is the oxidant efficiency (mole of epoxide produced per mole of H_2O_2 consumed).

amine gave an AEC of 0.5 meq/g as determined by use of a standardized K_2CrO_4 solution.

This solid was exchanged with the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ anion to give the active catalyst (Scheme 1). The most significant catalytic results are given in Table 3.

The $MCM\text{-}N^+/\{PO_4[WO(O_2)_2]_4\}^{3-}$ catalyst showed a considerable conversion of the alkene in combination with a very high epoxide selectivity (entry 1). However, the activity was lower than in the case of the amberlite material. This is not surprising as the AEC of the modified MCM material (0.5 meq/g for MCM-N$^+$) is about eight times lower than that of the amberlite. This leads to lower W loadings. Moreover, it is doubtful whether the entire pore volume of the modified MCM-41 is equally accessible for the PW complexes and for the reactant molecules. It is indeed known that surface modification of an MCM can reduce the average diameter of the mesopores, even into the microporous region. Nevertheless, the oxidant was consumed in an extremely efficient manner and the epoxidation reaction occurred in a heterogeneous way.

3.4. PW species on covalently linked phosphoramide groups

Instead of exchanging an isolated Venturello complex ($[PO_4[WO(O_2)_2]_4]((n\text{-}Bu)_4N)_3$) on a charged support, we also developed a catalyst in which the association between P and W is performed on the surface itself. For that purpose, a phosphoramide-grafted MCM material was developed in the following way (Scheme 1). Firstly, the silanols of MCM-41 were used to functionalize the support via reaction with alkoxysilyl amino compounds. Once anchored to the channel walls, the amino groups were reacted with $POCl_3$ in order to generate P–N covalent bonds. Finally, this material was treated with H_2O_2 and H_2WO_4 to give the epoxidation catalyst.

3.5. Characterization of the materials used

As for the amberlite catalysts, it is important to verify the presence of tungsten species and active peroxo groups on the catalyst material. For that reason, the catalyst underwent a vibrational study (IR and Raman). Moreover, solid state ^{31}P-MAS NMR measurements were performed on both the $MCM\text{-}NH(PO_3H_2)$ precursor and on the active catalyst to get a deeper insight in the catalyst composition. Information about the loading with the different surface groups was obtained by thermogravimetrical analysis (TGA) and EPMA.

3.5.1. TGA and EPMA

TGA and EPMA measurements were used to get a better insight into the loading of the phosphoramide-based catalyst. Thermogravimetry reveals that approximately 2 mmol of aminogroups are immobilized per gram of MCM-41. After treatment with $POCl_3$, the phosphoramide material obtained contains 0.66 mmol of phosphorous per gram silica, as determined by EPMA measurements. Thus, it seems that only part of the amine groups are phosphorylated. During the acidic washing, these unreacted $-NH_2$ groups are in the protonated form.

Furthermore, an EPMA study of the active catalyst material shows that the tungsten content is about 1.5 mmol/g catalyst. This suggests that the P/W ratio is about 1/2.3, whereas the Venturello anion ($\{PO_4[WO(O_2)_2]_4\}^{3-}$) has a typical ratio of 1/4.

3.5.2. IR and Raman spectroscopy

When comparing the IR spectra of the amine and the phosphoramide-functionalized MCM-41 materials (MCM-NH_2 and MCM-$NH(PO_3H_2)$), an additional band can be observed for the phosphoramide at 1233 cm^{-1}. This band can be assigned to a P=O stretching vibration of the phosphoramide moiety.

More interesting information can be obtained when studying the IR spectrum of the active epoxidation catalyst (MCM-$NH(PO_3H_2)$–W–peroxo). The most significant vibrations are summarized in Table 1. The typical peroxo vibration can be observed at about 835 cm^{-1} and the bands at 622 and 544 cm^{-1} can be assigned to asymmetric and symmetric tungsten peroxo vibrations. Due to overlap with the silica structure vibrations, however, the W=O band was not detectable. For that reason, we also performed Raman measurements on the active catalyst material (Fig. 1 and Table 1).

When comparing the spectrum of the active catalyst with that of the MCM-$NH(PO_3H_2)$ precursor, some new and distinct peaks are observable (956, 852, 795, 565 and 323 cm^{-1}). These vibrations can be assigned to W=O (956 cm^{-1}), O–O (852 cm^{-1}), W–O–O_{sym} (565 cm^{-1}) and W–(OH_2) (323 cm^{-1}) vibrations. These wavenumbers are very similar to literature data for $PW_4O_{24}^{3-}$ (in dilute H_2O_2) and $W_2O_{11}^{2-}$ (in H_2O) in Table 1 [7,8]. The small peak at 620 cm^{-1} is probably the asymmetric W–O–O vibration. One can conclude that IR and Raman spectroscopy give clear evidence for the existence of W–peroxo species on the synthesized catalyst material.

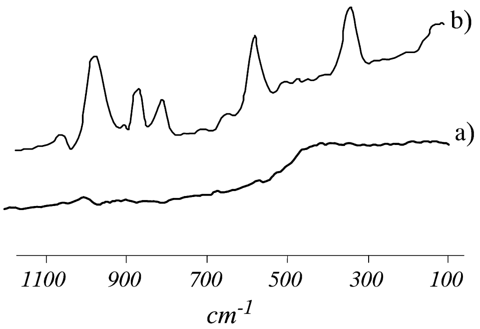


Fig. 1. Raman spectra of MCM-$NH(PO_3H_2)$ (a) and the active catalyst material (b).

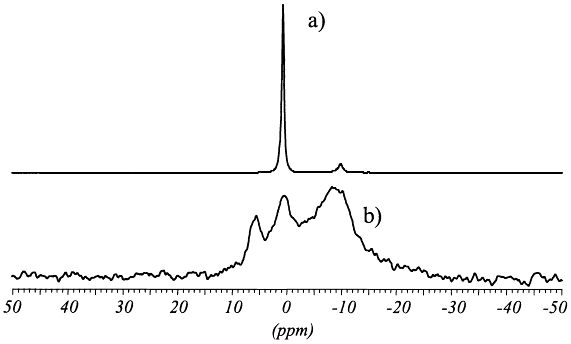


Fig. 2. ^{31}P-MAS NMR spectra of MCM-$NH(PO_3H_2)$ (a) and active catalyst (b).

3.5.3. Solid state ^{31}P-MAS NMR spectroscopy

In the solid state ^{31}P-NMR spectrum of the phosphoramide-functionalized MCM-41 (Fig. 2, spectrum a), one intense peak is observed at about 0 ppm. This value is consistent with phosphorous in fully protonated –NH–PO_3H_2 groups [15]. Importantly, only one type of phosphorous is detected in the synthesized material indicating that the $POCl_3$ reacts cleanly with the immobilized aminopropyl groups.

Addition of peroxo–W complexes leads to the spectrum of Fig. 2b with at least two new absorptions. This proves that the immobilized –PO_3H_2 groups react with the peroxo–W complexes with formation of P–O–W bonds. It is known that the ^{31}P shifts in PW complexes depend on the solvent, on the number of W atoms bound to P, and on the number of peroxo

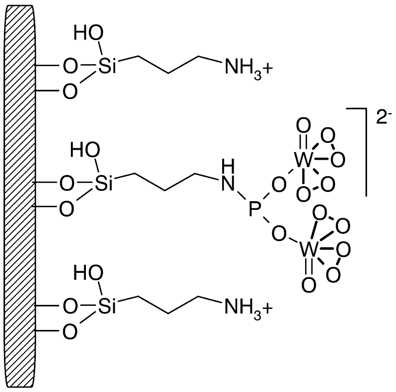


Fig. 3. Possible representation of the active catalyst with covalently anchored phosphoramide groups.

Table 4
Epoxidation of olefins by use of tungsten–phosphoramide-grafted MCM-41 catalysts[a]

Entry	Olefin	t (h)	Conversion (%)	S_{epox} (%)[c]	By-products[d]	E_{ox} (%)[e]
1[b]	*cis*-Cyclooctene	12	70	>95	Diol	>90
2[f]	Blank	24	0	–	–	–
3	Norbornene	20	64	93	Diol	>85
4	Geraniol	6	>99	95 (2, 3)	6,7-Epoxide	>85
5	Cyclohexene	20	30	60	Diol	>80
6[g]	Cyclohexene	20	28	85	Diol	>80

[a] Reaction conditions: 1.26 mmol of olefin in 4 ml acetonitrile, 1.89 mmol H_2O_2 (35% (w/w) in water), 0.01 g catalyst (7 wt.% on substrate base), 50°C.

[b] Leaching was about 2 ppm, as measured with ICP analysis, EPMA and checked by filtration experiments.

[c] Selectivity towards epoxide production.

[d] Major by-product of the epoxidation reaction.

[e] E_{ox} is the oxidant efficiency (mole of epoxide produced per mole of H_2O_2 consumed).

[f] MCM-NH(PO_3H_2) was used as catalyst material without added W, substrate: *cis*-cyclooctene.

[g] 0.252 mmol of pyridine was added.

ligands on these W atoms. Moreover, for isolated PW complexes such as $[PO_4[WO(O_2)_2]_4]((n\text{-Bu})_4N)_3$, ion pairing with the quaternary ammonium ion has a particularly strong influence on the ^{31}P shifts [8,16,17]. In the present heterogeneous catalyst, the negative charge of immobilized PW complexes may to some extent be balanced by unreacted, protonated aminopropyl groups close to the PW complex. Summarizing, while the presence of different types of immobilized PW complexes may give rise to overlapping lines, the ^{31}P spectrum gives clear evidence that peroxo–W groups are bound on immobilized P groups.

A possible active site of the catalyst is drawn in Fig. 3. The main elements that support this representation are: (i) one-third of the NH_2 groups are phosphorylated, (ii) between 2 and 3 W atoms are retained on the catalyst per P, and (iii) vibrational spectroscopy proves that the W atoms have coordinated peroxo ligands.

3.6. Catalytic results

For all reactions, 7 wt.% of active catalyst was used with a 1/1.5 ratio of olefin to oxidant. The most significant catalytic results are summarized in Table 4.

The catalytic epoxidation of bulky, cyclic olefins seemed to be very easy with the synthesized catalyst material. *cis*-Cyclooctene was converted for more than 70% after only 12 h of reaction time and this with a high selectivity towards epoxide formation (entry 1). Moreover, the oxidant was consumed in a surprisingly efficient way. Nearly the same catalytic results were obtained when using norbornene as the substrate for the epoxidation (entry 3). In addition, tungsten leaching could be limited to less than 2% of the total amount of tungsten present in the catalyst.

Another interesting reaction is the epoxidation of geraniol (entry 4). As can be derived from Table 4, the reaction was completed after only 6 h of reaction time. An interesting fact in this case is the nearly exclusive formation of the 2,3-epoxide. This behavior is typical for tungsten chemistry, where the OH function is known to coordinate on the transition metal center and olefin epoxidation occurs at the allylic alcohol. Also in this case, the efficiency of the oxidant use was high.

When a more acid sensitive epoxide was formed, like in the case of the cyclohexene epoxide, some diol formation was observed (entry 5). However, addition of an organic Lewis base (pyridine, entry 6) led to a significant reduction of diol formation (85% selectivity towards epoxide), maintaining nearly the same catalyst activity. Furthermore, oxidant consumption was very efficient.

4. Conclusions

In this work, several tungsten and phosphotungsten species were evaluated as epoxidation catalysts. PW complexes are by far the most active species and are therefore excellent candidates for immobilization on a catalyst support. Instead of using organic supports, two newly synthesized hybrid silicas were applied as supporting material. In the first case, the negatively charged PW complexes were immobilized on a modified MCM-41 by ion exchange. More interesting results were obtained when the tungsten species were immobilized on a covalently linked phosphoramide group. This material is capable of epoxidizing a broad variety of olefins in a heterogeneous way and holds great promise for the synthesis of valuable fine chemicals.

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