

Highly efficient recycling of a “sandwich” type polyoxometalate oxidation catalyst using solvent resistant nanofiltration†

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Received (in Cambridge, UK) 19th October 2004, Accepted 16th December 2004

First published as an Advance Article on the web 18th January 2005

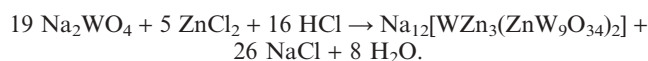
DOI: 10.1039/b416096g

A “sandwich” type polyoxometalate catalyst ([MeN(*n*-C₈H₁₇)₃]₁₂[WZn₃(ZnW₉O₃₄)₂]) was very efficiently recycled by nanofiltration with almost quantitative retention, using an α -alumina supported mesoporous γ -alumina membrane.

Catalyst recycling is often indispensable in order to arrive at economically acceptable catalyst costs per product unit. Recycling of homogeneous catalysts by filtration can be achieved by immobilization on a solid support.¹ Unfortunately, this often negatively affects catalyst performance. Alternatively, the molecular structure of homogeneous catalysts can be enlarged to such an extent that recycling by nanofiltration becomes feasible.^{2,3} Sufficiently high nanofiltration retentions are usually only obtained with large, shape-persistent structures that require a costly multi-step organic synthetic procedure.⁴ Accordingly, there is a need for readily accessible homogeneous catalysts with structural characteristics that enable highly efficient recycling through nanofiltration, thus combining the high performance characteristics of homogeneous catalysts with the ease of recycling of heterogeneous catalysts.

We have reported the use of the “sandwich” type polyoxometalate [WZn₃(ZnW₉O₃₄)₂]¹²⁻ (POM¹²⁻, Fig. 1) as a multi-purpose oxidation catalyst for transformations with aqueous H₂O₂, such as epoxidation,^{5,6} alcohol oxidation, and heteroatom oxidation.⁷ We already reported on the recycling of *water-soluble* Na₁₂POM by a simple phase separation.⁸ Herein we present the separation of *lipophilic* [MeN(*n*-C₈H₁₇)₃]₁₂POM (Q₁₂POM) from the organic reaction mixture by nanofiltration, and its subsequent reuse.

Dead-end nanofiltrations were performed in a cell equipped with an α -alumina supported mesoporous γ -alumina membrane with a pore size \ddagger of 5 nm.⁹ Toluene solutions of Q₁₂POM were prepared by addition of QCl (Aliquat 336) to aqueous Na₁₂POM, prepared in near-quantitative yield *via* self-assembly according to:⁶⁻⁸



Elemental analysis of the toluene solution showed that 60% of the POM¹²⁻ anions present in the aqueous layer were extracted

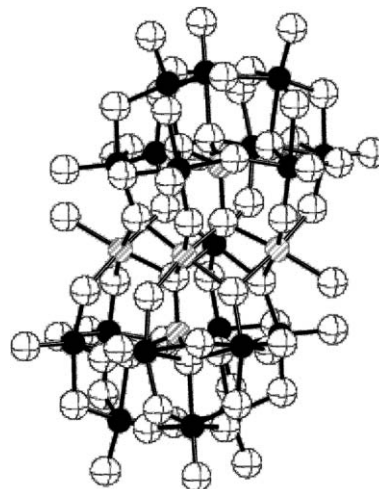


Fig. 1 The [WZn₃(H₂O)₂(ZnW₉O₃₄)₂]¹²⁻ polytungstate anion.

into toluene by addition of 12 equivalents QCl; *i.e.*, the Q₁₂POM toluene solution contains an excess of QCl relative to the POM.

The flux \ddagger of a toluene solution of Q₁₂POM is considerably lower than that of pure toluene (Fig. 2). This can be caused either by capillary condensation of water in the pores of the membrane,¹⁰ or by a higher viscosity of the POM solution. Although the Q₁₂POM concentration is too low to significantly influence the viscosity of the bulk solution, a local high concentration can be reached at the membrane surface. This so-called concentration polarization is a problem often observed in dead-end filtrations. For larger scale applications, it can easily be overcome by using a loop reactor.

The retention \ddagger of Q₁₂POM was nearly quantitative (>99.9%) over the pressure range of 5–13 bar. In accordance with that, XPS measurements on the membrane after nanofiltration indicate that the catalyst did not enter the pores of the membrane. Only very

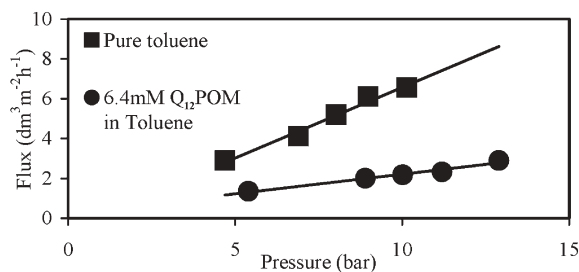


Fig. 2 Flux (dm³ m⁻² h⁻¹) versus pressure (bar).

† Electronic Supplementary Information (ESI) available: catalyst generation and analysis, membrane preparation and analysis. See <http://www.rsc.org/suppdata/cc/b416096g/>

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low atomic concentrations of W and Zn (0.6% and 0.3% respectively) were observed.¹¹

For the catalyst recycling,[§] we investigated the epoxidation of cyclooctene. This model reaction was chosen since analysis is accurate and simple because of the absence of by-products arising from allylic oxidation or epoxide ring opening. In order to make an accurate comparison of the different reaction cycles, we chose reaction conditions that did not lead to full conversion.

Fig. 3 shows the results for the recycling of Q₁₂POM in the cyclooctene epoxidation. The seemingly increasing activity of the catalyst after each recycling run is ascribed to the partial removal of the excess of QCl from the Q₁₂POM catalyst solution on each run.¹² This finding is in line with our earlier observation concerning the negative effect of an excess of QCl on the rate of Q₁₂POM catalyzed epoxidation of cyclooctene.⁶

Elemental analysis of the permeates showed nearly quantitative catalyst retentions for every recycling step, except for recycling run 3 (Table 1). The relatively high amount of Zn found in Permeate 3 is ascribed to experimental error, since Permeates 4 and 5 show again very high retentions.

In conclusion, we have shown that the Q₁₂POM polyoxometalate catalyst is retained almost quantitatively in organic solution by an α -alumina supported mesoporous γ -alumina nanofiltration membrane. This membrane is particularly suited for separations in organic media, to which it is very stable because of its ceramic nature. XPS measurements showed that the catalyst did not enter the pores of the membrane. This POM catalyst has all features necessary for obtaining a high retention in nanofiltration: it is

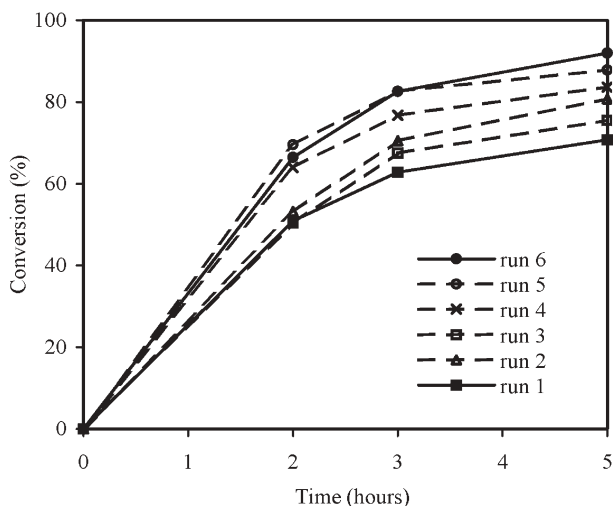


Fig. 3 Q₁₂POM catalyzed epoxidation of cyclooctene.

Table 1 Elemental analysis of permeates

	Amount Zn	Retention
Starting material ^a	10 mg	—
Permeate 1	4.5 μg	>99.9%
Permeate 2	<1.6 μg ^b	>99.9%
Permeate 3	140 μg	98.6%
Permeate 4	8.4 μg	>99.9%
Permeate 5	3.2 μg	>99.9%

^a Calculated amount, based on 32 μmol of Q₁₂POM. ^b Below detection limit.

highly ionic with a large POM anion that has a very rigid, shape-persistent structure. Shape-persistence is of prime importance in order to achieve the very high retentions required for industrial use.^{2,4} For efficient recycling and reuse, besides a high retention, also a high catalyst robustness is required. This is particularly hard to achieve in oxidation catalysis, since organic ligands are usually prone to oxidative degradation. The inorganic nature of the POM anion provides the required thermal and chemical stability. The foregoing features and its easy availability through self-assembly from readily available starting materials, make the Q₁₂POM catalyst a versatile and industrially attractive multi-purpose homogeneous catalyst for oxidations with aqueous hydrogen peroxide.

We thank the European Commission for support of this research (GIRD-2000-00347; Sustox project).

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Notes and references

‡ The pore size (d , in nm) is defined by $d = 2(r_K + t)$, where r_K is the Kelvin radius, and t the layer thickness of the t -layer (~ 0.3 nm). The flux (J , in $\text{dm}^3 \text{m}^{-2} \text{h}^{-1}$) is defined by $J = V_p/A_m T$, where V_p is the volume of the permeate, A_m the area of the membrane and T the time in which the permeate is collected. The retention (R , in %) is defined by $R = 100(1 - C_p/C_b)$, where C_p is the catalyst concentration in the permeate and C_b the concentration in the bulk.

§ Solvents and chemicals (including cyclooctene oxide, used as reference material for GC analysis) were commercial products used without purification. **Epoxidation:** 5 mL 6.4 mM Q₁₂POM in toluene (32 μmol), 10 mL toluene, 0.5 mL dodecane (internal standard) and 2.6 mL cyclooctene (20 mmol) were mixed and heated to 60 °C. 1.5 mL 50% H₂O₂ in H₂O (27 mmol) was added in 5 portions during a 2 hour period (300 μL per half hour) and the biphasic mixture was stirred at 60 °C. After 5 hours the stirring was stopped, the mixture was cooled to room temperature and the water layer was removed. **Nanofiltration:** The nanofiltration cell was charged with the organic layer of the epoxidation and pressurized (~ 10 bar). When ~ 15 mL permeate was collected, the cell was depressurized, which stopped the permeation. The retentate (~ 1 mL) plus 4 mL extra toluene was used for a subsequent epoxidation instead of the 5 mL Q₁₂POM stock solution. **GC-analysis:** GC samples (30 μL of the organic layer in 0.6 mL toluene) were taken at $t = 0, 2, 3, 5$ hours. GC spectra were measured on a HP6890 spectrometer, using a cross-linked 5% PH ME siloxane column. Conversions of run 2–6 were corrected for residual cyclooctene oxide in the retentates. **Catalyst analysis:** Catalyst concentrations were calculated from the Zn-content, measured by ICP-AES techniques after acidic destruction of the catalyst. ICP-AES measurements of stock solutions of Na₂WO₄ and Zn(NO₃)₂ in H₂O proved inaccurate in W-content ($\pm 20\%$), but accurate in Zn-content. ICP-AES measurements were performed on a Perkin Elmer Optima 3000, using a rhodium standard.

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- 11 It was not determined whether the small amount of metal found in the permeates or in the membrane was present as POM catalyst, or as another type of metal compound. Since Q₁₂POM was prepared *via* self-assembly from Na₂WO₄ and ZnCl₂, it is possible that small amounts of these salts are still present.
- 12 The retention of QCl in C₆D₅CD₃ is 65% as determined by ¹H NMR spectroscopy. The activity increase after the first run is as expected from this retention and the dependence of the rate on the Q/POM ratio (ref 6).