Catechol-functionalized (salen)Mn complexes can be supported on mesoporous anodized aluminium oxide disks to yield catalytic membranes that are highly active in the enantioselective epoxidation of olefins when being deployed in a forced-through-flow reactor.

Catalytic membrane reactors have attracted much attention over the last decade due to practical advantages over other reactor designs. They can potentially reduce the size of conventional reactors and cost of operation by combining two essential processes, chemical reaction and separation of the resulting products from the catalyst, in one stage. In particular, the catalytic membrane reactor configuration confers a significant advantage to oxidation reactions—the use of a catalytic membrane can provide a reactive interface for the oxidation to take place while avoiding long contact times of the desired product with catalysts, thereby minimizing over-oxidation.

Recent developments in the synthesis of inorganic materials have allowed chemists to create single-site catalysts and catalyst supports that provide a uniform environment around each active catalyst center. Among these inorganic materials, mesoporous anodic aluminium oxide (AAO) membranes have received great attention. They contain well-ordered, densely packed, nanoscale pores that naturally form when aluminium films are anodized in an acidic electrolyte. Although AAO membranes can be brittle, they are used in a number of diverse applications such as bioreactors, sensors, templates for quantum dots, nanowires, nanotubes, and nanofibers, and supports for metals and catalysts.

An attractive potential use for AAO membrane would be as a support for the immobilization of asymmetric homogeneous catalysts to generate an enantioselective catalytic membrane. Heterogenized asymmetric catalysts are intrinsically more economical and convenient to use than their homogeneous counterparts since they can provide a direct route to chiral products without costly separations. Among asymmetric homogeneous catalysts, chiral (salen)Mn complexes (Jacobsen–Katsuki catalysts) for the asymmetric epoxidation of olefins comprise one of the most widely immobilized classes of homogeneous catalysts. However, the ideal combination of activity, selectivity, and recyclability has not been achieved to date.

We have long been interested in the design of a catalytic system that can perform both a chemical transformation and a separation event within a single functionalized membrane material. To this end, we have explored the use of commercially available AAO membranes (Anodisc, Whatman) as the supporting materials for chiral (salen)Mn complexes. Being non-compressible and possessing high chemical and thermal stability, the AAO membranes can serve as a stationary phase suitable for incorporation into catalytic membrane reactors. In addition, their mono-disperse pores provide well-defined surfaces upon which site isolation of the supported catalyst can be more carefully controlled than in cross-linked polymers or other inorganic solid supports.

Herein, we report the fabrication of a chiral (salen)Mn-immobilized AAO membrane and demonstrate its use in a catalytic membrane reactor for enantioselective epoxidation. As anchoring groups for the (salen)Mn complexes, we have chosen catechol (1,2-dihydroxyphenyl), which has great affinity for Al ions and can adsorb strongly onto AlO3.

Our catechol-functionalized unsymmetrical chiral salen ligand can be prepared easily from (1R,2R)-diaminocyclohexane in good yield and then metallated with MnCl2/LiCl in air, resulting in complex 1. Immobilization of 1 was accomplished by stirring its ethanolic solution with an AAO membrane at 70 °C for 24 h, resulting in a brown membrane (1-AAO) (Fig. 1). The catalyst loading was determined by inductively coupled plasma (ICP) spectroscopy to be 4.1 μmol g⁻¹. The modified membrane was characterized by FT-IR, diffuse reflectance UV-Vis, and X-ray
Table 1  Catalytic performance of 1-AAO vs. 2 in the asymmetric epoxidation of 2,2-dimethyl-2H-chromene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield [%]</th>
<th>ee [%]</th>
<th>s [%](a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-AAO</td>
<td>79</td>
<td>81</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>1-AAO</td>
<td>72</td>
<td>76</td>
<td>99</td>
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<tr>
<td>3</td>
<td>1-AAO</td>
<td>62</td>
<td>73</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>1-AAO</td>
<td>51</td>
<td>69</td>
<td>95</td>
</tr>
<tr>
<td>5(^g)</td>
<td>2</td>
<td>82</td>
<td>86</td>
<td>100</td>
</tr>
</tbody>
</table>

\(a\) Reaction performed in a shell vial under ambient conditions using magnetic stirring. Molar ratio olefin/oxidant/catalyst = 100/2/1.

Table 2  Catalytic performance of 1-AAO in a liquid phase forced-through-flow reactor for the asymmetric epoxidation of 2,2-dimethyl-2H-chromene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cycle for membrane</th>
<th>Cycle for permeate</th>
<th>Flux [mL h(^{-1}) cm(^{-2})] (b)</th>
<th>Total TON(b)</th>
<th>Conversion [%] (c)</th>
<th>TOF [min(^{-1})] (d)</th>
<th>ee [%] (e)</th>
<th>s [%] (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>1174</td>
<td>47</td>
<td>20</td>
<td>86</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>4.5</td>
<td>1492</td>
<td>60</td>
<td>75</td>
<td>85</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>1(^e)</td>
<td>2</td>
<td>4.5</td>
<td>1174 (1st) + 820 (2nd)</td>
<td>80</td>
<td>n/a</td>
<td>85</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>7.5</td>
<td>1670</td>
<td>67</td>
<td>134</td>
<td>84</td>
<td>100</td>
</tr>
<tr>
<td>5(^g)</td>
<td>2</td>
<td>1</td>
<td>7.5</td>
<td>179</td>
<td>7</td>
<td>15</td>
<td>80</td>
<td>98</td>
</tr>
</tbody>
</table>

\(a\) Controlled by a syringe pump. \(b\) Total turnover number, based on conversion per catalyst. Molar ratio olefin/oxidant/catalyst = 10,000/2,500/1.

Fig. 2  Schematic diagram of the liquid-phase forced-through-flow catalytic membrane reactor for the enantioselective epoxidation of olefins.
membranes, which can then be used effectively in enantioselective catalytic membrane reactors. The supported catalytic membrane provided easy catalyst separation and recycling with comparable activity and selectivity to homogeneous counterparts. When used in a forced-through-flow reactor, it offered great flexibility in the control of substrate feed and product separation from the catalyst. Under optimized conditions, unusually high activity (TON = 1670, TOF = 135 min⁻¹) with high enantioselectivity and excellent chemoselectivity can be observed for olefin epoxidation. This strategy likely can be extended to other catalytic reactions, allowing for straightforward inexpensive isolation of valuable products as well as minimization of side reactions.

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Notes and references


11 Complex 2 is used in the control experiment instead of 1 because the latter is not very soluble in CH₂Cl₂ due to the exposed hydroxyl groups on the catechol moiety. In addition, the acidity of the phenolic protons of 1 can also cause side reactions with the epoxide products.

12 The use of excess oxidant was necessary because (a) high solubility of the oxidant (see ref. 12) as well as the high activity of the (salen)Mn⁺⁻O intermediate towards olefins.

13 Under the reaction conditions shown in Table 1, the first 40% of conversion occurred within 1 min, rendering the measurement of initial rate impractical. This fast reaction rate is due to the high solubility of the oxidant (see ref. 12) as well as the high activity of the (salen)Mn⁺⁻O intermediate towards olefins.

14 Due to phase-induced kinetic differences, the activities of salen-derived heterogenized catalysts for olefin epoxidation are often compared to those of their homogeneous counterparts in terms of TON or TOF, and not initial rate. See: (a) S. Keith and C.-H. Liu, Chem. Commun., 2002, 886–887; (b) F. Bigi, L. Moroni, R. Maggi and G. Sartori, Chem. Commun., 2002, 716–717.

15 Unlike AAO or mesoporous inorganic oxides with large pores, cross-linked polymer or small-pore zeolite supports may force the immobilized catalysts to adopt geometries that are significantly different from those of their homogeneous counterparts due to the limited size of the supporting cavities in these latter materials. See: (a) L. Canali and D. C. Sherrington, Chem. Soc. Rev., 1999, 28, 85–93; (b) F. Bedioui, Coord. Chem. Rev., 1999, 189–190, 69–91.


17 Although ICP analysis can yield the amount of manganese present in a membrane, not all of the Mn ions exist as supported (salen)Mn complex. The 83–87% of the initial Mn still present in the membrane after the 4th cycle represents an upper limit on the amount of (salen)Mn complex that has not been leached out, decomposed, or blocked.

18 Direct comparison of the batch reactor (Table 1) and the forced-through-flow reactor (Table 2) cannot be performed due to the differences in reagent concentrations and mass transport (flow through vs. diffusion).

