



Nanoporous alumino- and borosilicate-mediated Meinwald rearrangement of epoxides

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ABSTRACT

Nanoporous alumino- and borosilicate materials, produced using an evaporation-induced self-assembly approach (EISA), efficiently catalyse the Meinwald rearrangement of epoxides in dimethyl carbonate (DMC) to produce the corresponding carbonyl compounds in high yield and excellent selectivity.

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1. Introduction

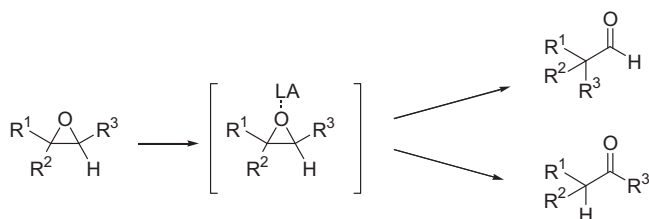
Epoxides are readily available and highly versatile intermediates which, due to their high reactivity, undergo Lewis acid catalysed nucleophilic ring-opening reactions in the presence of nucleophiles to yield valuable bifunctional compounds [1–4], or rearrangement reactions to produce cyclic [5–7] or carbonyl compounds [8,9]. This latter transformation, the Meinwald rearrangement has attracted considerable recent interest given the high efficiency of this protocol, and its potential for application in a range of synthetic and industrial processes (Scheme 1) [8,10–12].

The original synthetic protocols typically employed reagents with poor environmental profiles, such as boron trifluoride diethyl etherate, which have now largely been replaced by catalytic quantities of Lewis acids, such as palladium and gold salts, metalloporphyrin complexes, or indium trichloride and iridium trichloride, which have proven to be more efficient [13–17]. There remain, however, limitations to these protocols, whether it be due to

difficulties in recycling the catalyst, the requirement for prior synthesis of the catalyst, or the requirement to employ expensive or rare metals. The drive towards the development of more environmentally benign catalytic systems for the Meinwald rearrangement has coincided with the emergence of strategies to valorise waste biomass streams. Terpenic compounds are one important group of renewable feedstock chemicals derived from waste biomass, which can be converted into highly valuable flavour and fragrance components [12,18,19]. This in turn has led to considerable interest in the application of heterogeneous systems which catalyse the Meinwald rearrangement of α -pinene oxide, derived from α -pinene which is produced in large quantities as a by-product from paper and wood industry activities [20–24]. The most industrially useful product of this reaction, campholenic aldehyde, has found use as an odorant additive and as an intermediate in the synthesis of a number of sandalwood-like fragrances. We recently reported that nanoporous aluminosilicate materials produced by an evaporation-induced self-assembly (EISA) approach are effective catalysts both for the Meinwald rearrangement and for tandem Meinwald rearrangement-acetalisation reactions of epoxides [11,25]. We now wish to report an extension of our studies in this area to the synthesis, characterisation and catalytic

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Scheme 1.

activity of large pore nanoporous aluminosilicate and borosilicate materials produced by a modified EISA procedure and their ability to efficiently catalyse the Meinwald rearrangement reaction of epoxides in dimethyl carbonate (DMC).

2. Materials and methods

2.1. General methods

Commercially available reagents were used without further purification. Commercial zeolite materials were purchased in their NH_4^+ form and calcined at 500°C for 3 h to provide the H^+ form. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz in CDCl_3 at 25°C . High resolution mass spectra (HRMS) were obtained courtesy of the EPSRC Mass Spectrometry Facility, Swansea University, UK.

2.2. Catalyst preparation

A range of small pore aluminosilicate and borosilicate materials, in addition to the unmodified silica material (S-1-(2.02)), were synthesised as described previously using an evaporation-induced self-assembly (EISA) method [26,27]. In addition, a number of larger pore silicate materials were synthesised by a modification of this EISA protocol as described previously [28]. A typical preparation for the synthesis of the large pore borosilicate B-13-(3.54) catalyst is as follows: cetyltrimethylammonium bromide (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 mL, 0.1 M), ethanol (17.5 mL) and water (22.5 mL). Tetraethyl orthosilicate (25 mL, 112 mmol) was then added and the mixture stirred for 10 min at 40°C . The solution was cooled to room temperature and boric acid (553 mg, 8.95 mmol) was added in one portion. The mixture was stirred for 20 min and then left to age at room temperature for 24 h. The resultant white solid was crushed into a fine powder and calcined in air at 550°C for 6 h to remove the organic template to give a fine white powder. All materials were stored at 140°C for at least 24 h prior to use.

2.3. Catalyst characterisation methods

Specific surface areas were obtained by the BET method at liquid nitrogen temperatures using a Micromeritics Gemini or a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120°C under a flow of helium for 2 h prior to analysis. Pore sizes were obtained using a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120°C under vacuum for 3 h prior to analysis. Pore sizes were calculated by applying the non-local density functional theory (NLDFT) method to the N_2 sorption at -196°C employing Quantachrome AS-1 software data reduction parameters. Low angle XRD patterns were obtained using a Panalytical X'Pert Pro diffractometer. Measurements were performed in transmission mode at room temperature using monochromatic $\text{CuK}\alpha 1$ radiation. TEM analysis was performed on a Jeol 2100 operated at 200 kV. Samples were prepared by dispersion in methanol by sonication and deposited onto

lacey carbon coated 300 mesh copper grids. ATR FT-IR spectra were obtained using a Perkin Elmer Spectrum Two spectrometer. NH_3 -TPD experiments were carried out using a Quantachrome ChemBet TPR/TPD Chemisorption Analyser. Prior to the measurements, approximately 30 mg of sample was activated by heating at 100°C for 1 h. The sample was then cooled to room temperature before treating with ammonia for 30 min. Physically adsorbed ammonia was removed by purging with helium at 90°C for 1 h before the NH_3 -TPD analysis. The NH_3 -TPD of the samples was carried out by increasing the cell temperature linearly from 90°C to 900°C with a heating rate of $20^\circ\text{C min}^{-1}$ and a helium flow rate of $80\text{ cm}^3\text{ min}^{-1}$. Elemental compositions were obtained with a JOEL scanning electron microscope fitted with an EDX detector using a 20 keV accelerating voltage. MAS-NMR spectra were obtained courtesy of the EPSRC National Solid State NMR Service, Durham University. Aluminium spectra were obtained using a Varian VNMRS system, with direct excitation (DE) and the results are reported relative to an external 1 M aqueous $\text{Al}(\text{NO}_3)_3$ solution. Silicon spectra were obtained using a Varian Unity Inova spectrometer with a DE or cross polarisation (CP) from protons and the results are reported in ppm with respect to neat tetramethylsilane. Boron spectra were obtained using a Varian VNMRS system and results are reported relative to external $\text{BF}_3\cdot\text{Et}_2\text{O}$.

2.4. Catalyst testing and product analysis

All reactions were carried out in a stirred batch reactor. The catalyst was removed from the sample by filtration through a Celite plug, which was washed with DMC (2 mL \times 2 mL) and the combined solvents were removed under reduced pressure. Product mixtures were analysed using ^1H NMR and GC-MS techniques, and percentage conversions of reactions were determined by integration of the relevant signals from crude ^1H NMR spectra. Product distributions from reactions involving α -pinene oxide were also determined by GC analysis employing an FID detector with toluene as an external standard. These samples were analysed using a Varian Star 3800 Cx GC employing a 30 m CP-Wax 52 CB column. GC-MS analysis was performed using a Varian 450GC and Varian 300MS employing a VF-5ms capillary column (30 m, 0.25 mm i.d. and 0.25 μm) and a gradient temperature profile with an initial temperature of 50°C for 3 min rising to 280°C at a rate of $20^\circ\text{C min}^{-1}$.

2.5. General procedure for the Meinwald rearrangement of epoxides

The borosilicate catalyst B-13-(3.54) (25 mg) was added to a solution of styrene oxide (60 mg, 0.5 mmol) in DMC (2 mL) and the reaction heated to 40°C with vigorous stirring. On completion of the reaction, the catalyst was removed by filtration through a Celite plug which was washed with DMC (2 mL \times 2 mL) and the combined solvents were removed under reduced pressure to afford phenylacetaldehyde as a colourless oil; ν_{max} (film)/ cm^{-1} (neat) 2993, 1704, 1510, 1452 and 1127; ^1H NMR (400 MHz; CDCl_3) δ = 9.70 (1H, t, J = 2.0 Hz), 7.30–7.10 (5H, m), 3.60 (2H, d, J = 2.0 Hz); MS (EI) m/z 121 ($\text{M}+\text{H}$) $^+$; HRMS (EI) calculated for $\text{C}_8\text{H}_8\text{O}$ (M) $^+$ 120.0570, found (M) $^+$ 120.0568.

3. Results and discussion

3.1. Catalyst characterisation

All of the silicate materials generated displayed the expected large surface areas and narrow pore size distributions (Table 1). The nitrogen adsorption-desorption isotherms of all the materials appears to be a transition from type IV (mesoporous materials)

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