



Synthesis of nanoporous aluminosilicate materials and their application as highly selective heterogeneous catalysts for the synthesis of β -amino alcohols

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ABSTRACT

The ability of nanoporous aluminosilicate materials, synthesized using an evaporation-induced self-assembly (EISA) approach, to function as catalysts for the formation of β -amino alcohols from aromatic amines and epoxides was assessed. Materials containing high aluminium loadings displayed catalytic activity, giving the desired β -amino alcohols in high yield and with high selectivity for the Markovnikov addition product. These materials exhibited nanoporous pores, typically 1.34–1.49 nm, with a narrow pore size distribution and the expected large surface areas.

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1. Introduction

Since the initial disclosure of synthetic routes to ordered mesostructured silicate materials, surfactant directed self-assembly has developed into one of the most versatile and widely applied approaches for the synthesis of inorganic materials with controlled composition, structure and function [1,2]. Numerous studies have detailed the use of a range of templates which have been employed under a diverse range of reaction conditions for the synthesis of silicate materials in particular, providing access to materials with well-defined pore sizes and mesostructures [3–7]. One of the limitations, however, that is yet to be fully addressed in the continuing development of this field is the preparation of materials possessing regular pores in the 1.2–2.0 nm range, that is, materials with the pore size between the upper limit of zeolites and the lower end of mesoporous materials. Synthetic routes to silicas with pore sizes in this range are of considerable interest as, while numerous approaches to mesoporous materials with large pore sizes have been reported, the formation of ordered pores between 1.2 and 2.0 nm remains a significant challenge since there is only a limited number of template surfactants which can be employed

[4,8]. Although excellent progress has been made in this area, the current synthetic methods have several inherent drawbacks such as the requirement for hydrothermal conditions, poor control of the properties or poor reproducibility of the syntheses [8,9–12].

As part of our ongoing studies into the application of silicate materials as highly efficient and selective heterogeneous catalysts, we reported a simple and flexible route for the synthesis of nanoporous silicate and aluminosilicate materials using an evaporation-induced self-assembly (EISA) approach [13–15]. The EISA processes has proved to be one of the most straightforward methods for the preparation of highly ordered silicates, and offers a ready access point for the production of materials with a wide range of potential uses [16–18]. It has found application for the formation of thin films of surfactant-templated silicas, and has subsequently been employed for the synthesis of a variety of products including fibres and hollow spheres [5,19,20]. 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 simplicity of this approach. Our interest in this approach was stimulated by the work of Nagamine et al. who demonstrated that thin films of mesoporous silicates were produced using an EISA approach employing ethanol as the solvent [21]. Excellent control of the physical properties of the films was achieved by changing the ratios of the templating agent and inorganic precursor, or by controlling the rate of gelation by varying the ratio of acid to inorganic precursor. Thus, this approach

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Table 1
Physical characteristics of the nanoporous catalysts.

Catalyst	Si/Al (gel composition)	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-(44)	29	44	699	0.315	1.35
AS-(30)	23	30	580	0.266	1.34
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.

offers a potentially highly flexible, inexpensive, operationally simple and extremely versatile route to structured silicate materials. Importantly, it also addresses some of the limitations of previous methodologies for nanoporous silicate and aluminosilicate synthesis. In this paper we outline our recent progress in the synthesis of nanoporous aluminosilicate materials produced by the EISA approach, and their use as highly effective and selective heterogeneous catalysts for the addition reactions of aromatic amines 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.

2.2. Catalyst preparation and characterisation

Five nanoporous aluminosilicates (AS-(111), AS-(88), AS-(44), AS-(33) and AS-(14)), in addition to the unmodified silica material (S-1), were synthesized and characterised using a range of standard techniques (Table 1) as described previously [22]. 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). 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 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. 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.

2.4. General procedure for the aminolysis of epoxides

The aluminosilicate catalyst AS-(14) (120 mg) was added to a mixture of styrene oxide (118 mg, 0.98 mmol) and aniline (102 mg, 1.10 mmol) in dichloromethane (5 ml) which was stirred at room temperature. After 6 h the catalyst was removed by filtration

through a Celite plug which was washed with dichloromethane (2 × 5 ml). The combined solvents were removed under reduced pressure to give an oil that was purified by column chromatography (hexane → 20% ethyl acetate–hexane) to give the product a 19:1 mixture of 2-phenylamino-2-phenylethanol and 2-phenylamino-1-phenylethanol (150 mg, 70%) as a colourless oil; ν_{max} (film)/cm⁻¹ (neat) = 3394, 3026, 1600, 1499, 1315, 1064, 1026, 908, 748 and 691; ¹H NMR (CDCl₃, 400 MHz) δ = 7.47–7.11 (m, 6H), 6.74 (t, 2H, J = 8 Hz), 6.61 (d, 2H, J = 9 Hz), 4.53 (dd, 1H, J = 4 and 7 Hz), 3.96 (dd, 1H, J = 4 and 11 Hz), 3.77 (dd, 1H, J = 7 and 11 Hz), 2.03 (br s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ = 147.7, 140.6, 129.7, 129.6, 128.5, 127.2, 118.3, 114.3, 67.8, 60.3; MS (EI) m/z 213 (M)⁺; exact mass (ES) calculated for C₁₄H₁₆NO (M+H)⁺, 214.1226, found (M+H)⁺ 214.1225.

3. Results and discussion

3.1. Catalyst preparation and characterisation

The silica and aluminosilicate materials used in this study were produced using our previously reported procedure and were characterised using a range of standard techniques [13–15,22]. The nitrogen adsorption–desorption isotherms of all the materials displayed a reversible isotherm with no noticeable hysteresis (Fig. 1). The isotherms displayed a well-defined capillary condensation step at very low relative pressure (P/P_0 = 0.10–0.20), indicative of the formation of small pores less than 2.0 nm. The absence of any further adsorption and the lack of hysteresis at higher relative pressure regions indicate the absence of large macropores in the sample [23]. This was confirmed from the pore-size data (Fig. 2) calculated using the Barrett–Joyner–Halenda (BJH) method, which revealed a narrow pore size distribution for the aluminosilicate materials ranging between 1.34 and 1.49 nm (Table 1). While the reliability of this model has been the subject of some debate, the position of

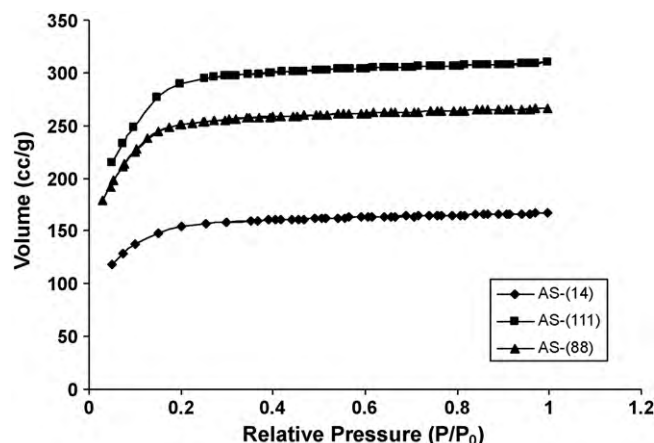
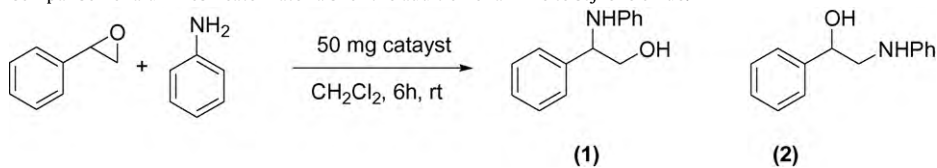


Fig. 1. Representative BET isotherm data.

Table 2
Comparison of aluminosilicate materials for the addition of aniline to styrene oxide.



Entry	Catalyst	Conversion (%) ^{a,b}	Selectivity (1:2) ^c
1	S-1	0	–
2	AS-(111)	28	95:5
3	AS-(88)	37	93:7
4	AS-(44)	30	95:5
5	AS-(30)	26	95:5
6	AS-(14)	37	95:5 ^d

^a Reactions employ 1 mmol of styrene oxide and 1 mmol of aniline in 5 ml CH₂Cl₂.

^b Conversion determined from ¹H NMR analysis of crude reaction mixtures.

^c Regioisomeric ratio determined from ¹H NMR analysis of crude reaction mixtures.

^d Regioisomeric ratio determined from ¹H NMR and GC–MS analysis of crude reaction mixtures.

the condensation step observed in our samples is a clear indication that the pore diameters in these materials are smaller than typical mesostructured silicates and so would appear to be generally valid in the size range under consideration [23–25].

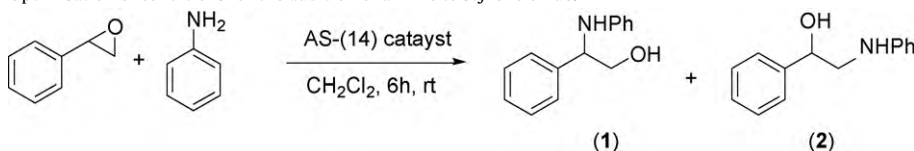
These observations are in good agreement with data originally reported by Nagamine et al. for thin silicate films synthesized using this approach [21]. The smaller pore sizes produced in this study are explained by the minor deviations in the reaction conditions, particularly the increased quantity of acid employed. The reduction in pore size and surface area for the high aluminium containing materials synthesized in this study is consistent with previous literature reports [26].

3.2. Catalytic activity and selectivity of nanoporous aluminosilicate materials

Epoxides are highly versatile synthetic intermediates and undergo a range of addition and rearrangement reactions [27–29].

The formation of β-amino alcohols from epoxides and amines is an important reaction in medicinal and organic chemistry as they are useful synthetic intermediates for the preparation of β-amino acids, in natural product synthesis and as chiral auxiliaries [30–32]. Typically, this transformation has been carried out using an excess of the amine nucleophile at elevated temperatures, however, these conditions are far from ideal as they are not tolerated by a number of functional groups, and the requirement to use an excess of the amine nucleophile impacts on the efficiency of the reaction [33]. Therefore, new methods which employ Lewis acid promoters, and which work at low temperatures employing near-stoichiometric amounts of amine, have continued to be of interest [34–38]. These approaches, however, also suffer from disadvantages, such as the toxicity of the Lewis acid catalyst employed, the extended reaction times or the requirement for protracted work-up procedures. Subsequent developments have focussed on the application of heterogeneous catalysts, and while these processes have greatly improved the overall atom efficiency of the process, they suffer

Table 3
Optimisation of conditions for the addition of aniline to styrene oxide.



Entry	Catalyst (mg/mmol epoxide)	Aniline (equiv.)	Conversion ^{a,b} (%)	Selectivity (1:2) ^b
1	50	1.1	37	95:5
2	50	1.1	28 ^c	95:5
3	50	1.1	53 ^d	95:5
4	50	1.4	33	95:5
5	50	1.8	29	95:5
6	50	2.1	30	95:5
7	50	1.1	26 ^e	88:12
8	50	1.1	33 ^f	90:10
9	50	1.1	66 ^{g,h}	80:20
10	50	1.1	33 ⁱ	82:18
11	100	1.1	53	95:5
12	120	1.1	70	95:5 ^j

^a Reactions employ 1 mmol of styrene oxide in 5 ml of CH₂Cl₂.

^b Determined from ¹H NMR analysis of crude reaction mixture.

^c Reaction at 40 °C.

^d Conversion after 24 h at room temperature.

^e Reaction in hexane.

^f Reaction in acetone.

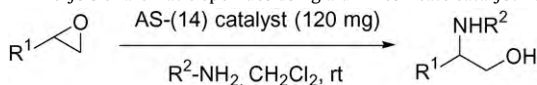
^g Reaction in ethanol.

^h Product contains 20% of 2-ethoxy-2-phenylethanol.

ⁱ Reaction in water over 2 h.

^j Determined by ¹H NMR and GC–MS analysis of crude reaction mixture.

Table 4
Aminolysis of aromatic epoxides using aluminosilicate catalyst AS-(14).



Entry	Epoxide	Aniline	Time (h)	Product	Yield (%) ^{a,b}
1		HNEt ₂	2		10 ^{c,d}
2			24		68 ^{e,f}
3			6		70 ^f
4			6		65 ^f
5			6		38 ^{f,g}
6			6		79 ^f
7			8		80 ^h

^a Isolated yield after column chromatography.

^b Reactions employ 120 mg of catalyst/mmol of epoxide and 1.1 equiv. of aniline in 5 ml of CH₂Cl₂.

^c Conversion from ¹H NMR analysis of crude reaction mixture.

^d Reaction at 40 °C using 50 mg of catalyst/mmol of epoxide in 5 ml of NHEt₂.

^e Reaction using 50 mg of catalyst/mmol of epoxide.

^f Product isolated as a 95:5 ratio of regioisomers. Major isomer shown.

^g Reaction at 40 °C.

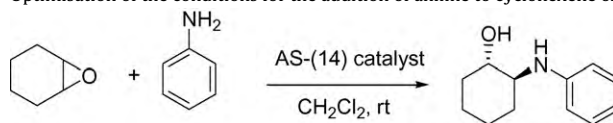
^h Product is an 85:15 ratio of regioisomers. Major isomer shown.

from limitations of their own [39–45]. We recently reported that nanoporous aluminosilicate materials function as highly efficient and selective heterogeneous catalysts for the preparation of β-alkoxy alcohols from epoxides and alcohols [13,46]. These reactions proceed rapidly under very mild reaction conditions and display excellent selectivity for the Markovnikov addition product. Given the obvious similarities in these transformations and the catalytic efficiency previously displayed by our nanoporous materials, we were interested in extending our initial studies to realise a new procedure for the preparation of β-amino alcohols from amines and epoxides under nanoporous aluminosilicate catalysis. We initially investigated the ability of five nanoporous aluminosilicate materials synthesized using the EISA approach, in addition to the plain silica material (Table 1), to catalyse the addition of aniline to styrene oxide (Table 2).

In line with our own and previous literature observations, the unmodified silica S-1 demonstrated no catalytic activity and the epoxide starting material was recovered unchanged (Table 2, entry 1) [46–48]. The incorporation of aluminium into the silica structure resulted in the production of effective catalysts for the addition reaction, and all of the aluminosilicate materials displayed activity to catalyse the addition reaction under the conditions employed. Importantly, all catalysts displayed high selectivity (typ-

ically 95:5) for the formation of the Markovnikov addition product 2-phenylamino-2-phenylethanol (**1**), over the anti-Markovnikov product 1-phenyl-2-(phenylamino)ethanol (**2**). Interestingly, and in contrast to our previous experience with addition reactions of alcohols to epoxides catalysed by these materials, no phenylac-

Table 5
Optimisation of the conditions for the addition of aniline to cyclohexene oxide.



Entry	Catalyst (mg/mmol epoxide)	Time (h)	Conversion ^{a,b} (%)
1	50	6	62 ^c
2	50	9	85
3	50	3	68 ^d
4	50	6	84 ^d
5	50	9	71 ^d
6	120	6	93

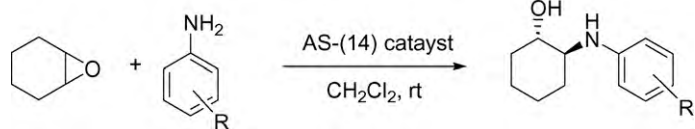
^a Reactions employ 1 mmol of epoxide and 1 mmol of aniline in 5 ml CH₂Cl₂.

^b Determined from ¹H NMR analysis of crude reaction mixture.

^c Determined from ¹H NMR and GC–MS analysis of crude reaction mixture.

^d Reaction at 40 °C.

Table 6
Aminolysis of cyclohexene oxide using aluminosilicate catalyst AS-(14).



Entry	Epoxide	Aniline	Time (h)	Product	Yield ^{a, b} (%)
1			12		65 ^{c, d}
2			6		85
3			6		65
4			18		61 ^d
5			12		69
6			6		53 ^{d, e}
7			12		57
8			12		61 ^{b, d}
9			24		61 ^{c, d}
10			6		81

^a Isolated yield after column chromatography.

^b Reactions using 120 mg of catalyst/mmol of epoxide and 1.1 equiv. of aniline in 5 ml of CH₂Cl₂.

^c Reaction at room temperature using 50 mg of catalyst/mmol of epoxide in 5 ml of CH₂Cl₂.

^d Conversion determined by ¹H NMR analysis of the crude reaction mixture.

^e Reaction at 40 °C using 50 mg of catalyst/mmol of epoxide in 5 ml of CH₂Cl₂.

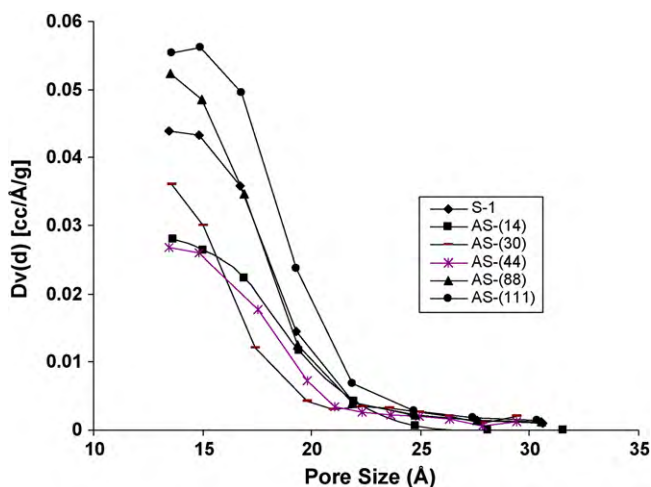


Fig. 2. Pore-size distribution of aluminosilicate catalysts.

etaldehyde was observed in the crude reaction mixture of these reactions. We have previously observed this product, formed by a competing Meinwald rearrangement reaction, in reactions in which the addition of the nucleophile is slow due either to its poor nucleophilicity or by competing steric factors [29,46,49].

3.3. Reaction optimisation and scope

We next optimised the reaction conditions using the addition of aniline to styrene oxide as a model reaction employing the AS-(14) material, and all subsequent reactions were undertaken with this catalyst. Reactions carried out with no catalysts present gave no addition products and the starting materials were recovered unchanged in these cases. Our initial reaction conditions replicated those we employed in our previous studies for the addition of alcohols to styrene oxide, and were carried out in dichloromethane at room temperature using 50 mg of catalyst/mmol of epoxide over 2 h (Table 3, entry 1).

These conditions, however, provided only moderate conversions to (1) even after extended reaction times (entries 1 and 3), albeit with high selectivity for the expected Markovnikov product. We envisage that the observed decrease in the conversion of epoxide to β -amino alcohol reflects the increased affinity of the amine for acidic sites in the aluminosilicate [50]. With this in mind, we next investigated reactions carried out at elevated temperatures, in different solvents or with increased quantities of aniline to assess whether these simple expedients would lead to improved conversions. Disappointingly, none of these measures provided an acceptable solution to resolve the limited reactivity observed (Table 3, entries 2 and 4–10). It was of interest, however, to observe that the reaction performed in water as the reaction medium (entry 10) gave conversions with selectivities that were comparable to reactions carried out in organic solvents. Indeed, only trace quantities of corresponding diol hydrolysis product were detected by ^1H NMR analysis of the crude reaction mixture. There has been considerable recent interest in the ring-opening reactions of epoxides in aqueous media, particularly those reactions involving amine nucleophiles [51–55]. Therefore, it is somewhat surprising that there appear to be no previous reports of similar protocols carried out using porous silicate catalysts.

We next studied reactions with increased quantities of catalyst, and under these conditions, we were gratified to observe that acceptable conversions of styrene oxide to aminolysis products were realised using near-stoichiometric quantities of the nucleophile at room temperature (entry 11). Further increasing the

quantity of catalyst to 120 mg/mmol of epoxide provided high isolated yields of the addition product which was obtained with excellent selectivity for the Markovnikov addition product (entry 12). With successful conditions established, the scope of the aluminosilicate catalysed addition was demonstrated with both a range of epoxides and amine nucleophiles (Table 4). All reactions proceeded to give the Markovnikov addition product with good to excellent selectivity, except in the case of the addition of aniline to 1,2-epoxy-3-phenoxypropane (entry 7) which gave the anti-Markovnikov product, derived from addition to the least hindered carbon of the epoxide, in accordance with literature reports [46].

We next studied the additional reactions of aniline to cyclohexene oxide. We have previously reported that for the addition of alcohols, these transformations proceed more rapidly than the corresponding reactions involving styrene oxide [13,46]. Therefore, a short additional optimisation study was completed which encompassed the effect of temperature, reaction time and catalyst quantity (Table 5). In line with our previous observations with this substrate, acceptable conversions were achieved using a lower quantity of catalyst (Table 5, entry 1), which were improved on extending reaction times (entry 2) or by carrying out the reactions at elevated temperatures (entry 3). It proved most expedient, however, to increase the quantity of catalyst to 120 mg/mmol of epoxide (entry 6), and under these conditions, the AS-(14) material again proved to be a highly effective catalyst for the addition of a diverse range of aromatic amine nucleophiles giving good to excellent isolated yields of β -amino alcohol products (Table 6).

4. Conclusions

In conclusion, we have demonstrated that both silica and aluminosilicates displaying pore sizes in the nano range, typically 1.3–1.5 nm, are easily and efficiently synthesized using a templated EISA approach. The process is operationally simple, requires no specialist equipment and gives materials with a narrow pore-size distribution and with the expected large surface areas. Synthetic routes to materials with pore sizes in this range are of considerable interest as, while numerous approaches to mesoporous materials with large pore sizes have been reported, the synthesis of materials with pore sizes between the upper limit of zeolites and the lower end of mesoporous materials remains a significant challenge. Our materials are highly flexible and well characterised heterogeneous solid acid catalysts, which efficiently catalyse the regioselective addition of aromatic amines to epoxides to produce β -amino alcohols in high yields and with excellent selectivity for the Markovnikov addition product. These silicate catalysts are highly stable, crystalline materials which are easy to handle, and the operationally simple protocol requires no special precautions, such as the exclusion of moisture or specialist equipment. Indeed, the reaction of styrene oxide with aniline carried out in water gives moderate conversion to the corresponding β -amino alcohol product with good selectivity. The addition reactions typically proceed at room temperature with near-stoichiometric quantities of the amine nucleophile to give good to excellent yields of the Markovnikov addition products from a range of epoxides and amines. The facile synthesis of these materials, their benign nature, their ease of handling, their high catalytic activity and the simplified reaction and isolation procedures make them a highly attractive alternative to current methodologies.

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References

- [1] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834–10843.
- [2] A. Taguchi, F. Schuth, *Micropor. Mesopor. Mater.* 77 (2005) 1–45.
- [3] T. Linsen, K. Cassiers, P. Cool, E.F. Vansant, *Adv. Colloid Interf. Sci.* 103 (2003) 121–147.
- [4] Y. Wan, D. Zhao, *Chem. Rev.* 107 (2007) 2821–2860.
- [5] P.J. Bruinsma, A.Y. Kim, J. Liu, S. Baskaran, *Chem. Mater.* 9 (1997) 2507–2512.
- [6] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* 279 (1998) 548–552.
- [7] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024–6036.
- [8] Z. Zhang, X. Yan, B. Tian, C. Yu, B. Tu, G. Zhu, S. Qiu, D. Zhao, *Micropor. Mesopor. Mater.* 90 (2006) 23–31.
- [9] S.A. Bagshaw, A.R. Hayman, *Micropor. Mesopor. Mater.* 44–45 (2001) 81–88.
- [10] R. Ryoo, I.S. Park, S. Jun, C.W. Lee, M. Kruk, M. Jaroniec, *J. Am. Chem. Soc.* 123 (2001) 1650–1657.
- [11] P.I. Ravikovitch, D. Wei, W.T. Chueh, G.L. Haller, A.V. Neimark, *J. Phys. Chem. B* 101 (1997) 3671–3679.
- [12] T. Sun, M.S. Wong, J.Y. Ying, *Chem. Commun.* (2000) 2057–2058.
- [13] M.W.C. Robinson, R. Buckle, I. Mabbett, G.M. Grant, A.E. Graham, *Tetrahedron Lett.* 48 (2007) 4723–4725.
- [14] M.W.C. Robinson, A.E. Graham, *Tetrahedron Lett.* 48 (2007) 2731–4727.
- [15] M.W.C. Robinson, D.A. Timms, S.M. Williams, A.E. Graham, *Tetrahedron Lett.* 48 (2007) 6249–6251.
- [16] D. Zhao, P. Yang, N. Melosh, J. Feng, B.F. Chmelka, G.D. Stucky, *Adv. Mater.* 10 (1998) 1380–1385.
- [17] Y.F. Lu, R. Ganguli, C.A. Drewien, M.T. Anderson, C.J. Brinker, W.L. Gong, Y.X. Guo, H. Soye, B. Dunn, M.H. Huang, J.I. Zink, *Nature* 389 (1997) 364–368.
- [18] Y. Klichko, M. Liang, E. Choi, S. Angelos, A.E. Nel, J.F. Stoddart, F. Tamanoi, J.I. Zink, *J. Am. Ceram. Soc.* 92 (2009) S2–S10.
- [19] M. Ogawa, N. Masukawa, *Micropor. Mesopor. Mater.* 38 (2000) 35–41.
- [20] C.J. Brinker, Y. Lu, A. Sellinger, H. Fan, *Adv. Mater.* 11 (1999) 579–585.
- [21] S. Nagamine, K. Kurumada, M. Tanigaki, A. Endo, *Micropor. Mesopor. Mater.* 49 (2001) 57–64.
- [22] M.W.C. Robinson, A.M. Davies, I. Mabbett, D.C. Apperley, S.H. Taylor, A.E. Graham, *J. Mol. Catal. A* 314 (2009) 10–14.
- [23] S.A. Bagshaw, A.R. Hayman, *Adv. Mater.* 13 (2001) 1011–1013.
- [24] J. Choma, M. Jaroniec, *Appl. Surf. Sci.* 253 (2007) 2287–5590.
- [25] T. Miyata, A. Endo, T. Ohmori, T. Akiya, M. Nakaiwa, *J. Colloid Interf. Sci.* 262 (2003) 116–125.
- [26] D.P. Serrano, R. van Grieken, J.A. Melero, A. García, *Appl. Catal. A* 319 (2007) 171–180.
- [27] D.J. Phillips, A.E. Graham, *Synlett* (2010) 769–773.
- [28] B.M. Smith, E.J. Skellam, S.J. Oxley, A.E. Graham, *Org. Biomol. Chem.* 5 (2007) 1979–1982.
- [29] D.D. Hughes, R. Buckle, M.W.C. Robinson, C. Torborg, M.C. Bagley, A.E. Graham, *Synth. Commun.* 38 (2008) 205–211.
- [30] D.J. Ager, I. Prakash, D.R. Schaad, *Chem. Rev.* 96 (1996) 835–875.
- [31] J. Joossens, P. Van der Veken, A.M. Lambeir, K. Augustyns, A. Haemers, *J. Med. Chem.* 47 (2004) 2411–2413.
- [32] P.G. Williams, W.Y. Yoshida, R.E. Moore, V.J. Paul, *J. Nat. Prod.* 65 (2002) 29–31.
- [33] M. Chini, P. Crotti, F. Macchia, *J. Org. Chem.* 56 (1991) 5939–5942.
- [34] E. Mai, C. Schneider, *Chem. Eur. J.* 13 (2007) 2729–2741.
- [35] F. Carrée, R. Gil, J. Collin, *Tetrahedron Lett.* 45 (2004) 7749–7751.
- [36] J.S. Yadav, A.R. Reddy, A.V. Narsaiah, B.V.S. Reddy, *J. Mol. Catal. A: Chem.* 261 (2007) 207–212.
- [37] A.T. Placzek, J.L. Donelson, R. Trivedi, R.A. Gibbs, S.K. De, *Tetrahedron Lett.* 46 (2005) 9029–9034.
- [38] G. Sekar, V.K. Singh, *J. Org. Chem.* 64 (1999) 287–289.
- [39] M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, *Eur. J. Org. Chem.* (2001) 4149–4152.
- [40] R.I. Kureshy, S. Singh, N.H. Khan, S.H.R. Abdi, E. Suresh, R.V. Jasra, *J. Mol. Catal. A: Chem.* 264 (2007) 162–169.
- [41] A.K. Chakraborti, A. Kondasar, S. Rudrawar, *Tetrahedron* 60 (2004) 9085–9091.
- [42] S.R. Kumar, P. Leelavathi, *J. Mol. Catal. A: Chem.* 266 (2007) 65–68.
- [43] L. Saikia, J.K. Satyarthi, D. Srinivas, P. Ratnasamy, *J. Catal.* 252 (2007) 148–160.
- [44] R. Chakravarti, H. Oveisi, P. Kalita, R.R. Pal, S.B. Halligudi, M.L. Kantam, A. Vinu, *Micropor. Mesopor. Mater.* 123 (2009) 338–344.
- [45] M. Hosseini-Sarvari, *Can. J. Chem.* 86 (2008) 65–71.
- [46] M.W.C. Robinson, A.M. Davies, I. Mabbett, S.H. Taylor, A.E. Graham, *Org. Biomol. Chem.* 7 (2009) 2559–2564.
- [47] K. Iwanami, J.-C. Choi, B. Lu, T. Sakakura, H. Yasuda, *Chem. Commun.* (2008) 1002–1004.
- [48] C. Ngamcharussrivichai, P. Wu, T. Tatsumi, *J. Catal.* 227 (2004) 448–458.
- [49] M.W.C. Robinson, K.S. Pillinger, A.E. Graham, *Tetrahedron Lett.* 47 (2006) 5919–5921.
- [50] R.G. Pearson, J. Songstad, *J. Am. Chem. Soc.* 89 (1967) 1827–1836.
- [51] A. Chanda, V.V. Fokin, *Chem. Rev.* 109 (2009) 725–748.
- [52] S. Liu, J. Xiao, *J. Mol. Catal. A* 270 (2007) 1–43.
- [53] N. Azizi, M.R. Saidi, *Tetrahedron* 63 (2007) 888–891.
- [54] H. Firouzabadi, N. Iranpoor, A. Khoshnood, *J. Mol. Catal. A* 274 (2007) 109–115.
- [55] S. Bonollo, F. Fringuelli, F. Pizzo, L. Vaccaro, *Synlett* (2008) 1574–1578.