Enantioselective epoxidations catalyzed by zeolite MCM-22 encapsulated Jacobsen's catalyst

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A novel method for the encapsulation of homogeneous catalysts within the supercages (7.1 × 18.2 Å) of zeolite MCM-22 has been developed. By way of example, the well known asymmetric oxidation catalyst (R,R)-N,N-bis(3,5-di-*tert*-butylsalicylidedene)-1,2-cyclohexanediaminemanganese(III) chloride, a.k.a Jacobsen's catalyst, was occluded in MCM-22 during the zeolite synthesis. This ship-in-a-bottle complex exhibited both higher activity and enantioselectivity for the epoxidation of α-methylstyrene compared with the homogeneous catalyst.

KEY WORDS: MCM-22; Jacobsen's catalyst; oxidation catalysis; ship-in-a-bottle complex

1. Introduction

Chiral manganese complexes based on Schiff base "salen" type ligands continue to generate interest as asymmetric oxidation catalysts [1]. The most widely studied complex is (R,R)-N,N-bis(3,5-di-*tert*-butylsalicylidedene)-1,2-cyclohexanediaminemanganese(III) chloride or Jacobsen's catalyst [2]. There is growing interest in heterogenizing this reasonably expensive catalyst for separation/recovery reasons as well as potential enhancements in stability, activity and selectivity. Although, there has been modest success in tethering this complex to organic [3–5] and inorganic supports [6], these strategies require modification of the ligand. Additionally, multimolecular deactivation pathways are not precluded. It has been suggested that a resting state for Jacobsen's catalyst is a μ-oxo bridged dimer, particularly at high pH [7]. Therefore, site isolation might also be a desirable feature for a supported catalyst of this type. Microporous metal oxide supports such as zeolites may provide this site isolation as well as size and shape selectivity. Complexes entrapped in zeolite pores but not necessarily bound to the oxide surface are often referred to as ship-in-a-bottle complexes [8]. Most of the aforementioned goals in oxidation catalysis such as enhanced activity, selectivity and stability have been realized with various ship-in-a-bottle complexes, however, further development of such systems has historically been self-limited by a rather poor choice of initial target substrates, *i.e.*, simple olefins and paraffins. Any practical application of ship-in-a-bottle complexes is most likely to be in a fine chemical process, where catalyst performance may outweigh the cost. For example, there would be merit in developing a heterogeneous asymmetric catalyst using the ship-in-a-bottle concept. Therefore, in this paper we report a novel method for encapsulating Jacobsen's catalyst in the large cages of zeolite MCM-22.

Previous attempts to immobilize chiral Mn(salen) complexes in zeolites were beset with two problems [9,10]. The synthetic zeolites having the FAU or EMT topologies have been employed as host matrices for ship-in-a-bottle complexes but these structures would not accommodate Jacobsen's catalyst. So the choice of chiral ligand was based largely on size. Therefore, the first challenge is to find a zeolite with a large enough pore size. The second problem was the method of encapsulation, which involved assembling the complex within the pores. Invariably, this strategy results in uncomplexed or partially complexed metal ions and ligands as well as an uneven distribution of occluded species. Not surprisingly, the catalytic results from these prior studies were disappointing. So the second challenge is to encapsulate the intact Jacobsen's catalyst so there is no doubt as to the nature of the guest molecules. In order to encapsulate Jacobsen's catalyst in a zeolite cage having apertures small enough to preclude leaching, the complex should be occluded during synthesis.

Zeolite MCM-22 [11–15], which has a very large cage (7.1 × 18.2 Å in diameter), has emerged as a viable host, in part because the synthesis of MCM-22 proceeds through a layered precursor [12]. At this stage in the synthesis, Jacobsen's catalyst can be intercalated between the layers. Then upon drying and heating to 280 °C the layers condense to form the crystalline MCM-22 structure and the associated large cages. The metal complex becomes encapsulated during this process with no possible means of escape through the 4 × 5.4 Å openings to the cage. Figure 1 shows the minimized structure of Jacobsen's catalyst within the MCM-22 cage. There are no close contacts in this orientation which

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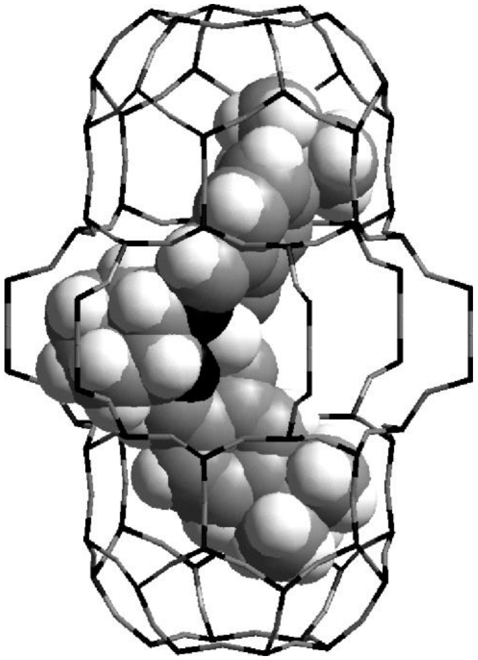

Figure 1. Structure of Jacobsen's catalyst minimized in an MCM-22 supercage calculated using Cerius^2 and the crystallographic parameters in [11].

still leaves ample room for oxidant and substrates. Preliminary characterization of the MCM-22 encapsulated complex and evaluation as a catalyst for the enantioselective epoxidation of α-methylstyrene is reported herein.

2. Experimental

The zeolite MCM-22 synthesis was based largely on a published procedure [13] using hexamethyleneimine (HMI) as the template, where a gel mixture having the molar ratio of $SiO_2/Al_2O_3 = 30$, $Na/SiO_2 = 0.18$, $HMI/SiO_2 = 0.35$, $H_2O/SiO_2 = 20.5$ was heated at 150 °C for 7 days with rotation (30 rpm). After cooling to room temperature the layered MCM-22 precursor was stirred with an ethanolic solution of Jacobsen's catalyst at RT overnight. The resulting product was suction filtered followed by drying in air overnight. MCM-22 was formed by heating a shallow bed of the dried precursor at 280 °C for 16 h. After calcination the MCM-22 was stirred in ethanol for 4 h and aqueous NaCl for 2 h to remove any surface species. The MCM-22 structure was verified by X-ray powder diffraction using a Scintag XDS 2000 diffractometer and Cu Kα radiation. The Si/Al ratio was 17 for the product MCM-22. The loading of metal complex was determined by elemental analysis (Galbraith Laboratory Inc., Knoxville, TN).

A typical oxidation reaction involved first preparing a solution of oxidant as follows: 6 ml of Clorox bleach mixed with 5 ml of 0.05 M of Na_2HPO_4 were cooled to 4 °C and the pH adjusted to 10.45 using 1 M NaOH. To this solution was added 250 mg of the ship-in-a-bottle catalyst mixed with 1 ml of α-methylstyrene (Aldrich) in 6 ml of acetonitrile. This mixture was stirred under N_2 at 4 °C and products were analyzed by capillary gas chromatography using a Chiraldex column. After reaction there is no evidence of complex leaching or loss in zeolite crystallinity as a result of the high pH.

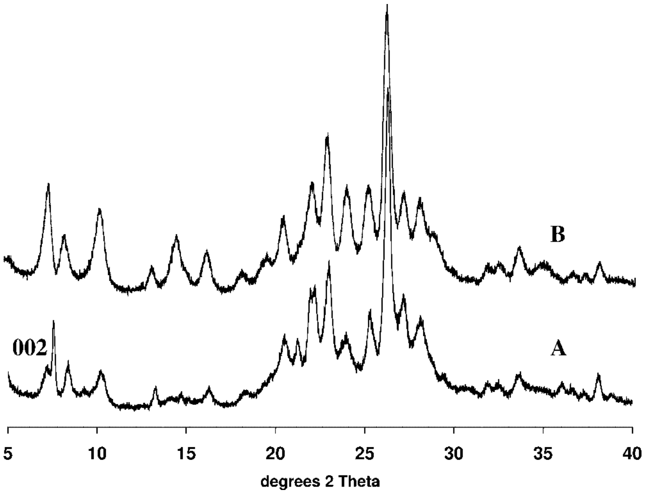

Figure 2. XRD patterns of (A) MCM-22 as-synthesized and (B) MCM-22 containing Jacobsen's catalyst after calcination at 300 °C.

3. Results and discussion

Zeolite MCM-22 has the MWW topology and consists of two independent pore systems. The first involves two-dimensional sinusoidal channels that are defined by 10-membered rings based on Si (Al) atoms. These channels should be partially occupied with HMI template under the conditions of this study since this section of template is apparently desorbed only above 400 °C [15]. The second pore system involves supercages 7.1 × 18.2 Å in diameter that are not connected with the other 10MR channels. Access to the supercages as seen in figure 1 is via six 10-membered rings, within the 2D layer that separates the other pore system. The HMI template is also located in the cages during synthesis but begins to desorb above 231 °C [15]. Additionally, HMI is probably lost during the intercalation process such that no residual template is expected to occupy any supercages after calcination at 280 °C. The supercages are formed as the layered MCM-22 precursor condenses with drying/heating. It is known that the MCM-22 layers can be swelled [16,17] or pillared [18,19]. So it was reasoned that metal complexes might be intercalated between the layers and would become entrapped during cage formation. It should be noted that the metal complexes must be added to the wet synthesis gel because once the MCM-22 precursor begins to dry the layers start to link and intercalation becomes impossible. After intercalation of Jacobsen's catalyst and heating at 280 °C, MCM-22 is formed as evidenced by the XRD pattern in figure 2. The 002 reflection may be used as an indicator in the transformation of the precursor phase to MCM-22 since the *c* parameter should decrease as the layers condense. The as-synthesized MCM-22 precursor and MCM-22 precursor containing Jacobsen's catalyst ex-

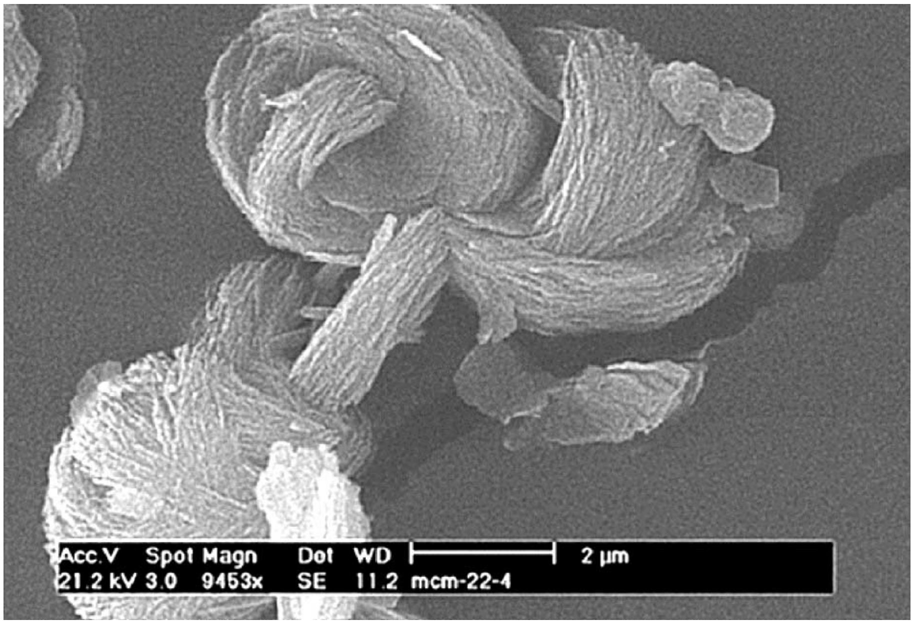

Figure 3. Scanning electron micrograph of MCM-22 containing Jacobsen’s catalyst.

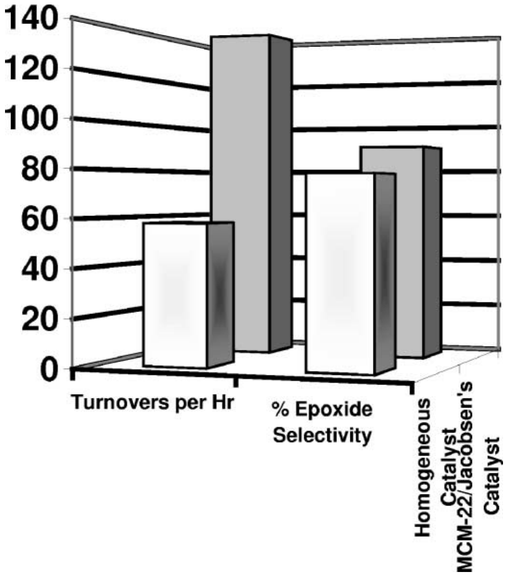

Figure 4. Plot of turnovers and percent epoxide selectivity for the oxidation of methylstyrene catalyzed by the homogeneous Jacobsen’s catalyst and MCM-22 encapsulated Jacobsen’s catalyst.

hibits 002 reflections at $d = 13.42$ and 13.7 Å, respectively. This corresponds to c parameters of 26.84 and 27.41 Å with and without complex. The slight increase between the layers may reflect the low loading of complex as well as some extraction of the HMI template with ethanol during the intercalation process. After heating at 280 °C the 002 reflections shift to a calculated d spacing of 12.60 and 12.30 Å for MCM-22 and MCM-22 containing the complex. The corresponding unit cells (25.2 and 24.6 Å) get smaller as the layers condense and certainly in the range of crystalline MCM-22.

The entrapped manganese complex should be stable to above 300 °C [20] and elemental analysis after heating reveals a loading of 1 complex per 22 supercages based on Mn content. Although, this might seem like a low loading, it is actually beneficial for maintaining diffusion pathways within this 2D pore system. The SEM shown in figure 3 reveals the morphology of the complex-loaded MCM-22 crystals as aggregates of thin round/hexagonal platelets. Presumably, access to the catalyst would be *via* the lamellae edges or the a direction. There are no obvious amorphous regions that could contain complex and influence catalytic results.

In order to probe the catalytic activity of the encapsulated complex, the oxidation of α-methylstyrene using hypochlorite as the oxidant was investigated. The reaction conditions mimic those previously reported for Jacobsen’s catalyst [2] and may not be optimal. However, the homogeneous reaction was run simultaneously for comparison and will be the benchmark for performance. The primary product of α-methylstyrene oxidation is the epoxide, with smaller amounts of the 2-phenylpropanol and 2-phenylpropanal. Figure 4 shows a plot of % selectivity for the epoxide product as well as the turnover frequency (moles product/moles catalyst per hour) after 4 h. Not only is the encapsulated catalyst more active than the homogeneous catalyst but the selectivity for the epoxide is also improved. The most remarkable feature of this ship-in-a-bottle system is the enantioselectivity, which is 91.3% ee *versus* 51% ee for the homogeneous catalyst. The origin of this dramatic enhancement in catalyst selectivity must be consequence of the steric constraints imposed supercage dimensions. This is further illustrated by the oxidation of cyclooctene, which should have a more difficult time negotiating the 4×5.4 Å pore openings. The homogeneous catalyst results in ~57% conversion largely to the alcohol after 20 h whereas the zeolite encapsulated complex produces less than 1% conversion under the same conditions. So not only does this confirm the intrazeolite location of Jacobsen’s catalyst but this also indicates that size and shape selectivity might be achieved with this MCM-22-based system. It should also be noted that MCM-22 calcined at 280 or 500 °C does not catalyze this reaction. There is also no change in enantioselectivity or conversion when the MCM-22 calcined at 280 °C is added to the homogeneous reaction. This indicates that any complex adsorbed on the outside surface of the zeolite would not be selective. Additionally, there was no further conversion of a reaction solution that was separated from the active ship-in-a-bottle catalyst after 4 h which indicates no leaching of complex. Again these observations are consistent with occlusion of the active catalyst in the MCM-22 cages.

4. Conclusion

We have presented the first example of a metal complex entrapped in zeolite MCM-22. This novel host zeolite and the method of encapsulation should prove to be a quite useful for the preparation of ship-in-a-bottle type catalysts. The immobilization of Jacobsen's catalyst in MCM-22 probably provides the first good example of a heterogeneous chiral "MnSalen" type catalyst that exhibits dramatically enhanced activity and enantioselectivity. These preliminary results certainly encourage further investigation of asymmetric oxidation reactions catalyzed with this system.

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