ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Nanoporous Aluminosilicate-Mediated Synthesis of Ethers by a Dehydrative Etherification Approach

Thomas E. Davies,[†] Jacqueline R. Kean,[‡] David C. Apperley,[§] Stuart H. Taylor,[†] and Andrew E. Graham*,[‡]

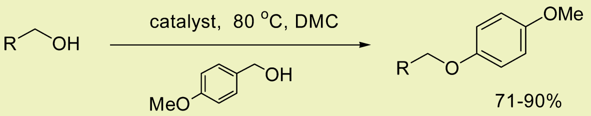
[†]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, U.K.

[‡]School of Applied Sciences, University of South Wales, Pontypridd, CF37 4AT, U.K.

[§]EPSRC Solid-State NMR Service, Department of Chemistry, Durham University, Durham, DH1 3LE, U.K.

Supporting Information

ABSTRACT: High aluminum containing nanoporous aluminosilicate materials, produced by an evaporation-induced self-assembly process, efficiently catalyze the formation of unsymmetrical ethers by a dehydrative etherification reaction in high isolated yields. By carrying out the reaction under dilute conditions, the quantities of reagents can be reduced to near stoichiometric quantities.



KEYWORDS: *Nanoporous aluminosilicates, Evaporation-induced self-assembly, Dehydrative etherification, Heterogeneous catalysis, Alcohol protecting groups*

INTRODUCTION

The development of new protocols and methodology for the protection of functional groups in synthetic sequences continues to be a vibrant research area, with a diverse array of strategies continuing to be reported.[1,2] The protection of alcohols and amines as benzyl and, in particular, *para*-methoxybenzyl (PMB) ethers has found widespread application due to their stability, their reluctance to undergo migration reactions, and their ease of removal. However, the formation of PMB ethers, and indeed the generation of ethers in general, poses significant synthetic and environmental challenges. The classical Williamson protocol generally employs an organohalide compound as the starting material which is unattractive due to its cost, toxicity, and their potential environmental impact.[3,4] Furthermore, these protocols also employ strongly basic conditions for the generation of the requisite alkoxide intermediate which can impose limitations on the substrate scope due to competing elimination reactions. Therefore, it is not surprising that there has been considerable interest both industrially and within the synthetic chemistry community in the development of methodology that produces ethers directly from alcohols by a dehydrative etherification approach. A number of elegant protocols employing activated benzylating agents[5−7] and both homogeneous[8−12] and heterogeneous catalysts[4,13,14] have been reported to be effective for the production of a wide range of structurally diverse ether products. In general, these approaches address many of the synthetic and environmental challenges outlined above but do have inherent limitations. In general, homogeneous catalysts can be problematic to recover and recycle, and activated benzylating agents can be expensive and prone to decomposition imposing limitations on their storage. Heterogeneous catalysts are more promising candidates for further development; however, the substrate range has typically been limited to the generation of symmetrical ethers. A major synthetic limitation common to all of these approaches is the requirement to use a large excess of one of the reagents to ensure high conversions and to limit the formation of unwanted self-condensation products which generate unproductive symmetrical ethers.

Our interest in this area was prompted by the chance observation that our nanoporous aluminosilicate materials generated significant quantities of furfuryl ethers from furfuryl alcohol and alkyl alcohols. With a few notable exceptions, aluminosilicate materials, such as zeolites, have proven to be disappointing promoters of dehydrative etherification reactions, with typical protocols displaying limited substrate scope or requiring high reaction temperatures or high pressures to achieve acceptable yields.[13,15−17] As part of our ongoing studies to develop new catalytic processes,[18−23] we undertook studies to assess the potential of these aluminiosilicate materials as catalysts for dehydrative etherification reactions, with the goal of developing a more efficient etherification protocol employing near stoichiometric quantities of reagents.

RESULTS AND DISCUSSION

A range of silicate (S-1) and aluminosilicate materials (Al-14-(2.42) and Al-56) displaying varying amounts of aluminum (Si/Al ratio 14:1 and 56:1, respectively) were synthesized using our previously reported evaporation induced self-assembly procedure (EISA)[18−20] and characterized using a range of standard techniques (Table 1 and pages S3−S15 of the Supporting

Received: November 25, 2013
Revised: January 14, 2014
Published: January 16, 2014

Table 1. Nanoporous Silicate Physical Properties

catalyst	Si/Al gel composition	Si/Al (EDX)[a]	BET surface area (m^{2}g^{-1})[b]	acidity (μmol g^{-1})[c]	pore width (nm)[d]
S-1			704	130	2.02
Al-14-(2.42)	13	12	489	440	2.42
Al-14-(3.18)	13	14	980	530	3.18
Al-56	54	56	639	230	1.87
zeolite Y-5	5	3	730[e]	nd[f]	nd[f]
ZSM-5-30	30	19	405[e]	nd[f]	nd[f]
ZSM-5-50	50	34	425[e]	nd[f]	nd[f]

[a] Determined by energy dispersive X-ray (EDX) analysis. [b] Obtained by the Brunauer–Emmett–Teller (BET) method. [c] Determined by temperature programmed desorption (TPD) analysis. [d] Determined by the nonlinear density function theory (NLDFT) method. [e] Manufacturers values. [f] Not determined.

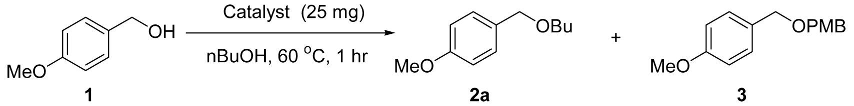
Information). The EISA process is a highly flexible, inexpensive, operationally simple, and extremely versatile route to structured silicate materials. Furthermore, it is highly reproducible and does not require specialized equipment or extended reaction times. An additional high aluminum content material (Al-14-(3.18)) which displays a significantly larger pore size (3.18 nm) than our standard aluminosilicate materials was also produced using a modification of the EISA protocol in which a 10-fold excess of water is used in the initial gel to generate the larger pore sizes.[24]

The ability of these materials and three commercial available zeolites to promote the etherification reaction of *para*-methoxybenzyl alcohol **1** (PMBA) to 1-butanol PMB ether **2a** was explored employing an excess of 1-butanol as solvent. The results for these experiments are summarized in Table 2. In line with previous reports, the silicate material S-1 and the two commercial ZSM-5 catalysts displayed little activity, and in these cases starting materials were recovered unchanged (Table 2; entries 1–3). This lack of ability to catalyze the etherification reaction may reflect the low acidity of these materials, although the involvement of structural factors, such as porosity, cannot be discounted. Interestingly, the Al-56 catalyst which contains an aluminum content comparable to the ZSM-5 catalysts, displayed significant activity giving moderate conversion to **2a** with high selectivity for the unsymmetrical ether product over the symmetrical self-condensation product **3** (Table 2; entry 4).

In line with previous reports, high aluminum materials provided the highest conversions[16] (Table 2; entries 5 and 6), and of these two materials, the larger pore size Al-14-(3.18) material was chosen for further study due to the higher selectivity observed for the generation of **2a**. Furthermore, it has been reported that diffusional problems can occur with microporous catalysts and bulky, polar products,[17] and it was envisaged that the use of the larger pore size material would be advantageous in these cases. We next investigated the potential to recover and reuse the catalyst in a series of reactions, and we were gratified to observe that the recovered material displayed excellent activity over the course of three reuses (Table 2; entries 7–9). The high aluminum containing zeolite Y (Table 2; entry 10) gave good conversions to **2a**, albeit with lower selectivity than both of the Al-14 materials. As expected, reactions containing no catalyst produced no ether products.

With effective conditions established for the dehydrative etherification reaction, we next investigated the ability of the Al-14-(3.18) material to catalyze the formation of unsymmetrical ethers from a series of activated alcohols, employing an excess of a range of simple aliphatic alcohols as both the solvent and reagent (Table 3). We were gratified to observe that PMBA reacted with all of the alcohols studied, generating the corresponding unsymmetrical PMB ethers in high yields and with excellent selectivity for the unsymmetrical ethers (Table 3; entries 1–6). The efficiency of this methodology is not diminished on gram scale reactions, giving comparable yields to small scale reactions (entry 4). In the case of *tert*-butanol (entry 7), the etherification reaction is considerably slower and requires protracted reaction times to achieve moderate conversions. Furthermore, the reduced nucleophilicity of the tertiary alcohol generated increased quantities of the symmetrical dimeric product **3**. In this case, it proved more efficient to add an additional quantity of the catalyst to ensure short reaction times and high selectivity. A small range of structurally diverse activated alcohols were also studied, with cinnamyl

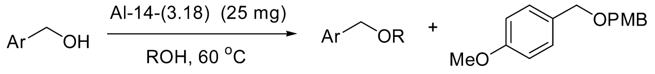
Table 2. Initial Catalyst Screening[a]



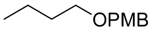
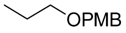
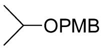
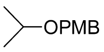
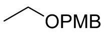
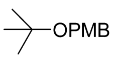
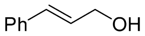
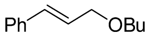
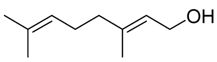
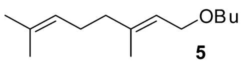
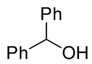
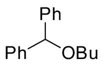
entry	catalyst	selectivity 2a:3 (%)[b]	conversion to 2a (%)[b]
1	S-1		0
2	ZSM-5-30		<10
3	ZSM-5-50		<10
4	Al-56	96	47
5	Al-14-(2.42)	95	>95
6	Al-14-(3.18)	97	86
7	Al-14-(3.18)	97	85[c]
8	Al-14-(3.18)	>98	85[d]
9	Al-14-(3.18)	>98	84[e]
10	zeolite Y-5	90	55

[a] Experimental conditions: The catalyst (25 mg) was added to a solution of **1** (1 mmol) in the specified alcohol (2 mL) and heated to 60 °C for the specified time. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Recycled catalyst first reuse. [d] Recycled catalyst second reuse. [e] Recycled catalyst third reuse.

Table 3. Nanoporous Aluminosilicate Mediated Synthesis of Ethers[a]

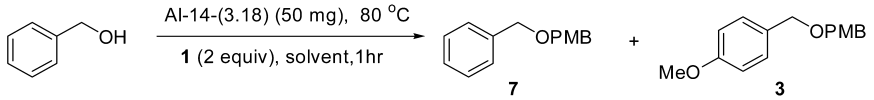


2a-2f and 4-6 **3**

Entry	ArOH	ROH	Time (h)	Product	Selectivity (%)[b,c]	Yield (%)[d]
1	**1**	^{n}BuOH	2	 **2a**	92	83
2	**1**	^{n}PrOH	2	 **2b**	94	89
3	**1**	^{i}PrOH	3	 **2c**	93	81
4	**1**	^{i}PrOH	4	 **2c**	91	79[e]
5	**1**	EtOH	1	 **2d**	92	84
6	**1**	MeOH	3	H_3C−OPMB **2e**	98	80
7	**1**	^{t}BuOH	4	 **2f**	91	69[f]
8		^{n}BuOH	5	 **4**	83	75
9		^{n}BuOH	2	 **5**	95	90[g,h]
10		^{n}BuOH	2	 **6**	100	82[i]

[a] Experimental conditions: the catalyst (25 mg) was added to a solution of **1** (1 mmol) in the specified alcohol (3 mL) and heated to 60 °C. [b] Percentage unsymmetrical ether product to dimer **3**. [c] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Compounds gave satisfactory spectroscopic data. [e] 15 mmol reaction. [f] An additional 25 mg of catalyst was added after 2 h. [g] Conversion determined by ^{1}H NMR analysis of the crude reaction mixture. [h] Crude reaction mixture contains a product identified by GC-MS as linalool butyl ether (~25%). [i] 50 mg of catalyst employed.

Table 4. Solvent Effects in the Etherification Reactions of Benzyl Alcohol[a]



7 **3**

entry	solvent	selectivity 7:3 (%)[b]	conversion (%)[b]
1	acetonitrile	53	50
2	ethyl acetate	46	45
3	chloroform	81	85
4	dimethyl carbonate	66	67

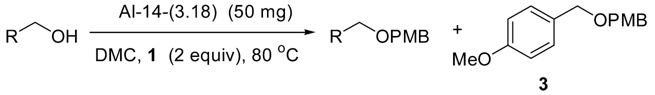
[a] Experimental conditions: The catalyst (50 mg) was added to a solution of **1** (2 mmol) and benzyl alcohol (1 mmol) in the specified solvent (2 mL) and heated to 80 °C for 1 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture.

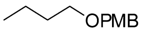
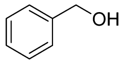
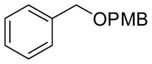
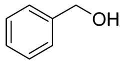
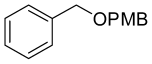
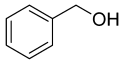
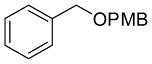
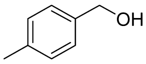
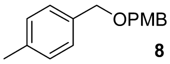
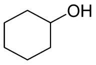
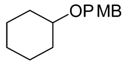
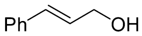
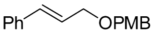
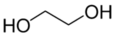
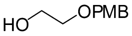
alcohol, geraniol, and diphenylmethanol (entries 8−10), giving good conversions to the corresponding unsymmetrical ether products (**4**−**6**). In the case of geraniol, however, isolated yields were limited by the formation of an additional product identified by ^{1}H NMR and GC-MS analysis to be the corresponding linalool butyl ether. This material is presumably generated by a competing rearrangement of either geraniol to linalool followed by subsequent etherification or rearrangement of the geranyl ether product itself.[25] In all the cases studied, no other self-condensation products except **3** were detected by GC-MS analysis of the crude reaction mixtures.

In all of these reactions, the ether products were isolated without the requirement for column chromatography, since only trace quantities of the self-condensation product **3** were present in these reactions. It was possible to remove residual PMBA from a hexane solution of the crude reaction mixture by adsorption onto chromatography silica, followed by filtration to give the ether products in high yield and high purity.

We next turned our attention to the most challenging goal of this work which involved the development of dehydrative etherification protocols employing near stoichiometric quantities of reagents. This initially required the identification of a suitable reaction solvent, and with this goal in mind, we initially screened a series of polar solvents employing stoichiometric quantities of **1** and benzyl alcohol to generate the PMB ether **7** to determine their suitability for further development. These reactions were noticeably slower in the absence of a large excess of the nucleophile and, to compensate for this, it was necessary to increase the quantity of catalyst. Furthermore, these reactions displayed poor selectivity which led to the consumption of **1** by self-condensation to give **3** which limited conversions to the desired PMB ether product **7**. This limitation was initially overcome by increasing the amount of

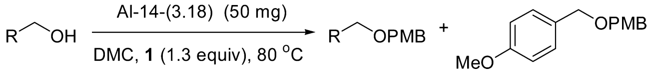
Table 5. Etherification Reactions under Concentrated Reaction Conditions[a]

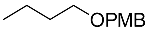
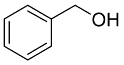
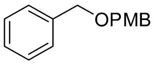
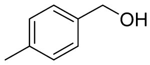
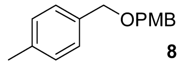
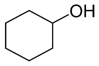
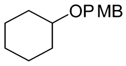
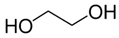
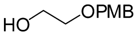
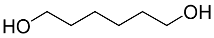
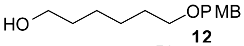
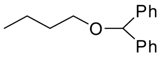
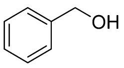
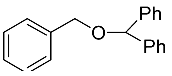


Entry	Alcohol	Product[a]	Time (h)	Selectivity (%)[b,c]	Conversion (%)[c]
1	^{n}BuOH	 2a	1	63	75
2		 7	1	66	67
3		 7	1	57	66[d]
4		 7	1	60	67[e]
5		 8	2	52	59
6		 9	2	52	71
7		 10	2	47	72[f]
8		 11	2	70	83[g]

[a] Experimental conditions: the catalyst (50 mg) was added to a solution of 1 (2 mmol) and the specified alcohol (1 mmol) in DMC (2 mL) and the reaction heated to 80 °C. [b] Percentage unsymmetrical ether product to dimer 3. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Recycled recalcined catalyst first reuse. [e] Recycled recalcined catalyst second reuse. [f] 75 mg of catalyst added as three equal portions at 30 min intervals. [g] 75:25 mixture of mono-PMB ether:bis-PMB ether by ^{1}H NMR analysis of the crude reaction mixture.

Table 6. Etherification Reactions under Dilute Reaction Conditions[a]



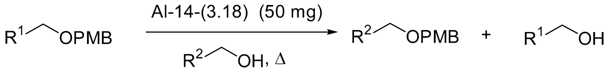
Entry	Alcohol	Product	Time (h)	Selectivity (%)[b,c]	Yield (%)[c]
1	^{n}BuOH	 2a	1	90	85
2		 7	3	85	82
3		 8	1	88	85
4		 9	2	80	75
5		 11	1	90	73[d]
6		 12	1	95	71[e]
7	^{n}BuOH	 6	1	100	90
8		 14	1.5	95	81

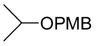
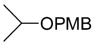
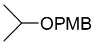
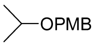
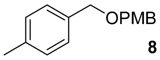
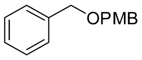
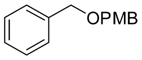
[a] Experimental conditions: A solution of 1 (1.3 mmol in 10 mL DMC) was added dropwise over 30 min to a solution of the specified alcohol (1 mmol) in DMC (2 mL) and the catalyst (50 mg) at 80 °C. [b] Percentage unsymmetrical ether product to dimer 3. [c] All compounds gave satisfactory spectroscopic data. [d] 90:10 mixture of mono-PMB ether:bis-PMB ether by ^{1}H NMR analysis of the crude reaction mixture. [e] No bis-PMB ether was detected by GC-MS analysis of the crude reaction mixture.

PMBA to two equivalents, and under these conditions, reasonable conversions to the unsymmetrical ether product 7 were produced with moderate to good selectivity in a range of solvents (Table 4).

Of the solvents investigated, chloroform (entry 3) displayed both high selectivity and high conversion to the corresponding PMB ether; however, this option was not pursued further due to the poor environmental profile of this solvent. Instead, dimethyl carbonate (DMC), a solvent which has been proposed as a sustainable and less toxic alternative to halogenated solvents,[26,27] and which also gave good conversions to 7, was selected for further development (entry 4). Importantly, only trace quantities of the corresponding methyl ethers, derived from reaction of DMC with the substrate alcohols were

Table 7. Nanoporous Aluminosilicate Mediated Transetherification Reactions[a]



Entry	PMB Ether	Alcohol	Time (h)	Temperature	Conversion (%)[b]
1	 **2c**	EtOH	3	reflux	0
2	 **2c**	EtOH	3	90°C[c]	42
3	 **2c**	BuOH	1	reflux	>98
4	 **2c**	BuOH	1	reflux	0[d]
5	 **8**	BuOH	1	reflux	>98
6	 **7**	BuOH	0.5	reflux	>98
7	 **7**	PrOH	4	reflux	88

[a]Experimental conditions: the catalyst (50 mg) was added to a solution of the PMB ether (1 mmol) in the specified alcohol (1 mmol) and the reaction heated to the specified temperature. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture. [c]Reaction carried out in a sealed reaction vessel. [d]No catalyst present.

detected by GC-MS analysis of the crude reaction mixtures. DMC has previously been reported to be an efficient and nontoxic methylating reagent for the synthesis of *N*-methyl amines from primary aromatic amines in the presence of zeolites.[28] The absence of this competing pathway is presumably due to the reduced nucleophilicity of the alcohols used, in addition to the lower reaction temperatures employed.

We next investigated the reactions of a range of simple alcohols with a small excess of **1** in DMC under what we termed "concentrated" conditions, that is, with all of the PMBA present at the start of the reaction. Under these conditions, the corresponding PMB ethers were produced with good conversions, albeit with moderate to poor selectivity (Table 5; entries 1−7). In the case of ethane-1,2-diol, the reaction not only produced quantities of **3** but also displayed only moderate selectivity for the formation of the mono-PMB ether **11** over the bis-PMB ether product (entry 8). Importantly, no symmetrical products derived from self-condensation of the substrate alcohol were detected by ^{1}H NMR or GC-MS analysis. We also took this opportunity to investigate the potential for catalyst recovery and recycling under these reaction conditions, using benzyl alcohol as a representative example. In this case, the recovered catalyst displayed some variation in reactivity, and it proved beneficial to subject the recovered material to a short recalcination step in order to achieve consistent results (entries 3 and 4). This process restored full catalytic activity without significantly changing the physical properties of the material (Supporting Information). In line with previous reports, deactivated alcohols, such as phenol and salicylaldehyde, produced only trace quantities of unsymmetrical ether products, with rapid consumption of PMBA generating **3** as the major product of these reactions.[13,29]

While this approach proved effective for the synthesis of the desired PMB ethers, it still required at least a 2-fold excess of PMBA to achieve acceptable conversions. Furthermore, the excess PMBA in the reaction was consumed by an unprofitable self-condensation reaction which produces an unrecyclable waste material. Obviously, it would be highly desirable if this pathway could be suppressed, which would allow the quantity of PMBA employed to be reduced to near stoichiometric levels. We reasoned that this may be achieved by adding the PMBA as a dilute solution to a mixture of the substrate alcohol and the catalyst (dilute reaction conditions). This approach would also exploit the lack of reactivity of the substrate alcohol toward self-condensation under the reaction conditions.

Our initial studies considered the reaction of 1-butanol in DMC with a small excess of PMBA added dropwise as a dilute DMC solution. We were highly gratified to observe that, not only was an excellent conversion obtained, but that the selectivity for the unsymmetrical product ether over the self-condensation product **3** was significantly improved (Table 6; entry 1). These observed high conversions and high selectivities were maintained for a range of structurally diverse alcohols and diols (entries 2−6). A further benefit of this approach was observed in reactions involving diols, where not only was the high selectivity for the PMB ether products achieved, but the ratio of the mono:bis products were also significantly improved (entries 5 and 6). Finally, we demonstrated that this methodology is also effective for the facile synthesis of diphenylmethyl (DPM) ethers, such as **6** and **13** (entries 7 and 8), which have also been proposed as a potential protecting group strategy for alcohols.[30,31]

We next explored the application of these materials as promoters of the corresponding transetherification reaction, with the goal of investigating this reaction as a potential protocol for the removal of the PMB protecting group. Numerous methods exist for PMB deprotection, including oxidative removal with ceric ammonium nitrate (CAN) or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or cleavage in the presence of a combination of a Lewis acid and a soft nucleophile, such as $AlCl_3$−EtSH, $MgBr_2$−Me_2S, or $SnCl_4$−PhSH. Of interest to us are reports that, while PMB ethers are stable under many acidic conditions, they may be cleaved in the presence of strong acids, such as trifluoroacetic acid, methanesulfonic acid, or triflic acid employing 1,3-dimethoxybenzene as a benzyl scavenger or transferred from alcohols to sulphonamides under triflic acid catalysis.[1,32,33] While a number of related transetherification reactions have been investigated for benzyl group deprotection,[34,35] protocols employing heterogeneous catalysts have attracted considerably less attention.[36] In our transetherification approach, it is envisaged that the aluminosilicate material would catalyze the transfer of the PMB group to a simple alkyl alcohol which is used in a large excess as a scavenger producing the corresponding alkyl PMB ether and so generating the desired free alcohol.

Our initial studies considered the reaction of isopropyl PMB ether **2c** in ethanol at reflux employing the Al-14-(3.18) material as catalyst. Disappointingly, under these conditions none of the corresponding ethyl PMB ether **2d** was observed; however, on increasing the reaction temperature, modest conversions to **2d** were achieved (Table 7; entries 1 and 2).

With this observation in hand, we were gratified to observe that, on changing to the higher boiling solvent 1-butanol, a rapid and complete transetherification of **2c** to **2a** was observed (entry 3). As expected, reactions in the absence of the catalyst gave no conversion to the transetherified product (entry 4). The reaction of PMB ethers **7** and **8** in 1-butanol was also effective and gave excellent conversions to **2a** in short reaction times (entries 5 and 6). The reaction was also successful in 1-propanol, although extended reaction times were required in this case (entry 7). GC-MS analysis of these reactions confirmed that only trace quantities of self-condensation products were formed during the reaction.

In conclusion, high aluminum containing nanoporous aluminosilicate materials are effective promoters of dehydrative etherification reactions both in alcohol solvents, or more usefully in DMC, providing access to a range of unsymmetrical ethers in high yield. The application of dilute reaction conditions leads to improved selectivity for unsymmetrical ether products and allows the use of near stoichiometric quantities of reagents. This methodology has been generalized for the synthesis of PMB and DPM ethers and performs well with a variety of substrate alcohols. These materials also effectively catalyze the corresponding transetherification reaction, providing a potential route for the deprotection of PMB ethers under mildly acidic conditions.

EXPERIMENTAL SECTION

Typical Procedure for the Dehydrative Etherification in Alcohol Solvents. The Al-14-(3.18) catalyst (25 mg) was added to a mixture of PMBA (138 mg, 1 mmol) in 1-butanol (3 mL) and heated to 60 °C with vigorous stirring. On completion of the reaction, the catalyst was removed by filtration through a Celite plug which was washed with additional 1-butanol (2 × 2 mL), and the solvent was removed under reduced pressure to give the product as a clear oil.

Typical Procedure for the Dehydrative Etherification under Concentrated Conditions in DMC. The Al-14-(3.18) catalyst (50 mg) was added to a mixture of benzyl alcohol (108 mg, 1 mmol) and PMBA (276 mg, 2 mmol) in dimethyl carbonate (2 mL) and heated to 80 °C with vigorous stirring. On completion of the reaction, the catalyst was removed by filtration through a Celite plug which was washed with additional dimethyl carbonate (2 × 2 mL), and the solvent was removed under reduced pressure to give the crude product as a clear oil.

Typical Procedure for the Dehydrative Etherification under Dilute Conditions in DMC. A solution of PMBA (179 mg, 1.3 mmol in 10 mL of DMC) was added dropwise over 30 min to a solution of benzyl alcohol (108 mg, 1 mmol) in DMC (2 mL) and the Al-14-(3.18) catalyst (50 mg) at 80 °C with vigorous stirring. On completion of the reaction, the catalyst was removed by filtration through a Celite plug which was washed with additional dimethyl carbonate (2 × 2 mL). The solvent was removed under reduced pressure to give the crude product which was purified by column chromatography (hexane → 2% ether:hexane) to give the product as a clear oil.

Typical Procedure for the Aluminosilcate Mediated Transetherification Reaction. The Al-14-(3.18) catalyst (50 mg) was added to a solution of isopropyl PMB ether (180 mg, 1 mmol) in 1-butanol (3 mL) and heated to reflux with vigorous stirring. On completion of the reaction, the catalyst was removed by filtration through a Celite plug which was washed with additional 1-butanol (2 × 2 mL), and the solvent was removed under reduced pressure to give the product as a clear oil.

ASSOCIATED CONTENT

Ⓢ Supporting Information

General methods, experimental procedures, catalyst characterization data, and spectroscopic data for all ether products. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: andrew.graham@southwales.ac.uk.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the EPSRC National Mass Facility Service, Swansea University, for high resolution mass spectra. Solid-state NMR spectra were obtained at the EPSRC UK National Solid-state NMR Service at Durham University.

REFERENCES

(1) Wuts, P. G. M.; Green, T. W. *Protective Groups in Organic Synthesis*; John Wiley and Sons: New York, 2006.

(2) Kocienski, P. J. *Protecting Groups*; Thieme: Stuttgart, 2003.

(3) Karas, L.; Piel, W. J. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1992; Vol. *9*, pp 860−876.

(4) Corma, A.; Renz, M. A general method for the preparation of ethers using water-resistant solid Lewis acids. *Angew. Chem., Int. Ed.* **2007**, *46*, 298−300.

(5) Nwoye, E. O.; Dudley, G. B. Synthesis of *para*-methoxybenzyl (PMB) ethers under neutral conditions. *Chem. Commun.* **2007**, 1436−1437.

(6) Wuts, P. G. M. 4-Methoxybenzyl 2,2,2-trichloroacetimidate. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley and Sons: New York, 1995; Vol. *5*, p 3329.

(7) Hanessian, S.; Huynh, H. K. Solution and solid phase *p*-alkoxybenzylation of alcohols under neutral conditions. *Tetrahedron Lett.* **1999**, *40*, 671−674.

(8) Yu, J.-L.; Wang, H.; Zou, K.-F.; Zhang, J.-R.; Gao, X.; Zhang, D.-W.; Li, Z.-T. Selective synthesis of unsymmetrical ethers from different alcohols catalyzed by sodium bisulfite. *Tetrahedron* **2013**, *69*, 310−315.

(9) Kayaki, Y.; Koda, T.; Ikariya, T. Halide-free dehydrative allylation using allylic alcohols promoted by a palladium−triphenyl phosphite catalyst. *J. Org. Chem.* **2004**, *69*, 2595−2597.

(10) Sharma, G. V. M; Mahalingam, A. K. A facile conversion of alcohols into *p*-methoxybenzyl ethers (PMB-ethers) using *p*-methoxybenzyl alcohol−Yb(OTf)$_3$. *J. Org. Chem.* **1999**, *64*, 8943−8944.

(11) Noji, M.; Ohno, T.; Fuji, K.; Futaba, N.; Tajima, H.; Ishii, K. Secondary benzylation using benzyl alcohols catalyzed by lanthanoid, scandium, and hafnium triflate. *J. Org. Chem.* **2003**, *68*, 9340−9347.

(12) Sherry, B. D.; Radosevich, A. T.; Toste, F. D. A mild C−O bond formation catalyzed by a rhenium-oxo complex. *J. Am. Chem. Soc.* **2003**, *125*, 6076−6077.

(13) Mitsudome, T.; Matsuno, T.; Sueoka, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Direct synthesis of unsymmetrical ethers from alcohols catalyzed by titanium cation-exchanged montmorillonite. *Green Chem.* **2012**, *14*, 610−613.

(14) Firouzabadi, H.; Iranpoor, N.; Jafari, A. A. Facile preparation of symmetrical and unsymmetrical ethers from their corresponding alcohols catalyzed by aluminumdodecatangstophosphate ($AlPW_{12}O_{40}$), as a versatile and a highly water tolerant Lewis acid. *J. Mol. Catal. A: Chem.* **2005**, *227*, 97−100.

(15) Hoek, I.; Nijhuis, T. A.; Stankiewicz, A. I.; Moulijn, J. A. Kinetics of solid acid catalysed etherification of symmetrical primary alcohols: zeolite BEA catalysed etherification of 1-octanol. *Appl. Catal. A: Gen.* **2004**, *266*, 109−116.

(16) Kim, J. W.; Kim, D. J.; Han, J. U.; Kang, M.; Kim, J. M.; Yi, J. E. Preparation and characterization of zeolite catalysts for etherification reaction. *Catal. Today* **2003**, *87*, 195−203.

(17) Lanzafamea, P.; Temi, D. M.; Perathoner, S.; Centi, G.; Macario, A.; Aloise, A.; Giordano, G. Etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol to biodiesel components using mesoporous solid acidic catalysts. *Catal. Today* **2011**, *175*, 435−441.

(18) Kubczyk, T. M.; Williams, S. M.; Kean, J. R.; Davies, T. E.; Taylor, S. H.; Graham, A. E. Nanoporous aluminosilicate catalyzed Friedel−Crafts alkylation reactions of indoles with aldehydes and acetals. *Green Chem.* **2011**, *13*, 2320−2325.

(19) Robinson, M. W. C.; Davies, A. M.; Mabbett, I.; Davies, T. E.; Apperley, D. C.; Taylor, S. H.; Graham, A. E. Synthesis of nanoporous aluminosilicate materials and their application as highly selective heterogeneous catalysts for the synthesis of β-amino alcohols. *J. Mol. Catal. A: Chem.* **2010**, *329*, 57−63.

(20) Robinson, M. W. C.; Davies, A. M.; Mabbett, I.; Apperley, D. C.; Taylor, S. H.; Graham, A. E. Synthesis and catalytic activity of nanoporous aluminosilicate materials. *J. Mol. Catal. A: Chem.* **2009**, *314*, 10−14.

(21) Robinson, M. W. C.; Pillinger, K. S.; Mabbett, I.; Timms, D. A.; Graham, A. E. Copper-mediated Meinwald rearrangement reactions of epoxides. *Tetrahedron* **2010**, *66*, 8377−8382.

(22) Robinson, M. W. C.; Davies, A. M.; Mabbett, I.; Taylor, S. H.; Graham, A. E. Epoxide ring-opening and Meinwald rearrangement reactions of epoxides catalyzed by mesoporous aluminosilicates. *Org. Biomol. Chem.* **2009**, *7*, 2559−2564.

(23) Smith, B. M.; Skellam, E. J.; Oxley, S. J.; Graham, A. E. Highly selective indium halide mediated cyclisation reactions of epoxyalkenes. *Org. Biomol. Chem.* **2007**, *5*, 1979−1982.

(24) Do, D. M.; Jaenicke, S.; Chuah, G.-K. Mesoporous Zr-SBA-15 as green solid acid catalyst for Prins reaction. *Catal. Sci. Tech.* **2013**, *5*, 247−254.

(25) Cori, O.; Chayet, L.; Perez, L. M.; Bunton, C. A.; Hachey, D. Rearrangement of linalool, geraniol, and nerol and their derivatives. *J. Org. Chem.* **1986**, *51*, 1310−1316.

(26) Tundo, P.; Selva, M. The chemistry of dimethyl carbonate. *Acc. Chem. Res.* **2002**, *35*, 706−716.

(27) Ferrer, B.; Alvaro, M.; Garcia, H. Application of dimethyl carbonate as solvent and reagent. In *Green Solvents 1: Properties and Applications in Chemistry*; Inamuddin, A. M., Ed.; Springer, 2012.

(28) Selva, M. Green approaches to highly selective processes: reactions of dimethyl carbonate over both zeolites and base catalysts. *Pure. Appl. Chem.* **2007**, *79*, 1855−1867.

(29) Luzzio, F. A.; Chen, J. Efficient preparation and processing of the 4-methoxybenzyl (PMB) group for phenolic protection using ultrasound. *J. Org. Chem.* **2008**, *73*, 5621−5624.

(30) Bikard, Y.; Mezaache, R.; Weibel, J.-M.; Benkouider, A.; Sirlin, C.; Pale, P. Diarylmethyl ethers and Pd salts or complexes: a perfect combination for the protection and deprotection of alcohols. *Tetrahedron* **2008**, *64*, 10224−10232.

(31) Namboodiri, V. V.; Varma, R. S. Iron-catalyzed solvent-free conversion of alcohols and phenols into diphenylmethyl (DPM) ethers. *Tetrahedron Lett.* **2002**, *43*, 4593−4595.

(32) Jung, M. E.; Koch, P. Mild, selective deprotection of PMB ethers with triflic acid/1,3-dimethoxybenzene. *Tetrahedron Lett.* **2011**, *52*, 6051−6054.

(33) Hinklin, R. J.; Kiessling, L. L. *p*-Methoxybenzyl ether cleavage by polymer-supported sulfonamides. *Org. Lett.* **2002**, *4*, 1131−1133.

(34) Weissman, S. A.; Zewge, D. Recent advances in ether dealkylation. *Tetrahedron* **2005**, *61*, 7833−7863.

(35) Ramanathan, M.; Hou, D. R. Cleavage of benzyl ethers by triphenylphosphine hydrobromide. *Tetrahedron Lett.* **2010**, *51*, 6143−6146.

(36) Petchmanee, T.; Ploypradith, P.; Ruchirawat, S. Solid-supported acids for debenzylation of aryl benzyl ethers. *J. Org. Chem.* **2006**, *71*, 2892−2895.