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Recovery of Homogeneous Polyoxometallate Catalysts from Aqueous and Organic Media by a Mesoporous Ceramic Membrane without Loss of Catalytic Activity

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Abstract: The recovery of homogeneous polyoxometallate (POM) oxidation catalysts from aqueous and non-aqueous media by a nanofiltration process using mesoporous γ-alumina membranes is reported. The recovery of $Q_{12}[WZn_3(ZnW_9O_{34})_2]$ ($Q = [MeN(n\text{-}C_8H_{17})_3]^+$) from toluene-based media was quantitative within experimental error, while up to 97% of $Na_{12}[WZn_3(ZnW_9O_{34})_2]$ could be recovered from water. The toluene-soluble POM catalyst was used repeatedly in the conversion of cyclooctene to cyclooctene oxide and separated from the product mixture after each reaction. The catalytic activity increased steadily with the number of times that the catalyst had been recycled, which was attributed to partial removal of the excess QCl that is known to have a negative influence on the catalytic activity. Differences in the permeability of the membrane for different liquid media can be attributed to viscosity differences and/or capillary condensation effects. The influence of membrane pore radius on permeability and recovery is discussed.

Keywords: epoxidation · homogeneous catalysis · membranes · nanofiltration · separation

Introduction

The recycling of catalysts is often essential to arrive at economically acceptable production costs. In the area of homogeneous catalyst recycling, much attention has been paid to catalyst immobilisation[1] and the development of enlarged catalysts.[2] However, this method is less attractive in view of the fact that additional synthetic steps are required to obtain these modified catalysts, which may display catalytic properties that are different from their homogeneous analogues.

A more promising approach is to make use of a pressure-driven nanofiltration process to separate the catalyst from the product. There are two mechanisms for separation by nanofiltration, namely size exclusion and/or electrostatic interactions between charged solutes and the native surface-charge on the membrane pore wall. Size exclusion is based on steric hindrance of solute molecules in the membrane pores, whereas the degree of electrostatic exclusion is determined by the sign and magnitude of the solute charge: ions with the same charge as the membrane surface (so-called co-ions) are repelled, while ions with opposite charge (counterions) are attracted. This leads to ion-concentration gradients at the membrane/solution interface, which generate an electrical potential difference known as the Donnan potential.[3] The Donnan potential difference is responsible for the repulsion of co-ions. Due to the requirement of electroneutrality, the counterions are then also rejected and thus separation of ionic solutes from the uncharged solutions occurs. The efficiency of this process is expressed in terms of the retention $R = (1-[A]_{perm}/[A]_{bulk})\cdot 100\%$, where $[A]_{bulk}$ and $[A]_{perm}$ are the salt concentrations in the liquid feed and permeated liquid, respectively.

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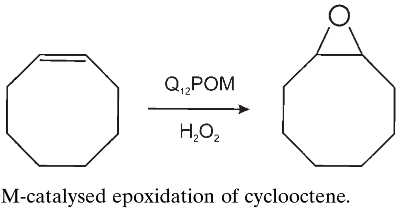
Nanofiltration membranes are known to allow for the recycling of non-enlarged homogeneous catalysts, although only low catalyst retentions are often achieved.[3–7] Polyoxometallate (POM) catalysts have all the features necessary for successful recycling by nanofiltration: they are large, they have a rigid structure,[8] which is charged,[9] and the lack of organic ligands makes them stable towards many different reaction conditions.[10] Herein, the recycling of a "sandwich"-type polyoxometallate oxidation catalyst from aqueous and non-aqueous media is described. The water-soluble sodium salt of the polyoxometallate catalyst $Na_{12}[WZn_3(ZnW_9O_{34})_2]$ was used for nanofiltration experiments from aqueous media, whereas exchange of the Na^+ ions with $[MeN(n\text{-}C_8H_{17})_3]^+$ moieties was necessary to make the POM anion $[WZn_3(ZnW_9O_{34})_2]^{12-}$ soluble in organic solvents like toluene.

Herein, we demonstrate that both the water-soluble (Na_{12}POM) and toluene-soluble (Q_{12}POM) POM oxidation catalysts can be recycled efficiently by a mesoporous ceramic γ-alumina membrane. These two "sandwich" POMs were chosen because we have demonstrated previously that they are very versatile "multi-purpose" catalysts for oxidations with aqueous hydrogen peroxide, such as epoxidation, alcohol oxidation and heteroatom oxidations.[10,14,17,18] From an industrial point of view, these "sandwich" POM catalysts offer the additional advantage that they are easily accessible by self-assembly from readily available inorganic compounds, as will be pointed out in the Experimental Section.

The influence of the γ-alumina membrane pore size and the nature of the solvent on the level of retention of the catalyst and the permeability of the membrane is also investigated.

The feasibility of this concept is demonstrated by repeated recycling (six sucessive runs) of Q_{12}POM from a model alkene epoxidation reaction mixture without any loss of catalytic activity. The epoxidation of cyclooctene (Scheme 1) was taken as a model reaction. It has the advantage that it forms one well-defined product, with little chance of unwanted side-reactions like allylic oxidation or epoxide ring opening.



Scheme 1. POM-catalysed epoxidation of cyclooctene.

Results and Discussion

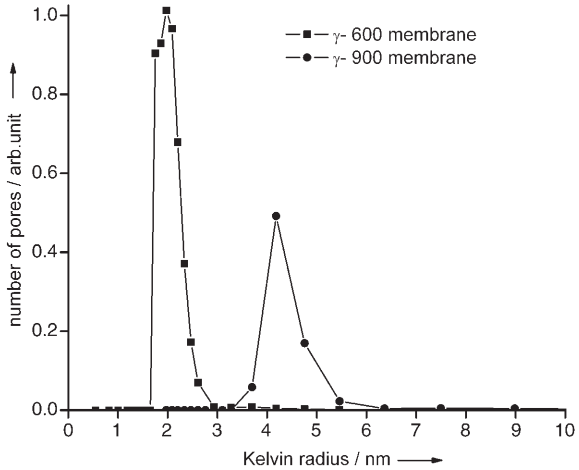


Figure 1. Pore-size distributions of γ-alumina membranes calcined at 600 and 900 °C.

Table 1. Retention of Q_{12}POM and Na_{12}POM solutions by different γ-alumina membranes.

Membrane	Pore radius r_p [nm]	Feed composition	Retention [%]
γ-600	2.3	Q_{12}POM (6.4 mM) in toluene	>99.9
γ-900	4.3	Q_{12}POM (6.4 mM) in toluene	93
γ-600	2.3	Na_{12}POM (10 mM) in water	97

Retention of Na_{12}POM and Q_{12}POM: The γ-alumina membranes calcined at 600 and 900 °C will be subsequently referred to as γ-600 and γ-900. The pore size distributions of γ-600 and γ-900 membranes are shown in Figure 1. The real pore radius, r_p, is related to the Kelvin radius, r_K, shown in Figure 1, by $r_p = r_K + t$, where $t \sim 0.3$ nm.[11] Hence the average pore radii of γ-600 and γ-900 are 2.3 and 4.0 nm, respectively. Table 1 lists typical retention values of Na_{12}POM and Q_{12}POM catalysts by γ-600 and γ-900 membranes. Nearly quantitative retention (>99.9 %) was obtained for toluene-soluble Q_{12}POM with a γ-600 membrane. The other retentions were lower, but were typically well above 90 %. Such high values that are relatively independent of experimental conditions suggest that retention by size exclusion is probably the dominant mechanism of separation. However, electrostatic interactions may also play a role. The retention behaviour of POM ions due to electrostatic interactions can be predicted qualitatively by the electrical double layer theory, which states that as the electrolyte strength increases the double layer thickness decreases. The thickness of the diffuse double layer can be estimated from the Debye screening length κ^{-1} [Eq. (1)]:[12]

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i z_i^2 n_i^0}} \tag{1}$$

where n_i^0 is the number density of ionic species, i, in the bulk of the electrolyte solution, and $\frac{1}{2}\Sigma z_i^2 n_i^0$ is the electrolyte strength.[12] ε_0 and ε_r are the dielectric constant of vacuum and the relative dielectric constant of the liquid medium, respectively, k_B is the Boltzmann constant, T is the absolute temperature and e is the elementary electron charge.

When $\kappa r_p < 1$, where r_p is the pore radius of the membrane, the dimensions of narrow-sized pores approach the thickness of the double layers such that double layer overlap occurs from opposite sides of the pore. The pore therefore becomes less permeable to ions with the same charge as the surface charge, thus increasing the retention of charged solutes.[12] Alternatively, under conditions at which $\kappa r_p > 1$, the double layer is confined to a small region near the channel wall and the centre of the channel is electrically uncharged, which means that the fluid in the centre of the pore contains both anions and cations, with the total amount of positive and negative charges being the same. Under these conditions both cationic and anionic species can be transported through the centre of the channel and the retention by electrostatic effects will be small.

The double layer thickness is not constant but decreases with electrolyte strength and increases with surface charge density, that is, with species having different degrees of ionisation, the double layer thickness will vary according to the number of ions present in the solution and the charge of these ions. Since we have no information about the degree of ionisation of $Na_{12}POM$ in water or $Q_{12}POM$ in toluene, we estimated the thickness of the double layer of a 10-mM $Na_{12}POM$ solution in water ($\varepsilon_r = 80$) and a 6.4-mM solution of $Q_{12}POM$ in toluene ($\varepsilon_r \sim 2.4$) by considering their different degrees of ionisation.

For the $Na_{12}POM$ salt in water, with a degree of ionisation between 8.3% ($Na^+ + [Na_{11}POM]^-$) and 100% ($12Na^+ + POM^{12-}$), the double layer thickness, κ^{-1}, was calculated to be between 3 nm and about 0.4 nm. For the $Q_{12}POM$ salt in toluene, with a degree of ionisation between 8.3% ($Q^+ + [Q_{11}POM]^-$) and 100% ($12Q^+ + POM^{12-}$), the double layer thickness varied between 0.7 nm and less than about 0.1 nm. This implies that $\kappa r_p > 1$ in all the experiments described above. Only if we assume a very low degree of ionisation of $Na_{12}POM$ (20% or less) can a considerable fraction of pores at the lower end of the pore size distribution be completely spanned by the electrical double layer. Since sodium salts are usually highly dissociated in aqueous solutions, such a low degree of dissociation is very unlikely. Hence, it can be concluded that the retention of $Na_{12}POM$ is due to size exclusion. Because of the even smaller double layer thicknesses calculated for $Q_{12}POM$ in toluene, $Q_{12}POM$ retention is also due to size exclusion by the membrane, despite the fact that the average pore sizes of the γ-600 and γ-900 membranes are larger than that of $Q_{12}POM$ and $Na_{12}POM$ moieties. The POM^{12-} ion is roughly 1.5 nm in size. Molecular dynamics (MD) calculations on $Q_{12}POM$ in toluene showed that it is present in associated form, that is, POM anions and Q-ammonium ions form loosely bound complexes in toluene that are about 3 nm in diameter. The hydrocarbon tails of the Q-ammonium ion have a favourable interaction with toluene molecules due to their organic character, and as the POM anion has a highly negative charge and polar character, the anion itself is unable to dissolve in toluene. Thus, the POM anion forms the core and the Q-ammonium cations form the shell layer of a large associated complex with the hydrophobic end-groups of the Q-ammonium cation exposed to the surrounding toluene phase.

The seeming contradiction between the high retention of the relatively small POM moieties by γ-alumina membranes with larger average pore sizes can be understood by considering that permporometry actually measures capillary condensation in a pore at equilibrium and thus gives the dimensions of a pore body, that is, the widest part of a pore. However, ceramic membranes have an undulating pore structure with wider and narrower parts, so the effective pore size for nanofiltration corresponds to the smallest openings in that structure and actually represents the pore neck size. The quantitative retention of $Q_{12}POM$ by γ-600 implies that the effective pore size must be smaller than about 3 nm, while the 97% retention of $Na_{12}POM$ by γ-600 suggests that the vast majority of transport paths through the γ-600 layer are even smaller than 1.5 nm. A 93% retention was obtained with γ-900 membranes with an average pore diameter of about 8 nm. This slightly lower retention is probably due to a larger effective pore size of the γ-900 membrane, which may allow some $Q_{12}POM$ molecules to pass.

Q_{12}POM catalyst recycling: To make an accurate comparison of the activity of $Q_{12}POM$ in subsequent cycles of cyclooctene epoxidation, reaction conditions were chosen that did not lead to full conversion. Although cyclooctene can easily be epoxidised with 100% conversion and selectivity, the main issues dealing with nanofiltration of large anions will not be influenced by the choice of substrate or reaction conditions.

Figure 2 shows the results for recycled $Q_{12}POM$ in cyclooctene epoxidation after different numbers of recycles. Elemental analysis of the permeate liquids showed nearly quantitative (>99.9%) catalyst retention for every recycling step except for recycle 3, where a retention of 98.6% was found. The relatively high amount of Zn found in permeate 3 is

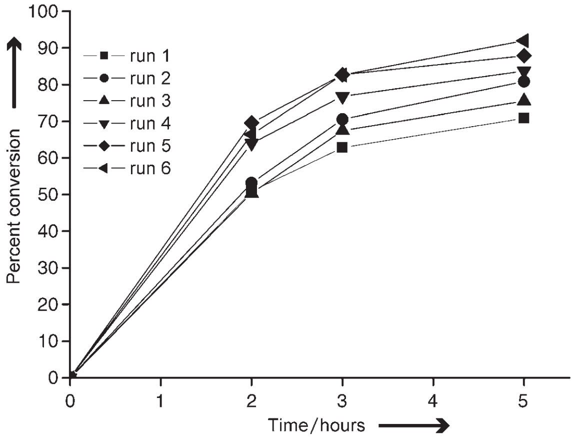


Figure 2. Q_{12}POM-catalysed epoxidation of cyclooctene after 0–5 recycles of the catalyst.

probably caused by an impurity, since permeates 4 and 5 again show very high retentions without any drop of catalyst activity in run 4 of the epoxidation reaction. Surprisingly, the activity of the catalyst increased after each round of recycling with the γ-600 membrane. This is most likely caused by removal of the excess of QCl from the Q_{12}POM catalyst solution generated in situ.[13] It has been reported previously that an excess of QCl (Aliquat 336) has a negative effect on the epoxidation of cyclooctene.[14] The retention of QCl dissolved in [D_8]toluene by a γ-600 membrane was found to be 65 %, as determined by ^{1}H NMR spectroscopy, which means that the excess of QCl present in the starting mixture decreases steadily after each recycling run.

XPS depth-profiling measurements on the γ-600 membrane after repeated nanofiltration experiments with Q_{12}POM indicated that the catalyst does not enter the pores of the membrane substantially. Only very low atomic concentrations of W and Zn (0.6 and 0.3 atom %, respectively) were observed. If we consider the specific surface area of γ-600 to be $285\ m^2g^{-1}$,[15] with W and Zn residing on the internal pore surface, the surface concentrations of W and Zn atoms per square nanometre of internal pore area are 0.6 and $0.3\ nm^{-2}$, respectively. Since one POM molecule contains 19 W atoms and 5 Zn atoms, a W/Zn ratio of 3.8 would be expected if POM were the only molecular species present inside the membrane pores. The experimentally observed W/Zn ratio of around 2 can be rationalised only if we assume that chemical species other than POM are also present. Since the POM catalyst was used as a mixture prepared in situ, it is very likely that small amounts of unreacted Zn- and W-containing materials are still present in the reaction mixture and adsorbed on γ-alumina. These could be the starting compounds Na_2WO_4 or $ZnCl_2$, or derivatives thereof. In view of the large size of the POM anion, its complete retention, within experimental error, and the fact that the W atoms in $[WZn_3(ZnW_9O_{34})_2]^{12-}$ are present in two oxidation states, while XPS detected W in the layer in only one oxidation state, it is very unlikely that POM is present at all. Although no retention measurements were performed on the starting compounds, it is expected that these much smaller molecules will pass through the membrane more easily than the large POM.

Membrane permeability: Figure 3 shows the volumetric flux of the toluene-based product mixture after reaction for five hours. The flux at a given applied pressure is considerably lower than that of pure toluene through a γ-600 membrane. This is either due to concentration polarisation of Q_{12}POM near the membrane surface and/or a result of capillary condensation of water in the pores of the membrane. Regarding the first option, it should be noted that the concentration of Q_{12}POM in the liquid bulk is too low to significantly influence the viscosity. However, concentration polarisation of the catalyst may occur at the membrane surface due to the retention of Q_{12}POM, leading to a highly viscous gel layer on the membrane surface. This gel layer presents an additional resistance to transport of solvent and is a problem that has often been observed in dead-end filtrations. In industrial applications it can easily be overcome by using a loop reactor.

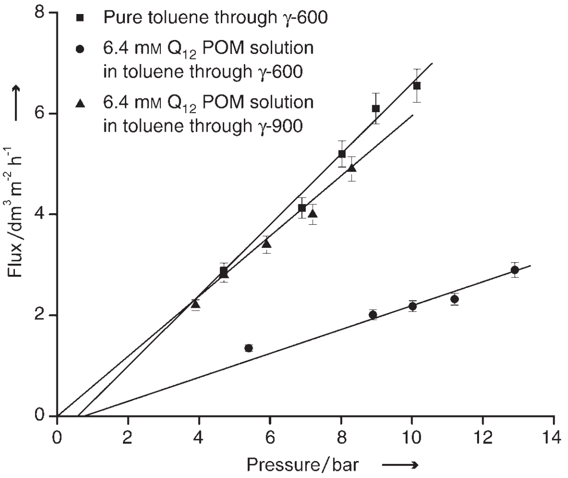


Figure 3. Volumetric flux of pure toluene and a toluene solution of Q_{12}POM through γ-alumina membranes calcined at 600 and 900 °C versus pressure applied on the liquid feed.

As for the second option, it has been reported that even very low levels of water (a few ppm) present in a non-polar solvent can significantly affect the permeability of the membrane by capillary condensation in small pores, thereby blocking those pores for further transport of the non-polar solvent.[15,16] In the present investigation a substantial amount of water was present in the reaction mixture; this originates from the H_2O_2 stock solution and is formed as a by-product of the reaction of H_2O_2 with cyclooctene. The phenomenon of capillary condensation is also thought to cause a non-zero threshold pressure that needs to be applied at least to initiate a net fluid flow across membranes with relatively small pores.[15] This threshold pressure is probably required to open up some of the water-blocked membrane pores by drainage working against the capillary pressure of the condensed water phase. A threshold pressure of about 1 bar can be observed in Figure 3 for the permeation processes involving γ-600 membranes, but not for the process involving the γ-900 membrane with larger pores, which is in agreement with earlier findings.[15]

The permeability coefficients, defined as the volumetric flux per unit of applied pressure, of the γ-600 and γ-900 membranes for the product mixture were 0.2 ± 0.02 and $0.57\pm0.01\ L\,m^{-2}h^{-1}bar^{-1}$, respectively. This difference is in good agreement with theory, which predicts that the permeability coefficient of a membrane towards a certain liquid is proportional to the second power of the membrane pore radius.[15] As the average pore radii of γ-600 and γ-900 are approximately 2.3 and 4.3 nm, respectively, the permeability coefficients are expected to differ by a factor of about 3.5; a difference of 2.9 times was found experimentally.

Figure 4 shows the volumetric flux versus applied pressure for pure water and a Na_{12}POM solution through the γ-600 membrane. In contrast to the results displayed in Figure 3,

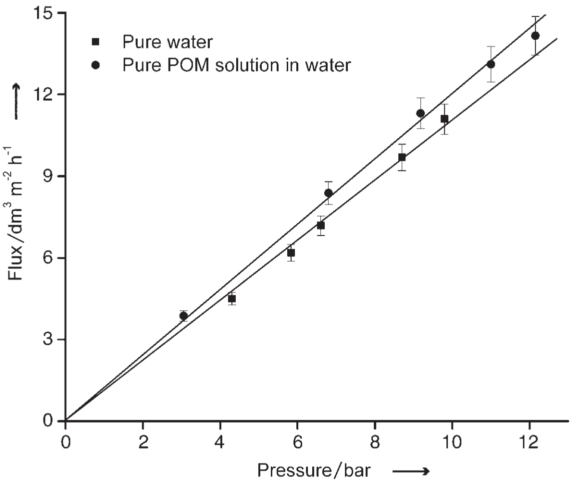


Figure 4. Volumetric flux versus applied pressure for pure water and a 10-mM $Na_{12}POM$ solution in water through the γ-600 membrane.

the permeability coefficients of the membrane for water and the aqueous $Na_{12}POM$ solution are very similar, that is, 1.1–1.2 $L\,m^{-2}\,h^{-1}\,bar^{-1}$. This agrees with the fact that the viscosities of pure water and the $Na_{12}POM$ solution in water are the same, and capillary condensation effects as observed in non-aqueous nanofiltration will not occur with aqueous media. Since the internal pore surface of γ-alumina has a relatively high density of hydroxy groups and is thus hydrophilic by nature, aqueous media will be able to pass more easily than hydrophobic solvents such as toluene. This explains the lower permeability of toluene of $0.7 \pm 0.01\,L\,m^{-2}\,h^{-1}\,bar^{-1}$, even though the viscosity of toluene at room temperature is substantially lower than that of water.

Conclusion

We have demonstrated that an industrially important homogeneous oxidation catalyst can be recovered quantitatively by nanofiltration through a mesoporous ceramic membrane without any loss of catalytic activity. In fact, the catalytic activity of the catalyst increases with the number of membrane recycles, probably because of removal of the excess of Aliquat 336 that is present in the catalyst stock solution. The retention of the catalyst in aqueous and non-aqueous solution was found to be due to size exclusion, which means that the catalyst can be recovered with very high retentions irrespective of the actual process conditions.

Experimental Section

Polyoxometallate catalyst preparation: Aqueous $Na_{12}[WZn_3(ZnW_9O_{34})_2]$ ($Na_{12}POM$) was prepared in near-quantitative yield by self-assembly according to the net reaction $19\,Na_2WO_4 + 5\,ZnCl_2 + 16\,HCl \rightarrow Na_{12}[WZn_3(ZnW_9O_{34})_2] + 26\,NaCl + 8\,H_2O$. [14,17,18] Thus, $Na_2WO_4{\cdot}2\,H_2O$ (62.5 g, 0.19 mol) was dissolved in water (175 mL) at 85 °C and aqueous 37 % HCl (13.3 mL, 0.16 mol) was added at this temperature. A yellow solid formed which dissolved almost immediately. The mixture was heated to 95 °C and a solution of $ZnCl_2$ (6.81 g, 50 mmol) in water (75 mL) was added dropwise over 4 h, whilst stirring, to form a 10-mM solution of $Na_{12}POM$. Since the crystallisation of $Na_{12}POM$ is very time-consuming and gives a very low yield, we skipped the catalyst purification step and used the prepared solution directly.

Toluene solutions of $Q_{12}[WZn_3(ZnW_9O_{34})_2]$ ($Q = MeN^+(C_8H_{17})_3$), subsequently referred to as $Q_{12}POM$, were prepared by addition of QCl (Aliquat 336) to the aqueous $Na_{12}POM$ solution. Thus, $[MeN(C_8H_{17})_3)]Cl$ (Aliquat 336; 40 g, 0.10 mol) was dissolved in toluene (300 mL) and the mixture was stirred for 6 h. The layers were separated, the aqueous layer was washed with pure toluene, and the combined toluene layers were dried over Na_2SO_4. Unfortunately, it is not possible to extract the POM^{12-} anion quantitatively into the organic phase by adding 12 equivalents of QCl to an aqueous solution of $Na_{12}POM$. Quantitative extraction as $Q_{12}POM$ requires an excess of QCl relative to the $Q_{12}POM$ stoichiometry.

Catalyst concentrations were calculated from the Zn content, as measured by ICP-AES techniques after acidic destruction of the catalyst. Measurements of stock solutions of Na_2WO_4 and $Zn(NO_3)_2$ in H_2O proved inaccurate with regards to W content (error ±20 %), but accurate for Zn content. ICP-AES measurements were performed with a Perkin Elmer Optima 3000, using a rhodium standard. The POM concentration in toluene was calculated to be 6.4 mM. This means that about 64 % of the POM^{12-} anions present in the aqueous layer are extracted into toluene upon addition of 12 equivalents of QCl, that is, the $Q_{12}POM$ solution in toluene contains an excess of QCl relative to POM.

Preparation of supported γ-alumina membranes: The γ-alumina membrane consisted of a macroporous α-alumina support and a thin mesoporous γ-alumina layer. The α-alumina supports were made by colloidal filtration of well-dispersed 0.3-μm α-alumina particles (AKP-30, Sumitomo). The dispersion was stabilized by peptizing with nitric acid. After drying at room temperature, the filter compact was sintered at 1100 °C. Flat disks with a diameter of 39 mm and a thickness of 2.0 mm were obtained after machining and polishing. The final porosity of these supports was about 30 % and the average pore diameter was in the range 80–120 nm. Three different mesoporous γ-alumina membranes with a thickness of about 3 μm were prepared by dip-coating the α-alumina supports in a boehmite sol, followed by drying and calcining at 600 or 900 °C (heating/cooling rates: $0.5\,°C\,min^{-1}$), respectively, for 1 h. These membranes are hereafter referred to as γ-600 and γ-900, respectively. The deposition/calcination cycle was carried out twice. The pore-size distribution of the γ-alumina membranes was determined by permporometry using a home-made setup.[11]

Epoxidation and POM catalyst recycling: $Q_{12}POM$ (5 mL of a 6.4 mM solution in toluene; 32 μmol), toluene (10 mL), dodecane (0.5 mL; internal standard) and cyclooctene (2.6 mL, 20 mmol) were mixed and heated to 60 °C. H_2O_2 (50 % solution in H_2O; 1.5 mL, 27 mmol) was then added in five portions over a period of 2 h (300 μL per half hour) and the biphasic mixture was stirred at 60 °C. GC samples (30 μL of the organic layer in 0.6 mL of toluene) were removed after 0, 2, 3 and 5 h. GC chromatograms were measured with an HP6890 chromatograph, using a cross-linked 5 % PH ME siloxane column. It should be noted that the conversions of runs 2–6 were corrected for residual cyclooctene oxide in the retentates. The stirring was stopped after 5 h, the mixture was cooled to room temperature and the water layer was removed. POM catalyst recycling was performed in a dead-end nanofiltration cell equipped with a supported γ-alumina membrane.[15] For the experiments with water-soluble POM, 10 mmol of pure and isolated $Na_{12}POM$ was dissolved in 1 L of deionized water to make the stock solution. A total volume of 50 mL was used as feed and about 8 mL of the permeate solution was collected. The recycling experiments were carried out over a range of 3–12 bar applied pressure.

For nanofiltration experiments with the epoxidation reaction mixture, the nanofiltration cell was charged with the organic layer separated after the epoxidation reaction and pressurized. After about 15 mL of permeate solution had been collected the cell was depressurized, which stopped the recycling process. The retained volume (retentate, approx. 1 mL) plus an additional 4 mL of toluene was used to catalyze the subsequent epoxidation reaction. The level of retention of Aliquat 336 in [D$_8$]toluene through a γ-600 membrane was determined by NMR spectroscopy using a Bruker DRX 500 spectrometer by determining the concentration of Aliquat 336 in the permeate.

X-ray photoelectron spectroscopy (PHI Quantera Scanning ESCA Microprobe, USA) was carried out on selected membranes after POM recycling experiments to identify the atomic concentrations of O, Al, Zn and W by measuring the O 1s, Al 2p, Zn 2p and W 4f spectra as a function of depth inside the layer at an Ar$^+$ sputter rate of 17.9 nm min^{-1}.

Acknowledgments

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