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**RING OPENING OF OXIRANES CATALYZED BY Mn-SALEN
IMMOBILIZED MESOPOROUS MATERIALS**

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Abstract: Mn-Salen immobilized mesoporous materials were found to be efficient solid catalysts for the nucleophilic ring opening of oxiranes with TMSN_3 , TMSCN and aniline.

Cyanohydrin trimethylsilyl ethers and azidosilyl ethers are industrially valuable and important intermediates in the synthesis of cyanohydrins, β -amino alcohols, α -amino acids and other biologically active compounds^{1,2} and substantial progress has been made recently in the development of catalytic methods for this class of compounds by the ring opening of epoxides. It is generally performed using various homogeneous and heterogeneous Lewis acid catalysts such as ZnI_2 ³, LaCl_3 ⁴, metal tartrates⁵ and KCN-18-Crown-6 or $\text{Bu}_4\text{N}^+\text{CN}^-$ ⁶ etc. Current interest

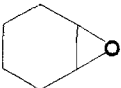
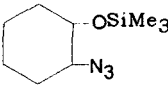
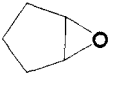
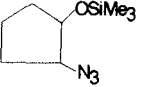
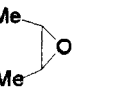
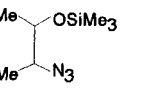
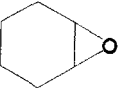
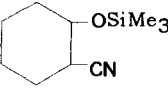
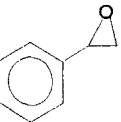
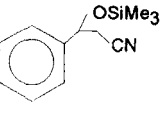
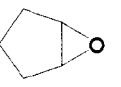
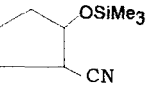
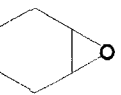
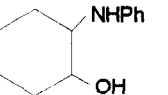
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is focused on the replacement of corrosive Lewis acids with environmentally friendly solid acids and bases. Zeolites⁷, clays^{8,9}, hydroxyapatite⁹, calcium fluoride⁹, and hydrotalcites¹⁰ are increasingly finding application in several important organic transformations including TMSCN addition reactions. Immobilization of metal complexes on solid supports can provide catalysts which are easier to handle and possibly exhibit improved activity, reusability and selectivity because of the support environment. Although few efforts have been made towards development of a variety of heterogenized Mn-salen complexes for asymmetric epoxidations^{11,12}, no effort has reportedly been made to date on the ring opening reactions. The recently discovered family of mesoporous material MCM¹³ possessing conceivable industrial application in fine chemical synthesis due to its tuneable larger pore size prompted us to design immobilized catalysts using MCM-41 as a support for ring opening reactions.

Herein we report Mn-salen immobilized mesoporous materials catalyzed nucleophilic ring opening reactions of oxiranes in very good yields (Table 1) for the first time. Trans products are obtained exclusively for entries (1, 2, 3). Robustness of the catalyst can be evident from the fact that this catalyst can be recycled for five times without any significant loss in activity. We have also investigated the ring opening reactions with the chiral Mn-salen complex immobilized on mesoporous materials. The azidosilyl ethers are obtained in good yields but in racemic form. Chiral Mn-salen complex¹⁴ also displayed no observable reactivity in ring-opening reactions whereas Cr-¹⁴ and Co-salen¹⁵ complexes are

Table 1. Ring opening of oxiranes by Mn-salen immobilized mesoporous materials

| Entry | Nucleophile | Substrate ^a | Product ^b | Catalyst | Yield (%) |
|-------|-------------------|---|---|----------|-----------------|
| 1 | TMSN ₃ |  |  | A | 76 ^c |
| | | | | C | 90 ^d |
| 2 | TMSN ₃ |  |  | A | 65 ^c |
| | | | | | |
| 3 | TMSN ₃ |  |  | A | 70 ^c |
| 4 | TMSCN |  |  | A | 60 ^c |
| | | | | B | 90 ^d |
| 5 | TMSCN |  |  | A | 90 ^d |
| | | | | B | 90 ^d |
| 6 | TMSCN |  |  | A | 90 ^d |
| | | | | B | 90 ^d |
| 7 | Aniline |  |  | A | 83 ^c |

^aSubstrates (1a-7a); ^bProducts (1b-7b); ^c Isolated Yields; ^d Yields determined by ¹H NMR.

A) Mn-salen mont.; B) Mn-salen MCM-41; C) Chiral Mn-salen mont;

Solvent : Benzene or n-heptane or DCM.

highly effective. Further work on ring opening reactions by chiral Cr- and Co-salen immobilized on mesoporous materials is under progress.

Experimental Section

Preparation of the catalysts :

(a) Mn-salen immobilized montmorillonite and MCM-41¹⁶ (Achiral) :

It was prepared by refluxing 2g of Na-K10 montmorillonite / Na-Al-MCM-41 and 1g of Mn-salen complex in 50 ml of water for 24 h. The solid catalyst was filtered, washed thoroughly with water, absolute ethanol, subjected to Soxhlet extraction in ethanol for 8h and then dried in vacuum for 24h at 100°C.

(b) Mn-salen immobilized montmorillonite (Chiral) :

It was prepared by refluxing 2g of Na-K10 montmorillonite and 1g of chiral Mn-salen complex in 50 ml of water and ethanol. The catalyst was filtered, washed with water-ethanol mixture, ethanol, subjected to Soxhlet extraction in ethanol for 8h and dried in vacuum for 24 h.

The plasma analysis results showed that the solids retained different amounts of manganese. A (2.05% of Mn), B (0.99% Mn), C (0.64% Mn). X-ray diffractogram of MCM-41 underwent no structural change during the preparation of the catalyst whereas Mn-salen immobilized montmorillonites (A and C) showed a basal region expansion (d_{001}) of 19.5-20.4Å° from 9.4Å° of montmorillonite which indicates the intercalation of Mn-Salen. The IR spectra of Mn-salen

immobilized montmorillonites and MCM-41 are in fair agreement with the IR spectra of homogeneous Mn-salen complex. UV-VIS spectra of the Mn-salen immobilized mesoporous materials (A-C) diluted in MgO show bands at 240, 280, 320, 390 and 500 nm similar to the absorption spectra of the corresponding Mn-salen complex. This further substantiated presence of Mn-salen complexes in the mesopores.

General procedure

0.150g Mn-salen exchanged montmorillonite and 0.2ml (2mmol) of cyclohexene epoxide were taken in benzene (10ml). To this solution 0.375ml (3 mmol) of TMSN₃ was added and stirred for 24 h. On completion of the reaction, the catalyst was filtered, concentrated and purified by column chromatography on silica gel. Yield : 326mg (76%). The products were characterised by ¹H NMR, IR, mass (1b-7b) and elemental analysis (4b, 5b and 6b). The spectral data of 1b, 2b, 3b and 7b are in accordance with the literature data⁵. Data of **1b**: IR (KBr), ν 2100 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz), δ 0.16 (s, 9H), 1.02-1.05 (m, 4H), 1.55-2.20 (m, 4H), 3.0-3.6 (m, 2H); MS, 213 (M⁺); **2b**: IR (KBr), ν 2100 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz), δ 0.12 (s, 9H), 1.23-2.25 (m, 6H), 3.4-3.7 (m, 1H), 3.78-4.10 (m, 1H); MS, 199 (M⁺); **3b**: IR (KBr), ν 2100 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz), δ 0.13 (s, 9H), 1.15 (d, 3H), 1.16 (d, 3H), 2.98-3.4 (m, 1H), 3.5-3.89 (m, 1H); MS, 187 (M⁺); **4b**: IR (KBr), ν 2200 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz), δ 0.16 (s, 9H), 1.02-1.05 (m, 4H), 1.55-2.20 (m, 4H), 3.0-3.6 (m, 2H); MS, 197 (M⁺); Anal. for C₁₀H₁₉NSiO: calcd.: C, 60.91; H, 9.64; N, 7.10; Found: C, 61.42;

H, 9.53; N, 6.9; **5b**: IR (KBr), ν 2200 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz), δ 0.3 (s, 9H), 2.7 (m, 2H), 4.4 (m, 1H), 6.9-7.4 (m, 5H); MS, 219 (M^+); Anal. for $\text{C}_{12}\text{H}_{17}\text{NSiO}$: calcd.: C, 65.75; H, 7.76; N, 6.39; Found: C, 66.02; H, 7.49; N, 7.57; **6b**: IR (KBr), ν 2200 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz), δ 0.12 (s, 9H), 1.23-2.25 (m, 6H), 3.4-3.7 (m, 1H), 3.78-4.10 (m, 1H); MS, 183 (M^+); Anal. for $\text{C}_9\text{H}_{17}\text{NSiO}$: calcd.: C, 59.01; H, 9.28; N, 7.65; Found: C, 61.23; H, 10.09; N, 8.3; **7b**: IR (KBr), ν 3400, 1580, 1500, 1280 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz), δ 1.00-1.52 (m, 4H), 1.55-1.88 (m, 2H), 1.88-2.24 (m, 2H), 2.86-3.45 (m, 2H), 3.34 (s, 2H), 6.48-6.5 (m, 3H), 6.96-7.23 (m, 2H); MS, 191 (M^+).

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