Development of porous materials for heterogeneous catalysis: kinetic resolution of epoxides

Leilani L. Welbes
Robert C. Scarrow
Haverford College, rscarrow@haverford.edu
A. S. Borovik

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Template copolymerization methods have been utilized to prepare porous materials with immobilized cobalt complexes that catalyze the hydrolytic kinetic resolution of epoxides.

Materials as heterogeneous catalysts are of interest because of ease of separation from the reaction mixture and reusability. Template copolymerization has shown promise for the design and preparation of heterogeneous catalysts. This process uses molecular precursors of known structure that are copolymerized in the presence of a porogen. The resulting materials contain immobilized sites that retain many of the structural properties present in the original template. Our group has shown that substitutionally inert metal complexes can serve as templates to prepare porous materials with sites having defined structure and geometry around the metal ion. Using 5 mol% template, we have achieved up to 90% site isolation and site accessibility. These materials reversibly bind small molecules, such as CO, NO and O₂.

In continuation of this work, we are developing methods that provide access to a wider range of materials from a common template. The ability to modulate the distance between template complexes is often an important parameter in the design of functional systems. Many chemical transformations require multiple complexes working in concert in order for the reaction to proceed while other chemical processes may be shut down if the complexes interact. We anticipated that varied structure of the immobilized sites can be obtained with a single template by adjusting the template: crosslinker ratio during the polymerization process to allow for the preparation of porous materials having different distributions of template and as a result, varying degrees of function for a specific chemical transformation. To evaluate this concept, we have prepared a series of porous polymers having varying concentrations of immobilized chiral cobalt–salen complexes to be used as heterogeneous catalysts for the hydrolytic kinetic resolution (HKR) of epoxides. Under homogeneous conditions, and on flexible solid supports, mechanistic studies suggest that two or more chiral metal complexes are necessary to achieve excellent resolution and selectivity. The results reported herein demonstrate the potential of this methodology in regulating the function of these materials by simply varying the concentration of template present.

The template used in this study, [CoIII1*(vpy)(dmap)]PF₆⁻, is a substitutionally inert metal complex where the dmap and vpy ligands are coordinated trans to each other in the axial positions. This template is a precatalyst with the active catalytic species (vide infra) being formed after template immobilization. Materials containing 5, 25, and 50 mol% template were prepared according to the procedure outlined in Scheme 1. The template is copolymerized with ethylene glycol dimethacrylate (EGDMA) to form the network copolymer, P-1*[(py)[CoCl₂]]. Chemical reduction of the CoIII sites to afford P-1*[(py)[CoII]] was achieved with butylpentamethylcyclopentadienyliron(n). This polymer contains immobilized CoII complexes, which were treated with acetic acid under aerobic conditions to produce the catalytically active polymer, formulated as P-1*[(py)[CoII(OAc)]].

The three polymers prepared with 50 mol% template were analyzed with XAS and EPR spectroscopies (Fig. 1). For P-1*[(py)[CoIII(dmap)]], XAS measurements are consistent with six-coordinate CoIII complexes immobilized within the porous EGDMA host. Both the X-ray absorption near edge spectrum (XANES) and extended X-ray absorption fine structure (EXAFS) data are superimposable with the results for [CoIII1*(vpy)(dmap)]++. XANES data on P-1*[(py)[CoII]] show the growth of an absorption shoulder at 7714 eV that is characteristic of four coordinate CoII complexes. Comparison of its intensity with that of P-1*[(CoIII(OAc)]++, a reference polymer containing immobilized CoIII(salen) complexes, suggests that somewhat less than half of the cobalt sites have been reduced in P-1*[(py)[CoII]]. EPR data corroborates the reduction of the immobilized cobalt complexes: the X-band EPR spectrum of P-1*[(py)[CoII]] at 77 K contains features at g-values of 3.2 and 1.97, which are consistent with a square planar CoIII complex having an S = 1/2 ground state. These findings imply that most of the immobilized sites in P-1*[(py)[CoII]] do not have the axial pyridine coordinated to the CoII centers; this agrees with the known weak interactions of template with copolymer chain.
binding of pyridine to Co$^{III}$(salen) complexes in solution and the solid state. $^{3,4}$ Reoxidation of the polymer in acetic acid under aerobic conditions results in a XANES spectrum very similar to that of the original P-1$^{1}\text{ppy}(\text{Co})^{III}(\text{dmap})$. In addition, oxidation leads to the expected loss of the low-spin Co$^{III}$ EPR signal (Fig. 1).

The function of these materials was probed in the HKR of epoxides using propylene oxide as a test substrate and the results of these studies are shown in Table 1. Entry 1 shows the result for the HKR of propylene oxide catalyzed with material containing 5 mol% template which has poor activity yielding only 6% diol, but with good selectivity. The low activity can be explained by the high degree of site isolation known to be exhibited in these types of materials, and mechanistic reports proposing a bimolecular pathway needed for function. $^{4,11}$

To improve the function of the material, we increased the concentration of the template in the polymer. Entries 2 and 3 demonstrate the effect of template concentration on the material’s ability to efficiently catalyze this reaction. The observed trend shows that as the percentage of the template increases within the material, the activity of the material increases. Of the three concentrations studied, materials containing 50 mol% template are the most active. Entries 3 and 4 show there is no difference between 24 and 48 h reaction times using materials that contain 50 mol% template. However, decreasing the reaction time to 12 h does affect the results considerably with very little diol formation observed (entry 5).

Entries 3, 6, and 7 point to the reusability of the material showing the results obtained for three consecutive cycles with material containing 50 mol% template. $^{5}$ The results show that the activity and selectivity is maintained during the recycling of the material (entries 6 and 7) and is enhanced compared to the first cycle (entries 3 and 6). One possible explanation for these observations is that dmap is not efficiently removed in the initial reduction of the material and is still present within the active site during the first cycle, thus blocking substrate access to the active sites. Support for this is given in the elemental analysis of the 50 mol% polymers, where there is no difference in nitrogen content between P-1$^{1}\text{ppy}(\text{Co})^{III}(\text{dmap})$ and P-1$^{1}\text{ppy}(\text{Co})^{II}$, indicating that little dmap is removed. With subsequent cycles there is a significant decrease in nitrogen within the polymer that can be attributed to the loss of dmap during work-up, allowing for the observed enhanced activity for the reused polymers. Consistent with reports for the homogenous systems, $^{6}$ we find that the immobilized cobalt centers are reduced following catalysis. After three cycles, XANES (Fig. 1) shows a much greater fraction of reduced cobalt than present after the initial reduction to form P-1$^{1}\text{ppy}(\text{Co})^{II}$ (Scheme 1). The greater fraction may be associated with the loss of dmap during turnover.

In summary, we have demonstrated that varying the percentage of the template complex, [Co$^{III}$(ppy)(dmap)]$, in the preparation of porous polymers leads to functionally different materials for the HKR of propylene oxide. Low template loadings produce polymers with isolated metal sites that are nearly inactive. Increasing the loadings to 50 mol% template gives reusable materials that catalyze the conversion of propylene oxide in moderate yield with good enantioselectivity. The results for these heterogeneous catalysts suggest that, in accordance with the previously proposed mechanism, a pathway involving more than one metal center may be necessary for catalysis. $^{4,11}$ However, the yields and enantioselectivities found for our heterogeneous polymers are lower than those reported for related homogeneous catalysts. $^{4,11}$ Improvements in the effectiveness of these materials by varying the template complex are currently under investigation.

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### Notes and references

$^4$ In control experiments, a 10–15% loss of propylene oxide is observed under normal experimental conditions in the absence of polymer; with polymer present, substrate loss is 15–20%. We attribute this loss to evaporation loss and transfer processes along with entrainment of the propylene oxide within the porous material, which increases as the amount of material increases (entries 1 & 2). In order to maintain constant cobalt concentration, less material was used as the template concentration within the polymer increased.

$^5$ There is less than 10% difference in results between independently prepared materials (see supplementary information).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Template</th>
<th>Cycle #</th>
<th>Time (h)</th>
<th>% Yield of epoxide</th>
<th>% Yield of diol</th>
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<td>6 (74)</td>
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<td>3</td>
<td>24</td>
<td>50 (42)</td>
<td>31 (86)</td>
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</table>

$^6$ Reactions run at room temperature in neat propylene oxide with water (0.55 equivalents) and polymer (0.002 equivalents of Co sites).

$^7$ % ee determined by chiral GC analysis; the (R)-epoxide and the (S)-diol are the major enantiomers. $^*$ Average results.

14. Abbreviations: dmap, 4-dimethylaminopyridine; vpy, 4-vinylpyridine; H$_2$1+, (R,R)-N,N'-bis(4-(4-vinylbenzoyloxy)-3-tert-butylsalicylidene)-1,2-cyclohexanediamine; XAS, X-ray absorption spectroscopy; EPR, electron paramagnetic resonance spectroscopy; H$_2$J, N,N'-bis(4-(4-vinylbenzoyloxy)salicylidene)-1-ethylimidazoline.