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### Nanocatalysts: Properties and applications

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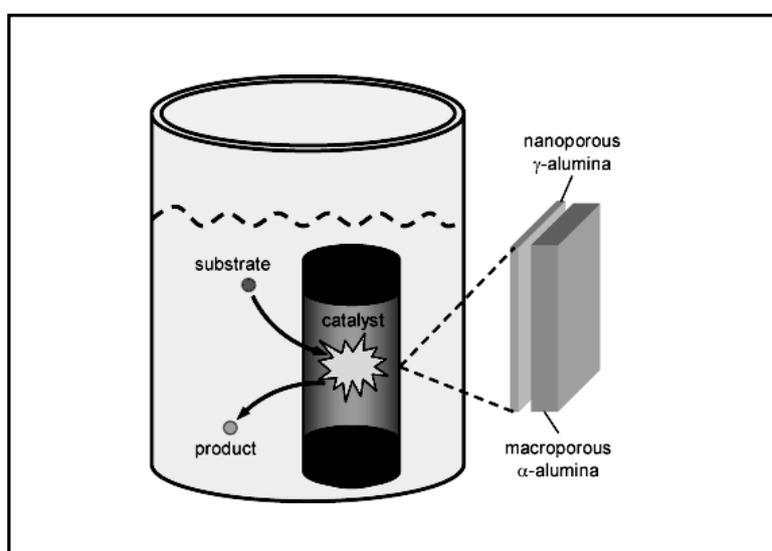
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## Chapter 6

### *‘Cat-in-a-cup’: Facile separation of nanocatalysts using ceramic membranes*



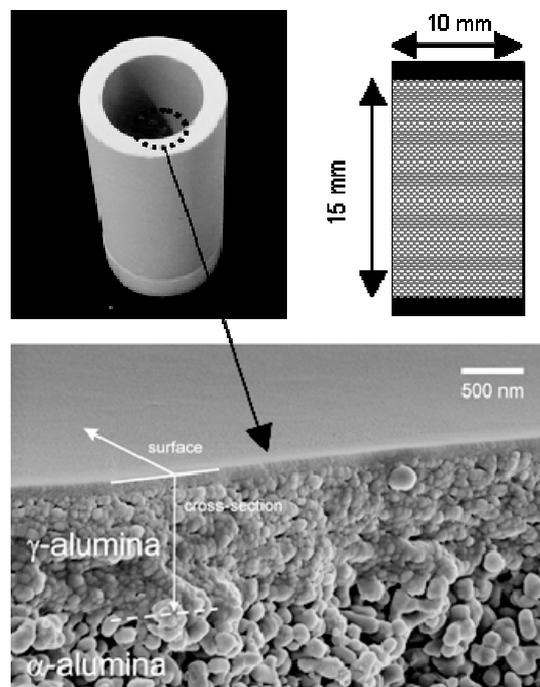
Part of this work is published as “Cat-in-a-cup: Facile separation of large homogeneous catalysts”, A. V. Gaikwad, V. Boffa, J. E. ten Elshof, G. Rothenberg, *Angew. Chem. Int. Ed.*, **2008**, *47*, 5407.

**Introduction**

Catalyst separation and recycling is the bane of homogeneous catalysis. This is true for both lab-scale experiments and large industrial processes.<sup>[1]</sup> A variety of ingenious solutions is available: selective product crystallisation, catalyst precipitation and filtration, flash distillation of the product, or extraction of the catalyst using e.g. supercritical solvents<sup>[2]</sup> (one can also tether the homogeneous complex onto a solid support, e.g. polymers<sup>[3-5]</sup>, zeolites<sup>[6, 7]</sup> or silica,<sup>[8]</sup> but then it is no longer homogeneous catalysis). One relatively new concept combines nanoporous membranes and high molecular weight transition-metal complexes.<sup>[9]</sup> Such membranes can effectively filter species a few nanometers in diameter (nanofiltration) to tens and hundreds of nanometers (ultrafiltration).<sup>[10]</sup> These diameters match with those of dendrimers and macromolecules, respectively. Current applications include hydrovinylation,<sup>[11]</sup> allylic amination,<sup>[12]</sup> and Kharasch addition.<sup>[13]</sup>

Unfortunately, many of these solutions require dedicated membrane reactor technology, which is often incompatible with conventional laboratory equipment. Moreover, organic polymer membranes are prone to swelling and leaching. To solve this problem, we turned to ceramic membranes.<sup>[14-17]</sup> As we recently showed, these can be designed and tailored to nanometric dimensions.<sup>[16, 17]</sup> In this communication, we present a novel and simple tool for separating homogeneous catalysts, using a multi-layered porous membrane cylinder (Figure 1). We demonstrate the utility of this “cat-in-a-cup” concept in the ruthenium-catalysed asymmetric transfer hydrogenation of acetophenone.

Our porous membrane cups are basically cylinders made of a thin nano-porous  $\gamma$ -alumina layer, coated on a macro-porous  $\alpha$ -alumina membrane (Figure 1).<sup>[18, 19]</sup> They are closed with Teflon caps on both sides. The cups are 15 mm tall, with an inner diameter of 7 mm. The molecular weight cut-off of the  $\gamma$ -alumina layer is 1000 Da. Although this is higher than most homogeneous complexes, it is well within the size range of dendrimers and oligomers.



**Figure 1.** (top) Photo and schematic of the two-layered porous catalyst separation cup (4 nm pore diameter) with MWCO 1000 Da; (bottom) HRSEM image of a cross-section of the membrane cup, showing the  $\alpha$ -alumina and  $\gamma$ -alumina layers.

### Experimental Section

**Methods and Instrumentation:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX 300 spectrometer at 300.1 MHz and 75.2 MHz, respectively. Inductive Coupled Plasma (ICP) measurements were performed on a Perkin Optima 3000 XL ICP instrument. Samples were first dried under vacuum at 65 °C and then digested using 6 ml of HCl and 2ml of HNO<sub>3</sub> and heated at 220 °C for 51 min. GC analysis was performed using an Interscience GC- 8000 gas chromatograph with a fused silica chiral capillary column (DBEXm, permethylated  $\beta$ -cyclodextrin doped into 14% cyanopropylphenyl / 86% dimethyl polysiloxane, 30 m  $\times$  0.25 mm  $\times$  0.25 mm ). GC conditions: isotherm at 80 °C (5 min); ramp at 5 °C/ min to 150 (5 min); ramp at 15 °C/ min to 220 min (15 min). Pentadecane was used as internal standard. All products are known compounds and were

identified by comparison of their GC retention times to those of authentic samples and by MS analysis. Chemicals were purchased from commercial firms (>99% pure).

**Procedure for preparing the bilayer porous membrane cup:** A porous  $\alpha$ -alumina tube of 10 mm outer diameter, 1.5 mm wall thickness, and with an average pore size of 80-120 nm (Pervatech, Netherlands) was coated on the inside with a boehmite sol, following a procedure described elsewhere in more detail.<sup>[15]</sup> The layer was dried in air and then heat-treated at 600°C, so that the boehmite film transformed into a  $\gamma$ -alumina phase with a porosity of ~55% and a pore diameter of 4.5-5 nm. A second layer of boehmite was deposited and transformed into  $\gamma$ -alumina using the same procedure. Then the tube was cut into segments of 2.0 cm length with a circular diamond saw blade. The cups were prepared from these segments by clamping flat Teflon disks on both sides of the segments.

**SEM analysis:** The thickness and morphology of the  $\gamma$ -alumina layer of the reactors were analyzed by Scanning Electron Microscopy (SEM) using a LEO 1550 FEG SEM. The SEM picture shows the cross section of the inner part of the tube. The  $\gamma$ -alumina layer can be seen to have a total thickness of about 1.2  $\mu\text{m}$ . The top part of the  $\gamma$ -alumina layer is very smooth, relatively dense and featureless, and has a thickness of about 150 nm. The remaining part of the  $\gamma$ -alumina layer has a spherical morphology and some larger macropores are visible in the picture. The semi-permeability of the membrane depends completely on the thin top layer.

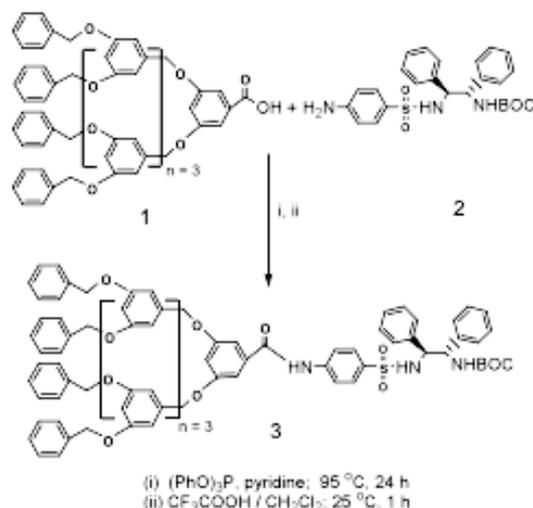
**General procedure for preparing the dendritic Ru<sup>II</sup> catalyst:** All reactions were carried out in standard Schlenk vessels under nitrogen. Third generation dendrimer 1 was prepared exactly as described by Fréchet.<sup>[24]</sup> Ligands **2**, **3** were prepared using the method described by Chen *et al.*<sup>[27]</sup> Then,  $[\text{RuCl}_2(\text{cymene})]_2$  (6.5 mg, 0.01 mmol), dendritic ligand **3** (1.1 equiv of Ru), and  $\text{NEt}_3$  (6.5  $\mu\text{L}$ , 0.04 mmol) were stirred in THF at room temperature for 2 h. All the intermediate dendrimers and ligands were analyzed using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

**Procedure for asymmetric transfer hydrogenation of acetophenone in the membrane reactor:** The membrane pellet was kept under vacuum overnight to remove the air from the pores and thus prevent any interference of oxygen. Then it was immersed in the distilled and dry *i*-PrOH under nitrogen for 2 h. The catalyst solution in 0.6 ml THF was injected into the cup under nitrogen, and the cup was sealed with a Teflon cap. The cup was placed on the stand in the membrane reactor. 20 ml of *i*-PrOH was injected in the

reactor and then acetophenone **4** (0.23 ml, 2 mmol), pentadecane (internal standard, 1 mmol) and *i*-PrOK (0.1 ml, 10 mmol) were added, and samples were analyzed by GC.

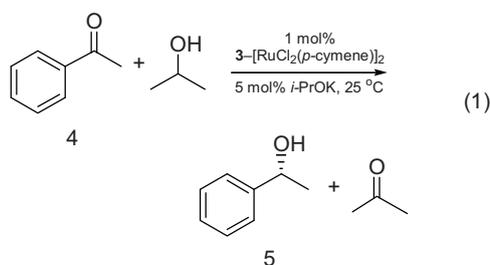
### Results and Discussions

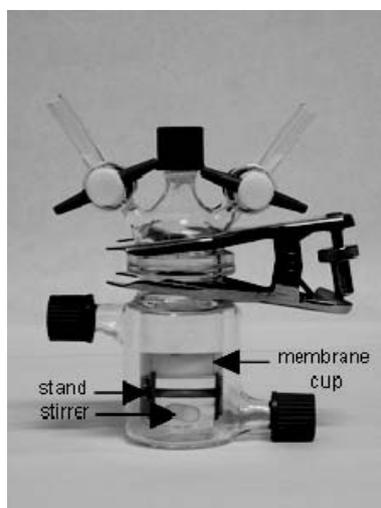
There are different approaches for making high-molecular-weight homogeneous catalysts, e.g. the covalent binding of ligands to soluble oligomers or polymers demonstrated by Plenio and co-workers.<sup>[5, 20]</sup> Here, we chose to attach a 'dendrimer anchor' to the homogeneous complex.<sup>[21-24]</sup> This creates a dendritic catalyst, with a controllable structure, that can be separated using nanofiltration.<sup>[25]</sup> We synthesised a third-generation Fréchet-type dendrimer scaffold (Mw 1240 Da),<sup>[24]</sup> attaching to it a Ru(II) complex with (*s,s*)-*N*-arenesulfonyl-1,2-diphenylethylenediamine ligands (TsDPEN). This complex, developed by Noyori and Ikariya,<sup>[26]</sup> is known as a good asymmetric transfer hydrogenation catalyst. Moreover, Chen et al. showed that attaching this complex to a dendrimer did not diminish its catalytic activity.<sup>[27-29]</sup> The core functionalized dendritic ligand was prepared by condensing the chiral (*s,s*)-DPEN **2** with third-generation polyether dendrons **1**, followed by deprotection of the BOC group (Scheme 1). The dendritic ruthenium complex was prepared by mixing the dendrimer ligand with [RuCl<sub>2</sub>(cymene)]<sub>2</sub> at 25 °C in THF (see supporting information for full experimental details).



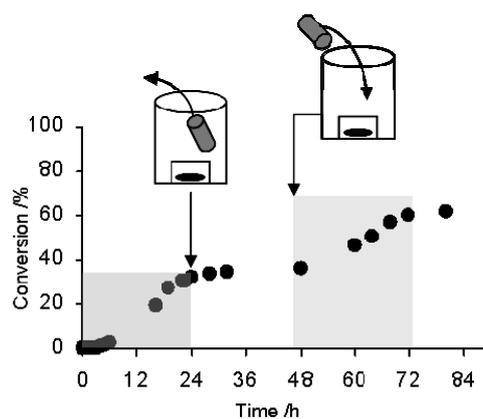
**Scheme 1.** Ts-DPEN ligand formation with third generation dendrimer.

We then tested the catalyst in the asymmetric transfer hydrogenation of acetophenone **4** with *i*-PrOH, in the presence of *i*-PrOK as base (eq 1). The reaction reached 65% conversion after 48 h, with high selectivity to (*s*)-1-phenylethanol **5** (95% *ee*). No reverse reaction was observed. Subsequently, we tested the same catalyst using our cat-in-a-cup system, under otherwise identical reaction conditions. For this, we used a 25 ml glass reactor, constructed in-house, where the alumina cylinder rests on a stainless steel stand above the magnetic stirrer (Figure 2). The membrane ‘cup’ was first placed under vacuum to remove oxygen from the pores. Then, it was immersed in *i*-PrOH for 2 h,<sup>[30]</sup> after which 0.6 ml of the Ru(II) complex were injected into the cup under N<sub>2</sub>. The cup was then sealed with a teflon cap, and placed in the reactor, together with 20 ml of *i*-PrOH. The reagents and base were added, and the mixture was stirred at 25 °C. Samples were taken every 2 h and analysed using GC. After 24 h, the membrane cup was removed and kept in *i*-PrOH under N<sub>2</sub> for 24 h. During this period, we continued sampling the reaction mixture. The cup was then replaced in the reactor and the reaction was continued for another 24 h. Figure 3 shows the results. The clear step-wise behaviour of the reaction profile supports our hypothesis that the catalyst indeed stays inside the membrane cup (ICP analysis of the reaction mixture at the end of the reaction showed that < 0.3% of the Ru leached into solution). The slight increase observed in the second 12-hour period is well within the experimental measurement error limits.





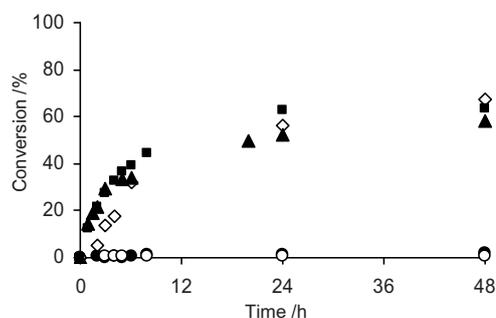
**Figure 2.** Photo of the reactor used for the ‘cat-in-a-cup’ experiments.



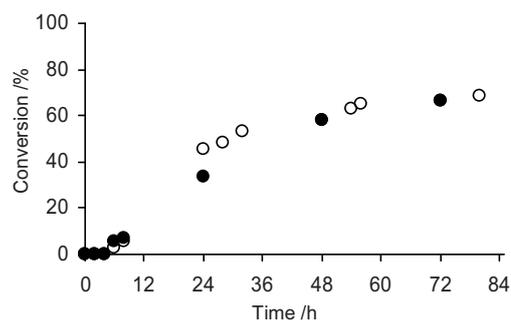
**Figure 3.** Stepped reaction profile for acetophenone conversion, showing the removal and replacement of the membrane cup at 24 h intervals. Reaction conditions: Acetophenone (0.23 ml, 2 mmol), pentadecane (internal standard, 1 mmol) and *i*-PrOK (0.1 ml, 10 mmol) stirred under N<sub>2</sub> in 20 ml of *i*-PrOH at 25 °C under nitrogen.

A series of control experiments was run to examine the background reaction effects (Figure 4). No conversion was observed in the absence of catalyst (‘○’ symbols), or when only the dendritic ligand was present (‘●’ symbols). Reactions in the presence of

the ruthenium precursor salt, the Ru complex, and the Ru-dendrimer complex (‘◊’, ‘■’, and ‘▲’ symbols, respectively) all gave similar conversions, but only the latter two showed enantioselectivity (93–95 *ee* in both cases). These reactions were also repeated without the membrane cup, placing the various catalysts in standard Schlenk reactors. The results were identical, affirming that the lack of enantioselectivity in the last three cases is not due to diffusion processes through the membrane. A separate series of extraction experiments followed by ICP analysis showed that the membrane cup retained > 99.7% of the Ru metal after stirring for 3 days in *i*-PrOH. Preliminary studies show that the ceramic membrane is highly stable at  $3 < \text{pH} < 7$ , and that no membrane fouling was observed.



**Figure 4.** Reaction profiles of the control experiments: ‘o’ symbols: reaction without catalyst; ‘•’ symbols: dendritic ligand only; ‘◊’ symbols: ruthenium salt precursor only; ‘■’ symbols: with catalyst but without dendritic ligand; ‘▲’ symbols: with catalyst and dendritic ligand. Reaction conditions are as in Figure 3.



**Figure 5.** Time resolved reaction profiles for two consecutive experiments using the same catalyst “cup” (‘•’ and ‘o’ symbols denote the first and second run, respectively) Reactions conditions for both runs are same as in Figure 3.

Indeed, catalyst recovery is only part of the problem in homogeneous systems. Recovery *per se* is often doable if you allow for catalyst destruction. Conversely, recovery and recycling is more challenging. Our concept has the potential to allow this, as shown by the recycling experiments in Figure 5. Here, the same catalyst “cup” was employed in two different runs, giving practically identical conversions, selectivities, and reaction rates. These results also show that the Ru catalyst retained in the membrane remains in the form of the dendrimer-supported complex. Note that the experimental system was cleaned carefully between the two runs, precluding any possibility of residual activity due to catalyst contamination.

### **Conclusion**

We showed that multilayered ceramic membranes can be combined with large molecular ligands, giving a simple and effective separation tool for homogeneous catalysis research. We hope that this cat-in-a-cup approach will be adopted and applied by the general catalysis community.

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