



Editor Choice Paper

Synthesis and catalytic activity of nanoporous aluminosilicate materials

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ABSTRACT

A range of nanoporous aluminosilicates varying in their aluminium content were synthesised using an evaporation-induced self-assembly (EISA) approach under acidic conditions. The nanoporous materials produced display narrow pore size distributions and the expected large BET surface areas. The activity and selectivity of these materials to function as Lewis acid catalysts for the addition of alcohols to styrene oxide and cyclohexene oxide were assessed and found to be optimum using high aluminium containing materials.

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1. Introduction

The preparation of inorganic solids with controlled pore size and surface properties has attracted considerable recent attention [1,2]. In particular, routes to silicate-based mesoporous materials which use surfactant templating approaches have proved to be popular, and a number of synthetic procedures employing a diverse range of reaction conditions have been reported [3–5]. These procedures, however, often lack good reproducibility, require long reaction times or utilize specialist equipment for the synthesis of relatively small quantities of the mesoporous material. As part of our studies into the use of silicate materials as heterogeneous catalysts, we required a simple and flexible route for the synthesis of silicate and aluminosilicate materials and were attracted to the simplicity of utilizing an evaporation based approach [6–8]. Evaporation-induced self-assembly (EISA) processes has proved to be one of the most straightforward methods for the preparation of highly ordered mesoporous silicate materials, and offers a ready access point to the production of silicate materials with a range of potential applications [9–11]. The EISA method has previously been employed for the formation of thin films of surfactant-templated silica, and has subsequently been employed for the synthesis of a variety of products including fibres and hollow spheres [5,12–14].

Typically, a solution of an inorganic silicate precursor and a template are mixed and the inorganic precursor is hydrolysed in the presence of small quantities of a mild acid. On evaporation of the solvent, the polymerisation of the silicate precursor is facilitated and ordered mesostructures are produced. Of particular interest to us was the report by Nagamine et al. that thin films of mesoporous silicas were produced by an EISA approach which was achieved by hydrolysing tetraethylorthosilicate (TEOS) under acidic conditions using ethanol as the solvent [15]. The physical properties of these films were controlled by varying the ratios of the template and inorganic precursor, or by controlling the rate of gelation by varying the ratio of acid to inorganic precursor. It is surprising that the use of EISA approaches for the synthesis of bulk silicate and aluminosilicate materials for catalytic applications has received relatively little attention given the apparent simplicity of this approach. In this paper we outline our recent progress in the synthesis and characterisation of aluminosilicate materials produced by the EISA approach and their use as highly effective heterogeneous catalysts for the addition reactions of alcohols to epoxides.

2. Experimental

2.1. Materials

All chemicals employed were purchased from the Aldrich Chemical Company and were used as received without further purification.

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2.2. Catalyst preparation

Three nanoporous aluminosilicates (AS-(111), AS-(88) and AS-(14)), in addition to the unmodified silica material (S-1), were synthesised using a modification of the method reported by Nagamine et al. [15]. A typical preparation for the synthesis of the aluminosilicate AS-(14) 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) and ethanol (17.5 ml). TEOS (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 aluminium nitrate nonahydrate (3.35 g, 8.95 mmol) was added in one portion. The mixture was stirred for 20 min and then left to age at room temperature for 1 week. The resultant orange solid was crushed into a fine powder, dried overnight at 90 °C and then calcined in air at 550 °C for 12 h to remove the organic template to give a fine white powder.

2.3. Characterisation

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 room temperature under a stream of helium for 3 h prior to analysis. Pore sizes were calculated from the desorption branch of the isotherm by the BJH Dv(d) method and pore volumes were determined using the DH method. Elemental compositions were obtained with a JOEL scanning electron microscope fitted with an EDX detector using a 20 keV accelerating voltage. Powder X-ray diffraction (PXRD) profiles of the mesoporous aluminosilicates were recorded on a Philips X'Pert diffractometer. 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 a DP pulse sequence and results are reported in ppm using a 1 M aqueous AlCl₃ solution as internal reference. Silicon spectra were obtained using a Varian Unity Inova spectrometer with a DP pulse sequence and results are reported in ppm with respect to tetramethylsilane.

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 dichloromethane (2 × 5 ml) and the combined solvents were removed under reduced pressure. Product mixtures were analysed using ¹H NMR, GC or GC-MS techniques and percentage conversions of reactions were determined by integration of the relevant signals from crude ¹H NMR spectra.

2.5. General procedure for the methanolysis of epoxides

The aluminosilicate catalyst AS-(14) (50 mg) was added to a solution of styrene oxide (120 mg, 1 mmol) in methanol (10 ml) and the reaction was stirred for 2 h at room temperature. On completion of the reaction, the catalyst was removed by filtration through a Celite plug which was washed with dichloromethane (2 × 5 ml) and the combined solvents were removed under reduced pressure to afford 2-methoxy-2-phenylethanol (114 mg, 95%) as a colorless oil; ν_{\max} (film) cm⁻¹ (neat) 3421, 2933, 1454, 1109, 1062, 1025, 757, 699 and 544; ¹H NMR (400 MHz; CDCl₃) δ = 7.44–7.29 (5H, m), 4.34 (1H, dd, *J* = 4 and 9 Hz), 3.74–3.59 (2H, m), 3.34 (3H, s), 2.45 (1H, br s); ¹³C NMR (100 MHz; CDCl₃) δ = 138.7, 129.4, 128.9, 127.5,

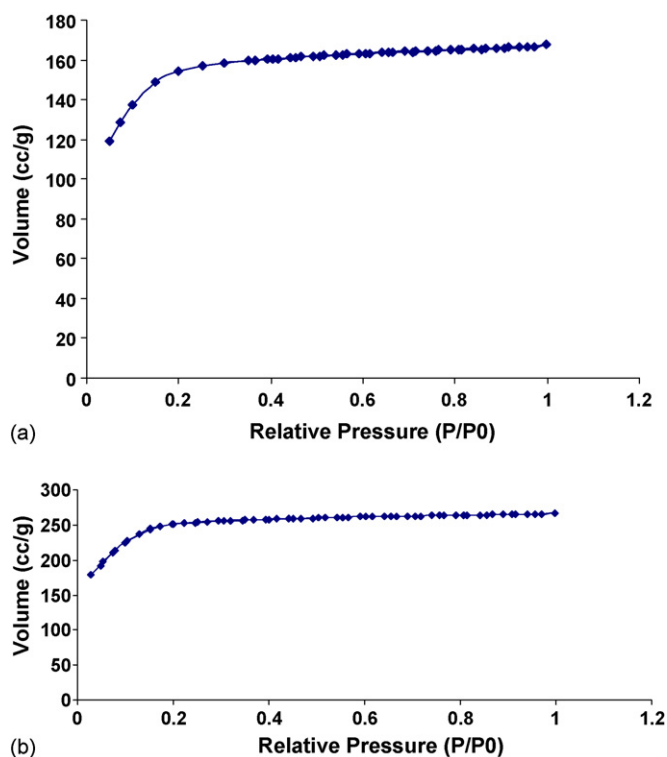


Fig. 1. BET isotherm of aluminosilicate: (a) AS-(14) and (b) AS-(88).

85.1, 67.8 and 57.3; MS (EI) *m/z* 152 (M)⁺; HRMS (ES) calculated for C₉H₁₆NO₂ (M+NH₄)⁺ 170.1176, found (M+NH₄)⁺ 170.1176.

3. Results and discussion

3.1. Characterisation

The nitrogen adsorption–desorption isotherms of all the materials displayed a reversible isotherm with no noticeable hysteresis (Fig. 1). Interestingly, the isotherms displayed a well-defined capillary condensation step at very low relative pressure (*P/P*₀ = 0.10–0.20), which is lower than those generally reported for mesostructured silica materials and is more typical of small-pore

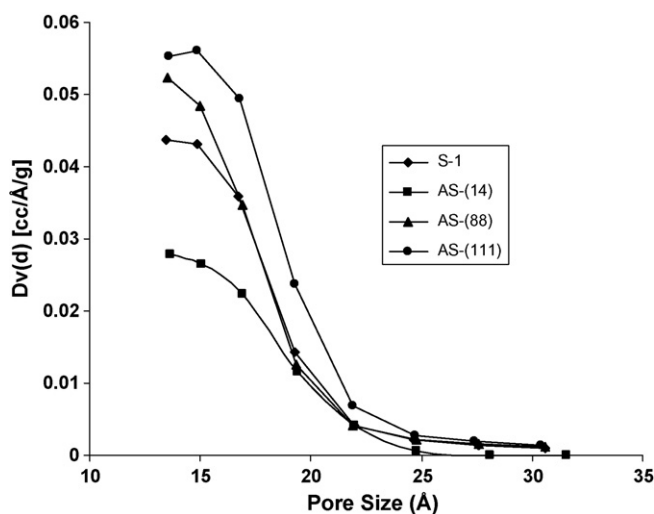


Fig. 2. Pore size distribution of aluminosilicate catalysts AS-(111), AS-(88), AS-(14) and S-1.

Table 1
Physical characteristics of the mesoporous catalysts AS-(111), AS-(88), AS-(14) and S-1.

Catalyst	Si/Al (nominal)	Si/Al (EDX) ^a	BET Surface area (m ² g ⁻¹) ^b	Pore volume (cm ³ g ⁻¹) ^c	Pore width (nm) ^d
S-1	–	–	704	0.277	1.49
AS-(111)	102	111	927	0.375	1.48
AS-(88)	72	88	789	0.298	1.35
AS-(14)	13	14	588	0.168	1.37

^a Determined by EDX analysis.

^b Surface areas were obtained by the BET method.

^c Pore volumes determined by the DH method.

^d Pore width determined by the BJH method.

mesoporous materials, suggesting that the samples have uniform and well ordered small mesoporous channels [16]. This was confirmed from the pore size data (Fig. 2) and surface areas for the samples calculated using the BJH method from adsorption branch of the isotherms. These results revealed a narrow pore size distribution for the silica material S-1 with a value of 1.49 nm and for the aluminosilicate materials AS-(111), AS-(88) and AS-(14) at values of 1.48, 1.35 and 1.37 nm, respectively indicative of a uniform small-pore mesostructure (Table 1 and Fig. 2). These results are in good agreement with the surface areas and pore volumes originally reported by Nagamine et al. for thin silicate films synthesised using this approach. The smaller pore sizes produced in this study are explained by the minor deviations in the reaction conditions, particularly the increased quantity of acid employed. The reduction in pore size and surface area for the high aluminium containing materials synthesised in this study is consistent with previous literature reports [17]. The PXRD data obtained were also similar to those reported by Nagamine et al. for the CTAB/TEOS ratio used in these studies. Small-angle PXD pattern (Fig. 3b) of the as-synthesised sample shows two well-resolved diffraction peaks ($2\theta=2.55^\circ$ and 3.86°) in the small-angle region suggestive of an ordered 2D hexagonal symmetry. After calcination, the PXRD pattern shows one broad diffraction peak at $2\theta=2.57^\circ$, revealing that long-range ordered nanostructure is retained (Fig. 3a).

EDX analysis demonstrated that aluminium was efficiently incorporated into the silicate material structure during the EISA process (Table 1), an observation that was further confirmed by MAS-NMR analysis of the samples. The ²⁷Al MAS-NMR for the calcined aluminosilicate sample AS-(14) (Fig. 4a) shows a broad resonance at 51 ppm due to tetrahedrally coordinated (framework) aluminium and a broad resonance at –1 ppm due to octahedrally coordinated (non-framework) aluminium in-line with previous reports [18]. The ²⁹Si MAS-NMR for the calcined aluminosilicate sample AS-(14) (Fig. 4b) shows a broad signal around –107 ppm accompanying a shoulder at –100 ppm which can be assigned to the Q⁴ and Q³ environments of silicon, respectively. A third weaker

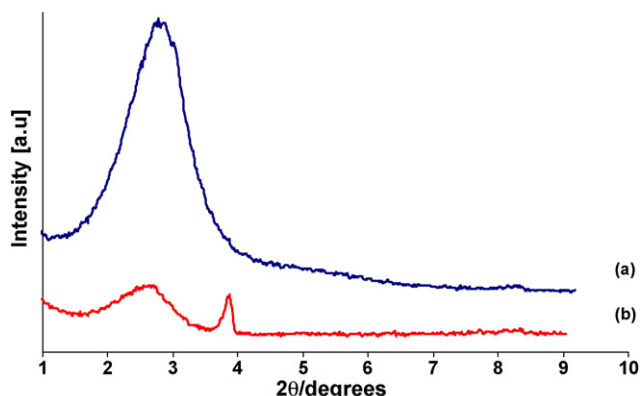


Fig. 3. Typical XRD pattern of: (a) calcined AS-(88) and (b) uncalcined AS-(88).

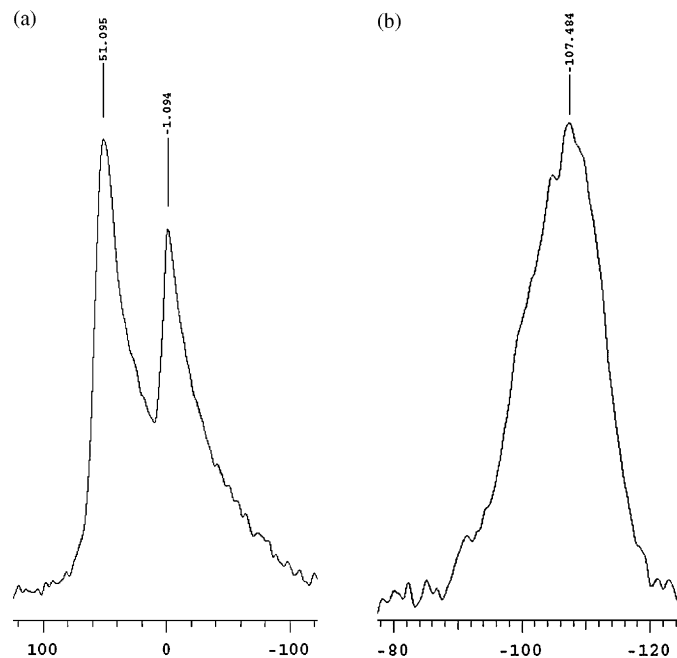


Fig. 4. (a) ²⁷Al MAS-NMR spectra of AS-(14) and (b) ²⁹Si MAS-NMR spectra of AS-(14).

shoulder at –92 ppm is present which is associated with the Q² environment [18]. The broadness of the signals is indicative of the noncrystalline nature of the siloxane network in the silicate materials [19] but can be deconvoluted to give three distinct resonances.

3.2. Catalytic activity

Epoxides are highly versatile synthetic intermediates and their ability to undergo ring-opening reactions with a variety of nucleophilic species with high regio- and stereoselectivity has been well

Table 2
Comparison of catalyst conversion for the formation of 2-methoxy-2-phenylethanol.

Entry	Catalyst	Conversion ^a	Selectivity ^b
1	S-1	0	–
2	AS-(111)	55	99:1
3	AS-(88)	88	97:3
4	AS-(14)	94	95:5

^a Reactions carried out using 1 mmol of styrene oxide in 10 ml methanol using 50 mg/mmol of catalyst.

^b Ratio of 2-methoxy-2-phenylethanol to phenylacetaldehyde was determined from ¹H NMR and/or GC-MS analysis of crude reaction mixture.

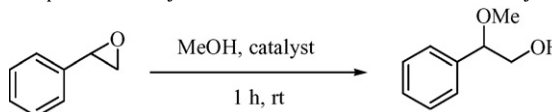
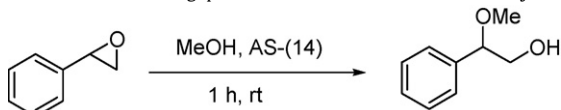
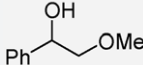
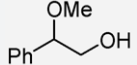
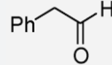


Table 3

The effect of increasing quantities of methanol on the selectivity of formation of 2-methoxy-2-phenylethanol and phenylacetaldehyde from styrene oxide.



Entry	MeOH (equiv.)	Conversion (%) ^{a,b}	% Composition		
					
1	0	5	–	–	100
2	2	35	20	60	20
3	4	28	17	70	13
4	8	22	9	79	12
5	Neat	94	–	95	5

^a Reactions carried out using 1 mmol of styrene oxide in 10 ml CH₂Cl₂ at room temperature for using 50 mg/mmol catalyst.^b Product selectivity determined from ¹H NMR and/or GC–MS analysis of crude mixture.

established [20–22]. The addition of alcohols to epoxides is a widely employed route β-alkoxyalcohols [23], however, the poor nucleophilicity of alcohols requires the use of strongly acidic or basic conditions or Lewis acid promoters. These protocols are often far from ideal, and suffer from disadvantages such as the high toxicity and corrosiveness of the acids employed, the requirement to use stoichiometric quantities and long reaction times or inconvenient handling procedures [24–26]. Therefore, the introduction of new methods for the nucleophilic ring-opening of epoxides that work under mild conditions is of continuing interest and the use of heterogeneous catalysts in particular has attracted considerable attention [27–29].

The ability of the nanoporous aluminosilicate materials to catalyze the formation of 2-methoxy-2-phenylethanol from styrene oxide and methanol was studied initially (Table 2). As expected, the unmodified silica S-1 demonstrated no catalytic activity and the starting material was recovered unchanged [30,31]. The incorporation of aluminium into the silica structure resulted in the production of highly effective catalysts and all of the aluminosilicate materials displayed good activity and high selectivity for the addition product. In all of these cases, trace quantities of phenylacetaldehyde (~1–5%), formed by a competing Meinwald rearrangement product were observed [32]. All subsequent reactions were undertaken with the AS-(14) material as this proved to be the most efficient catalyst in terms of overall conversion and selectivity for the addition product over the rearranged material [32]. Reactions carried out with no catalysts present gave no addition products and the starting materials were recovered unchanged in these cases.

3.3. Effect of the number of equivalents of MeOH

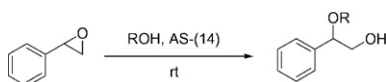
Experiments utilizing reduced quantities of methanol in non-polar co-solvents, such as dichloromethane, were undertaken using the AS-(14) catalyst and the selectivity for the β-alkoxyalcohol product was determined by analysis of the crude reaction mixture by ¹H NMR and/or GC–MS analysis (Table 3). It was observed that in the presence of a small excess of methanol (2–4 equiv.), poor conversion of the epoxide was observed and these reactions also displayed poor selectivity for the β-substituted product with significant quantities of the anti-Markovnikov addition product being generated. In addition, yields of the β-alkoxyalcohol product were further limited by the formation of phenylacetaldehyde produced in a competing Meinwald rearrangement reaction. Reactions carried out using larger quantities of methanol (8 equiv.) gave improved selectivity for the Markovnikov addition product and further improvements in both epoxide conversion and selectivity for the β-alkoxyalcohol product were achieved by carrying out the reactions in neat methanol which resulted in a complete suppression of the anti-Markovnikov addition pathway.

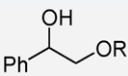
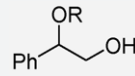
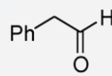
3.4. Addition reactions of higher alcohols

We next investigated the addition reactions of a range of different alcohols to styrene oxide (Table 4). It was observed that there was a decrease in both the formation of the Markovnikov addition product and a reduction in the selectivity in these cases, which is attributed to the increased steric bulk and decreased nucleophilicity of these alcohols. This leads to the requirement to employ

Table 4

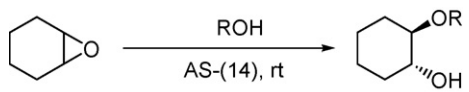
Selectivity for the addition of higher molecular weight alcohols to styrene oxide.



Entry	Nucleophile	R	Time (h)	Conversion ^{a,b} (%)	% Composition		
							
1	MeOH	Me	2	100	–	95	5
2	EtOH	Et	2	92	–	86	14
3	ⁱ PrOH	ⁱ Pr	3.5	64	14	73	13
4	^t BuOH	^t Bu	6	44	33	23	44
5	AcOH	Ac	23	73	–	40	60

^a Reactions carried out using 1 mmol of styrene oxide in 10 ml solvent and 50 mg/mmol AS-(14) catalyst.^b Product ratios determined from ¹H NMR and/or GC–MS analysis of crude mixture.

Table 5
Alcoholysis reactions of cyclohexene oxide.



Entry	Alcohol	R	Time (h)	Conversion (%) ^a	Selectivity ^b
1	MeOH	Me	1	100	100
2	EtOH	Et	1	100	75 ^c
3	ⁱ PrOH	ⁱ Pr	2	100	93 ^c
4	^t BuOH	^t Bu	2	100	96 ^c
5	AcOH	Ac	21	100	95 ^c

^a Reactions were carried out using 1 mmol of cyclohexene in 10 ml alcohol using 50 mg/mmol catalyst.

^b Determined from ¹H NMR and/or GC–MS analysis of crude mixture.

^c Mass balance is polymeric material.

extended reaction times and a subsequent increase in the quantities of anti-Markovnikov product and products derived from the competing Meinwald rearrangement. This was particularly pronounced in the case of *tert*-butanol, which required elevated temperatures in order to obtain satisfactory conversions and which gave phenylacetaldehyde as the major product. The use of acetic acid as a nucleophile generated the corresponding protected β -substituted alcohol, however, due to its reduced nucleophilicity, long reaction times were required with concomitant formation of significant quantities of the rearrangement product.

The additional reactions of a range of alcohols to cyclohexene oxide were also studied and these transformations proceeded more rapidly than the corresponding reactions involving styrene oxide and, in most cases, the reactions were complete within 2 h giving excellent conversions to the β -substituted alcohols (Table 5). In contrast to the styrene oxide case, these reactions proceeded to give products derived from anti-addition of the alcohol in all cases and no products derived from rearrangement reactions were observed [32].

4. Conclusions

In conclusion, we have shown that nanoporous aluminosilicates are easily synthesised using an EISA approach using ethanol as the solvent. The process is operationally simple requiring no specialist equipment and produces nanoporous silicate and aluminosilicate materials with pore sizes in the 1.3–1.5 nm range and with the expected large surface areas. Pore engineering of these materials is of considerable interest and, while many mesoporous materials with pore size greater than 2.5 nm have been prepared, the synthesis of materials with pore sizes between the upper limit of zeolites (1.2 nm) and the lower end of mesoporous materials has remained a significant challenge as only a limited range of template surfactants can be employed for their synthesis [33–36]. While a limited number of approaches for the synthesis of such materials have been reported, they typically suffer from such limitations as poor reproducibility, high cost or poor control of the physical properties of the final material [16,19,37,38]. The development of simple routes to such materials provides a significant advance potentially allowing for shape selective catalysis of organic molecules that are too large to access the pores of traditional zeolite catalyst technologies. Furthermore, these larger molecules are becoming increasingly more commercially important for heavy fraction crude oil processing, new specialty chemical development and new pharmaceutical precursor syntheses [39–41].

Our current interest in this area is concerned with the development of these materials as efficient heterogeneous catalysts and we have demonstrated that the aluminosilicates produced by this approach efficiently catalyze the regioselective addition of alcohols

to epoxides to produce β -alkoxyalcohols in high yields and with excellent selectivity. The facile synthesis of these catalysts, their benign nature, the ease of handling and the simplified reaction and isolation procedures make them a highly attractive alternative to current methodologies.

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