

Silica tethered with poly(ethylene and/propylene) oxide as supports for polyoxometalates in catalytic oxidation

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Abstract

Use of the sol–gel technique has allowed the preparation of silicates with polyfunctionalized surfaces. In this way, silicates containing combinations of hydrophilic poly(ethylene oxide) (PEO), hydrophobic poly(propylene oxide) (PPO) and cationic quaternary ammonium (Q^+) groups were prepared. These silicates coupled with polyoxometalates led to active catalytic assemblies. In one application, $H_5PV_2Mo_{10}O_{40}$ was complexed to PEO–SiO₂ and used to catalyze the oxydehydrogenation of dihydroanthracene with improved activity and selectivity compared to the non-supported catalyst. Recycle of the assembly was possible. In a further use, $[ZnWm_2(ZnW_9O_{34})_2]^{12-}$, bound by a Q^+ moiety to the silicate surface modified also with polyethers formed an assembly catalytically active, with excellent recycle for the epoxidation of alkenes with aqueous 30% H₂O₂. A silicate with a hydrophobic (PPO)/hydrophilic (PEO) balance showed the highest activity due to the optimal contact of the apolar hydrocarbon and the aqueous oxidant. Dispersion of the silicate in a solvent depended much on the polyether tether. Hydrophilic PEO–SiO₂ formed a homogeneous gel in water but was not dispersed in chloroform. For hydrophobic PPO–SiO₂, the opposite was observed. Maximal dispersion together with ease of recovery was possible with intermediate 10% PEO, 10% PPO–SiO₂. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Sol–gel; ORMOSIL; Polyoxometalate; Oxidation; Polyether

1. Introduction

The concept of heterogenization of homogeneous catalysts is still an important goal for chemists interested in catalysis designed to take advantage of the many possibilities of molecular design and optimization of reaction selectivity inherent to the use of homogeneous catalysts together with the practical advantages of simple post-reaction work-up indigenous to heteroge-

neous catalysis. Over the years, many ideas and methods have been considered for heterogenization of homogeneous catalysts and these are still studiously being explored [1,2]. One heterogenization technique is known as supported liquid (aqueous) phase catalysis (SLPC) [3,4], wherein catalysts, dissolved in solvents, are strongly adsorbed unto supports such as silica. In such systems, considering the liquid state of the catalyst containing phase, contact with a reactant in a fluid phase is maximized. Typically, hydrophilic solvents such as water, ethylene glycol and even polyethylene oxide (PEO) have been used [5–10]. Recently, we reported on our pre-

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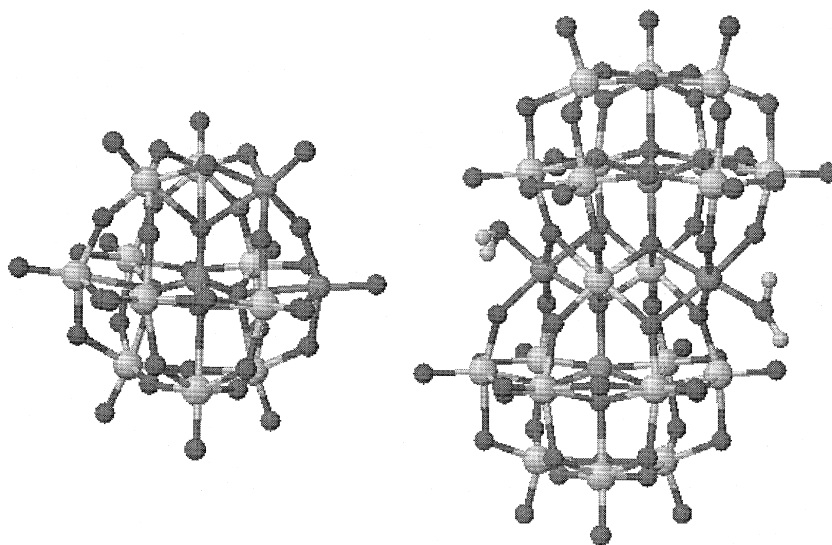
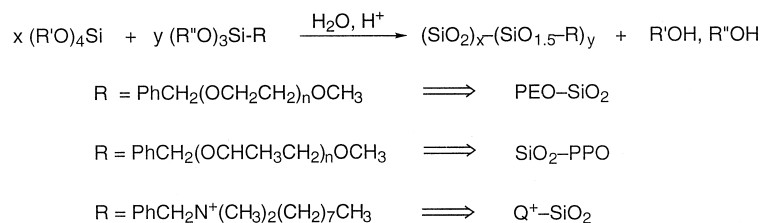


Fig. 1. Structure of the $PV_2Mo_{10}O_{40}^{5-}$ (left) and $[ZnWMn^{II}(ZnW_9O_{34})_2]^{12-}$ (right) polyanions.

liminary research describing an extension of the SLPC method used to immobilize oxidation catalysts onto silica supports [11,12]. In our newer system, a solvent, poly(ethylene and/or propylene) oxide was covalently anchored to a silica surface. This tethering of poly(ethylene and/or propylene) oxide onto silica supports has the perceived additional advantages of enabling the anchoring of both hydrophilic and hydrophobic solvents, and of preventing leaching of the solvent phase and the associated catalyst from the heterogeneous support. This anchoring of the solvent is in actuality somewhat analogous to the use of bonded phase columns in gas chromatography in place of simple physically adsorbed phases used previously.

Since a major focus of our research group over the last decade has been to develop polyoxometalates as stable catalysts for oxidation with environmentally friendly oxidants [13–15], we have sought to test the use of soluble polyoxometalates in a heterogenized reaction system. Presently, we have concentrated on two catalysts, Fig. 1, the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate or heteropoly acid of the Keggin structure useful for oxidative dehydrogenation reactions [16–18] and the $[ZnWMn^{II}(ZnW_9O_{34})_2]^{12-}$ transition metal substituted polyoxometalate which is effective for hydrogen peroxide activation and epoxidation of alkenes [19–21]. Since polyoxometalates are anionic species, their attachment to silica can also be



Scheme 1. The preparation of functionalized (tethered) silica.

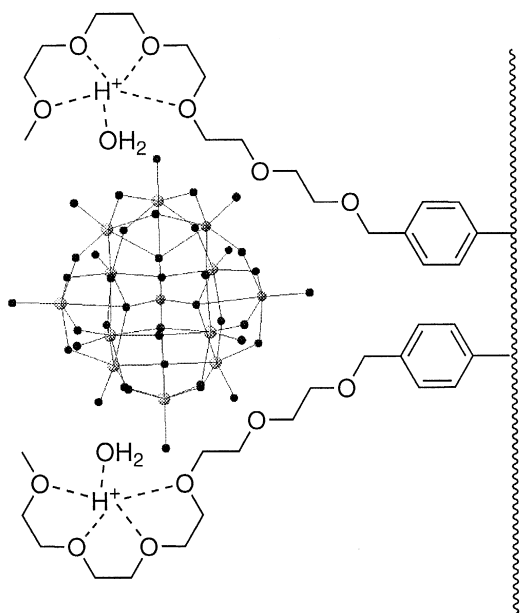


Fig. 2. An illustration of $H_5PV_2Mo_{10}O_{40}$ complexed by PEO- SiO_2 .

achieved by use of silica functionalized with quaternary ammonium salts [22].

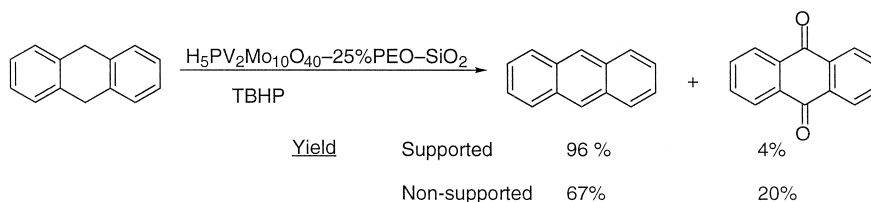
2. Results and discussion

The general approach used in this research to prepare functionalized silica with appropriate tethers has been to use the sol-gel synthesis [23] with alkoxy silanes as reagents, Scheme 1. The use of a non-hydrolysable substituent (R) leads to formation of the desired functionalized silica. Three substituents or combinations thereof

were contemplated: (a) PEO, known as a hydrophilic polyether, (b) poly(propylene oxide) (PPO), known as a hydrophobic polyether and (c) a quaternary ammonium salt which renders the silica cationic and attractive for ion-pair binding of polyoxometalates.

The first example of the utility of the polyoxometalate-functionalized silica paradigm was to take advantage of the known complexation of Keggin type heteropoly acids with diethylether [24] and other similar polyethylethers [25] in a system where organic substrate and oxidant are soluble in the same organic phase. In this way, the *strong* complexation [25] of an acidic heteropoly acid oxidation catalyst, $H_5PV_2Mo_{10}O_{40}$, to a PEO functionalized silica could be considered, Fig. 2. The oxidative dehydrogenation in toluene of dihydroanthracene to anthracene with *t*-butylhydroperoxide as oxidant and 25% PEO- SiO_2 containing $H_5PV_2Mo_{10}O_{40}$, Scheme 2, showed that the supported catalytic assembly was superior to the control, non-supported reaction in terms of both catalytic activity and selectivity. At the completion of the reaction, the catalytic assembly was filtered off, washed and dried. Recycle of the catalytic assembly yielded quantitative conversions and selectivities to anthracene of 96, ~ 100, 97 and 97% for four consecutive runs with out any evidence of loss of catalytic species (UV-Vis and AA).

A considerably more complex experimental situation is encountered when a hydrocarbon is to be reacted with a water soluble reagent as,



Scheme 2. Oxidative dehydrogenation using a heteropoly acid complexed to a PEO- SiO_2 support. Reactions were carried out by mixing 0.2 mmol dihydroanthracene in 0.1 ml toluene, 0.4 mmol 70% TBHP, and 15 mg catalyst particle containing 0.002 mmol $H_5PV_2Mo_{10}O_{40}$ (supported) or just 0.002 mmol $H_5PV_2Mo_{10}O_{40}$ (non-supported) at room temperature for 24 h.

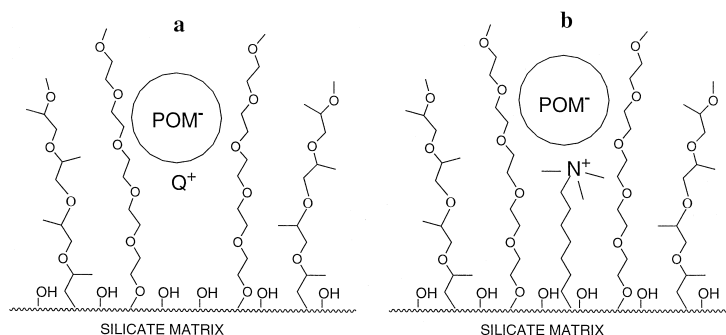


Fig. 3. An illustration of $[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ immobilized on functional silica; (a) $\text{Q}_{12}[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]$ dissolved in PE(P)O–SiO₂. (b) $[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ bound to Q^+ –PE(P)O–SiO₂.

for example, in the epoxidation of alkenes with 30% aqueous hydrogen peroxide. The immiscibility of the two reaction components in this situation requires that the supported catalyst be available to both reactants. This can be achieved by tethering silica with both PEO and PPO, Fig. 3a. As opposed to the previous example, the $[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ polyoxometalate was not strongly complexed to the tethers, but only dissolved within the anchored solvent phase. This increases the likelihood that during the reaction in the post-reaction work-up, polyoxometalate will wash into one of the liquid phases. In order to overcome this problem, the silica surface may additionally be functionalized by a quaternary ammonium moiety leading to a cationic surface advantageous for binding the anionic polyoxometalate. An illustration of such a catalytic assembly, Q^+ –PE(P)O–SiO₂– $[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]$, is presented in Fig. 3b. In the model epoxidation of cyclooctene with 30% H₂O₂ and in the absence of an organic solvent, Fig. 4, one can observe that non-bonding dissolution, Fig. 3a, of $[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ within the anchored solvent phase yields the most active catalytic system. When the polyoxometalate is additionally bound to the silicate surface, catalytic activity is lower, however, comparable or slightly better than the common biphasic, alkene in 1,2-dichloroethane/30% H₂O₂ system. Significantly, catalytic activity is maximized when the silica surface is tethered with both PEO and PPO, Figs. 4 and 5. Under

these conditions the hydrophilic/hydrophobic balance of the anchored solvent phase enables improved contact of the catalyst with both reaction phases. Furthermore, the polyether functionalization of the silica surface enables one to form thin films of these seemingly insoluble assemblies (see below), so that the hydrophilic/hydrophobic balance can also be appreciated by measurement of the wetting angle of 25% PPO–SiO₂, 10% PPO, 10% PEO–SiO₂ and 25% PEO–SiO₂. Indeed, wetting angles of 79, 54 and 38°, respectively, were measured as compared to 90° for pure PPO and 20° for pure

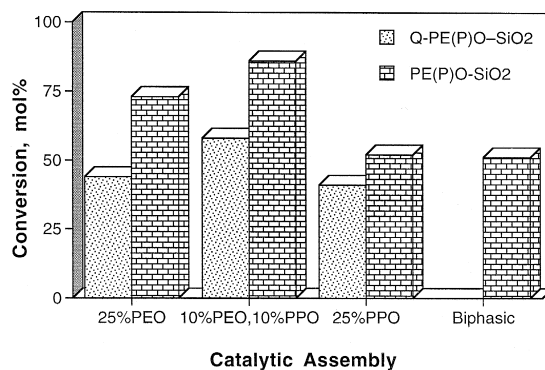


Fig. 4. Epoxidation of cyclooctene with 30% H₂O₂ with various catalytic assemblies. Reaction conditions: 1 mmol cyclooctene, 2 mmol 30% H₂O₂, 1 μmol $[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ added as 30 mg of functionalized silicate (20 wt.% loading), ambient temperature, 24 h. For the biphasic reaction, 1 mmol cyclooctene, 2 mmol 30% H₂O₂, 1 μmol $\text{Q}_{12}[\text{ZnWMn}_2^{\text{II}}(\text{ZnW}_9\text{O}_{34})_2]$ (Q = tricaprilmethyl ammonium), 1 ml 1,2-dichloroethane, ambient temperature, 24 h. Analysis was by GLC and cyclooctene oxide was the sole product.

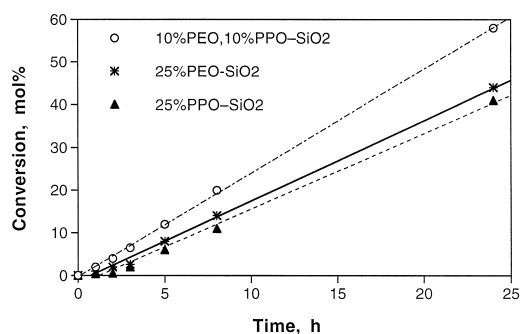


Fig. 5. Kinetic profiles of the epoxidation of cyclooctene with $Q^+-PP(E)O-SiO_2$ catalytic assemblies. Reactions conditions: 1 mmol cyclooctene, 2 mmol 30% H_2O_2 , 1 μ mol $[ZnWMn^{II}(ZnW_9O_{34})_2]^{12-}$ added as 30 mg of functionalized silicate (20% loading), ambient temperature, 24 h. Cyclooctene oxide was the sole product.

PEO. Despite the fact that the dissolved non-bonded catalytic system, Fig. 3a, showed higher activity than the bonded assembly, Fig. 3b, there was indeed leaching in the former system of the polyoxometalate into the organic substrate/product phase and loss of catalytic activity upon catalyst recycle. Leaching of the polyoxometalate in the later case was not discernible by either UV-Vis and atomic absorption spectroscopy. In fact, complete recycle of the catalytic assembly was possible without loss in catalytic activity; conversions of cyclooctene to cyclooctene oxide of 58, 54, 60, 52 and 58 mol.% were obtained for five cycles measured, under conditions described in Fig. 4.

A further experimental finding which is important to emphasize deals with the timing of the addition of the $[ZnWMn^{II}(ZnW_9O_{34})_2]^{12-}$ polyoxometalate during the preparation of the polyoxometalate bound assembly. The functionalized silica as indicated in Scheme 1 is synthesized by copolymerization of the relevant monomers in an aqueous alcoholic solvent, coupled with addition of $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$. In the first stage a sol is formed. In this stage the quaternary ammonium moiety is relatively free for anion exchange with the polyoxometalate and high incorporation can be measured, Table 1. As the copolymerization of the siloxane monomers continues, the silicate

gels by cross-linking, making the anion exchange sterically more difficult. However, early addition of $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$ also reduces access to the polyoxometalate in the final catalytic assembly because of the 3-D structure of the silicate. Therefore, a functionalized silicate with maximum catalytic activity is obtained in an intermediate situation where $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$ is added after 3 h. The $Q^+-PE(P)O-SiO_2-[ZnWMn^{II}(ZnW_9O_{34})_2]$ heterogenized catalytic assembly, Fig. 3b, was also used for the epoxidation of a range of alkenes, Table 2. As may be noticed, the immobilized catalyst consistently gave improved results compared to the 'classic' biphasic reaction system.

In order to more completely judge the usefulness of the solvent anchored silicates, it was valuable to observe their behavior upon contact with liquid phases. For example, the hydrophilic 25% PEO-SiO₂ was contacted with both water and chloroform, Fig. 6. It is very noticeable that in water, 25% PEO-SiO₂ is very well dispersed; the mixture has a homogeneous, slightly gelled appearance. On the other hand in chloroform, 25% PEO-SiO₂ is averse to dispersion in the solvent. Instead, distinctly, the silica particles are not dispersed in the solvent and act as a

Table 1

Incorporation and catalytic activity of $Q^+-PE(P)O-SiO_2-[ZnWMn^{II}(ZnW_9O_{34})_2]$ as a function of the timing of the addition of $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$

| Timing of addition (h) | Catalytic activity (conversion, mol.%) | POM incorporation (Cl ⁻ exchange) |
|------------------------|--|--|
| 0 | 20 | 86 |
| 1 | 36 | 77 |
| 3 | 58 | 60 |
| 5 | 17 | 22 |

The timing of addition refers to the time elapsed between the beginning of the copolymerization of the monomeric siloxanes and the addition of $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$ to the polymerizing mixture (see Section 3 for more detail). The catalytic activity was evaluated using the cyclooctene epoxidation as described in Fig. 4. $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$ incorporation was measured by titration of exchanged Cl⁻ relative to the maximum theoretical amount assuming each mole of $Na_{12}[ZnWMn^{II}(ZnW_9O_{34})_2]$ can exchange 12 equivalents of Cl⁻.

Table 2

Epoxidation of alkenes with the $Q^+ - 10\%$ PEO, 10% PPO-SiO₂-[ZnWMn^{II}(ZnW₉O₃₄)₂] catalytic assemblies and in 'classic' biphasic reactions

| Substrate | Turnovers, catalytic assembly | Turnovers, biphasic |
|---------------------|-------------------------------|---------------------|
| cyclohexene | 345 | 610 |
| 1-methylcyclohexene | 260 | 670 |
| cyclooctene | 580 | 510 |
| 1-octene | 100 | 135 |
| 3-nitrostyrene | 50 ^a | 310 |

Reaction conditions: For the catalytic assembly—1 mmol alkene, 2 mmol 30% H₂O₂, 1 μmol [ZnWMn^{II}(ZnW₉O₃₄)₂]¹²⁻ Q⁺-10% PEO, 10% PPO-SiO₂-[ZnWMn^{II}(ZnW₉O₃₄)₂], ambient temperature, 24 h. For the biphasic reaction—1 mmol alkene, 2 mmol 30% H₂O₂, 1 μmol Q₁₂[ZnWMn^{II}(ZnW₉O₃₄)₂] (Q = tricaprylmethyl ammonium), 1 ml 1,2-dichloroethane, ambient temperature, 24 h.

^a3-Nitrobenzaldehyde was 15% impurity.

typical insoluble solid. For 25% PPO-SiO₂, the same picture is obtained in reverse. There is excellent dispersion in chloroform, but in water

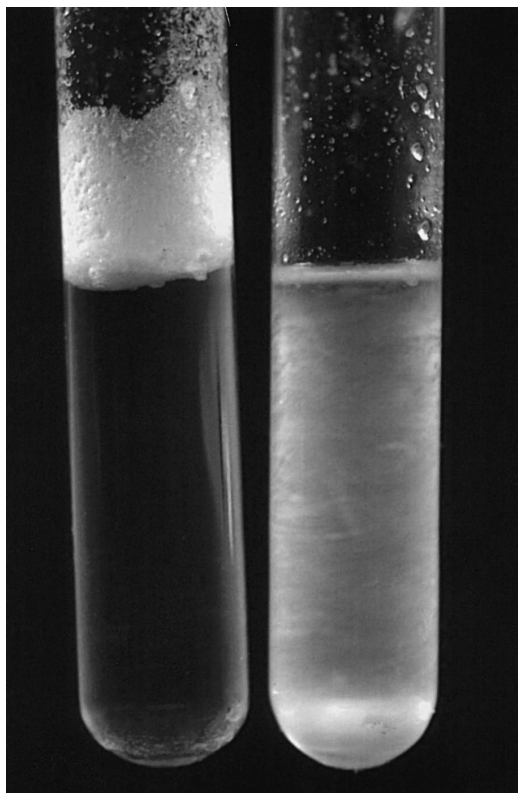


Fig. 6. A 25% PEO-SiO₂ in chloroform (left) and water (right).

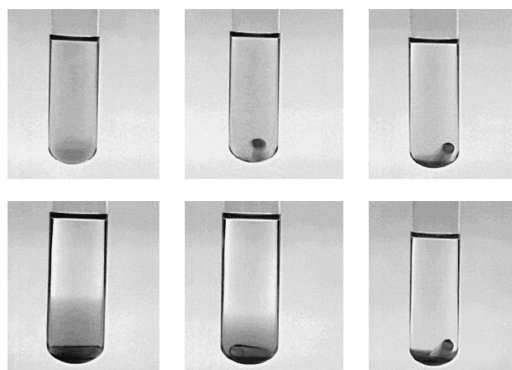


Fig. 7. A 10% PEO, 10% PPO-SiO₂ in toluene. Top left—stirred solution and then clockwise, the separation and precipitation after discontinuation of the stirring.

the silica lies on the surface. Non-dispersed assemblies are poor vehicles for catalysis. The excellent dispersion of 25% PPO-SiO₂ in organic solvents and 25% PEO-SiO₂ in aqueous solvents, while allowing for high reactivity in the respective solvents, however, also led to difficulties in the recovery of the catalytic assembly. Here, the use of 10% PEO, 10% PPO-SiO₂ allows both excellent dispersion but also easy separation. In Fig. 7 (10% PEO, 10% PPO-SiO₂ in toluene) one can see that upon even gentle mixing (top left), the solution appears homogeneous with excellent dispersion of the functionalized silica. Once the stirring is stopped, the functionalized silica, slowly, over a period of 10–15 min, separates from the solution. The 10% PEO, 10% PPO-SiO₂ has the same behavior when in contact with an aqueous phase (not shown). Therefore, not only do the 10% PEO, 10% PPO-SiO₂ based catalytic assemblies have the highest activity but they also are most easily recovered from the reaction mixture.

3. Experimental

3.1. Preparation of siloxane monomers

(CH₃O)₃SiPhCH₂(OCH₂CH₂)_nOCH₃ ($n_{\text{ave}} = 7-8$) was prepared by reacting 25 mmol (CH₃O)₃SiPhCH₂Cl with 25 mmol CH₃-(OCH₂CH₂)_nOH (MW = 350) in 100 ml ace-

tone in the presence of 125 mmol solid K_2CO_3 at reflux for 18 h. The solid salts (KCl , K_2CO_3) were filtered off by centrifugation and the solvent was evaporated off. No further purification was made at this point. 1H NMR in $CDCl_3$ (ppm)—7.66, d, 2H; 7.44, d, 2H; 3.5–3.8, m, 39H; 3.31, s, 3H. Similarly, $(CH_3O)_3SiPhCH_2-(OCH(CH_3)CH_2)_nO(CH_2)_3CH_3$ (n_{ave} 4–5) was prepared by reacting 25 mmol $(CH_3O)_3SiPhCH_2Cl$ with 25 mmol $HOCH(CH_3)-CH_2O(CH_2)_3CH_3$ (MW = 340) in 100 ml acetone in the presence of 125 mmol solid K_2CO_3 at reflux for 18 h. The solid salts were filtered off by centrifugation and the solvent evaporated and again no further purification was made. 1H NMR in $CDCl_3$ (ppm)—7.66, d, 2H; 7.44, d, 2H; 3.25–3.6, m, 29H; 3.1, t, 2H; 1.50, m, 2H; 1.32, m, 2H; 1.15, s, 20H; 0.88, t, 3H. $(MeO)_3SiPhCH_2N^+(CH_3)_2(CH_2)_7CH_3Cl^-$ was prepared by reacting 10 ml (0.4 mol) $(MeO)_3SiPhCH_2Cl$ with a equimolar amount of octyldimethylamine dissolved in 60 ml of petroleum ether (100–120) at reflux overnight [22]. After cooling, the product was filtered off (yield 65%) and used as is.

3.2. Preparation of functional (tethered) silicates

In general, the functionalized silicates were prepared by dissolving the desired or appropriate amounts (total 5 mmol) of $(CH_3O)_3SiPhCH_2(OCH_2CH_2)_nOCH_3$, $(CH_3O)_3SiPhCH_2-(OCH(CH_3)CH_2)_nO(CH_2)_3CH_3$, $(MeO)_3SiPhCH_2N^+(CH_3)_2(CH_2)_7CH_3Cl^-$ and $Si(OEt)_4$ in 20 ml acetone. Ten equivalents of water and 0.01 equivalents of dibutyltin dilaurate were added to initiate the polymerization. The mixture was held at 60°C for 3 h and left to slowly evaporate for 2 days at room temperature. More specifically, for the preparation of 25% PEO– SiO_2 – $H_5PV_2Mo_{10}O_{40}$, 25% PEO– SiO_2 was prepared as above (3.75 mmol $Si(OEt)_4$ and 1.25 mmol $(CH_3O)_3SiPhCH_2(OCH_2CH_2)_nOCH_3$). A total of 1.5 g 25% PEO– SiO_2 was then wet impregnated by addi-

tion of 440 mg $H_5PV_2Mo_{10}O_{40} \cdot xH_2O^{10}$ (0.2 mmol) dissolved in 10 ml acetone, the solvent evaporated and the 25% PEO– SiO_2 – $H_5PV_2Mo_{10}O_{40}$ assembly was then dried overnight under vacuum at room temperature. Similarly, for catalytic assemblies PEO and/or PPO– SiO_2 containing dissolved $Q_{12}[ZnWMn^{II}_2(ZnW_9O_{34})_2]$ (Q = tricaprylmethyl ammonium), Fig. 3a, 1.6 mg of PE(P)O– SiO_2 was impregnated with 400 mg $Q_{12}[ZnWMn^{II}_2(ZnW_9O_{34})_2]$ (20 wt.% loading) as above.

For catalytic assemblies $Q^+-PE(P)O-SiO_2$ with incorporation of $[ZnWMn^{II}_2(ZnW_9O_{34})_2]^{12-}$, the procedure was modified as follows: 0.43 mmol $(MeO)_3SiPhCH_2N^+(CH_3)_2-(CH_2)_7CH_3Cl^-$ were reacted with the appropriate amounts of $Si(OEt)_4$, $(CH_3O)_3SiPhCH_2-(OCH_2CH_2)_nOCH_3$, $(CH_3O)_3SiPhCH_2(OCH(CH_3)CH_2)_nO(CH_2)_3CH_3$ (the later three components totalling 4.57) in 20 ml acetone. Ten equivalents of water and 0.01 equivalents of dibutyltin dilaurate were added to form a sol. After 3 h (see optimal timing in Table 1) at 60°C, $Na_{12}[ZnWMn^{II}_2(ZnW_9O_{34})_2]$ (28.7 μ mol, 189.2 mg) was added. The solution was heated for an additional 10 min and left to cool. After slow evaporation of the solvent (2–3 days), the $Q^+-PE(P)O-SiO_2-[ZnWMn^{II}_2(ZnW_9O_{34})_2]$ catalytic assemblies were washed with an excess amount water and dried under vacuum. The water wash was analyzed by titration for Cl^- anions to estimate the anion exchange.

3.3. Catalytic oxidation and determination of wetting angles

Typical oxidation reactions were carried out in 5 ml magnetically stirred vials. Material quantities and reaction conditions are given in the tables and figures. Analysis of the reaction mixtures was by GLC in a HP 5890 instrument using a 30-m, 0.32-mm ID, 0.25- μ m methylsilicone coating (RTX-1) column. Catalyst recovery was by filtration of the catalyst, followed by washing to remove reaction remnants and drying.

Wetting angles were measured using a goniometer (Rame-Hart) by forming a film on a clean glass substrate from the sol formed from a solution of $(\text{CH}_3\text{O})_3\text{SiPhCH}_2(\text{OCH}_2\text{CH}_2)_n\text{-OCH}_3$, $(\text{CH}_3\text{O})_3\text{SiPhCH}_2(\text{OCH}(\text{CH}_3)\text{CH}_2)_n\text{-OCH}_3$, and $\text{Si}(\text{OEt})_4$ (total 5 mmol), 50 mmol water, 0.05 mmol dibutyltin dilaurate in 20 ml acetone after 3 h at 60°C.

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