

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

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1. General Methods

Commercially available reagents were used without further purification. Flash chromatography was carried out using Merck Kieselgel 60 H silica. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF254 that were visualized under UV light (at 254 and/or 360 nm) or using potassium permanganate solution (1% in water) followed by charring. Infra-red (IR) spectra were recorded in the range 4000–600 cm^{-1} as neat oils or solids and are reported in cm^{-1} . Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz in CDCl_3 at 25 °C and are reported in ppm; *J* values are recorded in Hz and multiplicities are expressed by the usual conventions. Low-resolution mass spectra (MS) were determined by electron impact ionization (EI). High resolution mass spectra (HRMS) were obtained courtesy of the EPSRC Mass Spectrometry Facility, Swansea University, UK. GC-MS analysis was performed using a Varian 450GC and Varian 300MS employing a VF-5ms capillary column (30m, 0.25mm i.d. and 0.25 μm) and a gradient temperature profile with an initial temperature of 50°C for 3 minutes rising to 280°C at a rate of 20°C/minute. Removal of solvent refers to evaporation at reduced pressure using a rotary evaporator followed by the removal of trace volatiles using a vacuum pump. The commercial zeolite materials were purchased in their NH_4^+ form and calcined at 500°C for 3 hours to provide the H^+ form.

2. Catalyst Preparation

The aluminosilicate materials AS-54 and AS-14-(2.42), in addition to the unmodified silica material (S-1), were synthesized as described previously.^{1a-c} A typical preparation for the synthesis of the aluminosilicate AS-14-(3.18) catalyst is as follows: cetyltrimethylammonium bromide (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 mL, 0.1 M), ethanol (17.5 mL) and water (22.5 mL). Tetraethyl orthosilicate (25 mL, 112 mmol) was then added and the mixture stirred for 10 minutes 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 minutes and then left to age at room temperature for 24 hours. The resultant orange solid was crushed into a fine powder and calcined in air at 550 °C for 6 hours to remove the organic template to give a fine white powder. All materials were stored at 120 °C for at least 12 hours prior to use.

3. Catalyst Characterization Methods

Specific surface areas were obtained by the BET method at liquid nitrogen temperatures using a Micromeritics Gemini or a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120 °C under a flow of helium for 2 hours prior to analysis. Pore sizes were obtained using a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120 °C vacuum for 3 hours prior to analysis. Pore sizes were calculated by applying the non-local density

functional theory (NLDFT) method to the N₂ sorption at 77K employing Quantachrome AS-1 software data reduction parameters. NH₃-TPD experiments were carried out using Quantachrome, ChemBet TPR/TPD Chemisorption Analyser. Prior to the measurements, approximately 30 mg of sample were activated by heating at 373 K for 1 h, and after cooling for 15 min to 253 K, ammonia adsorption was carried out. Physically adsorbed ammonia was removed by purging with helium at 363 K for 1 h before the NH₃-TPD analysis. The physisorbed ammonia and the ammonia associated with weak acid sites were removed by purging with helium at 363 K for 1 h. The NH₃-TPD of the samples was carried out by increasing the cell temperature linearly from 363 to 1173 K with a heating rate of 20 K min⁻¹ and a helium flow rate of 80 cm³ min⁻¹. Elemental compositions were obtained with a JOEL scanning electron microscope fitted with an EDX detector using a 20 KeV accelerating voltage. MAS-NMR spectra were obtained courtesy of the EPSRC National Solid State NMR Service, Durham University. Aluminium spectra were obtained using a Varian VNMRS system, with a DP pulse sequence and results are reported in ppm using a 1M aqueous AlCl₃ solution as internal reference. Silicon spectra were obtained using a Varian Unity Inova spectrometer with a DP or CP pulse sequence and results are reported in ppm with respect to tetramethylsilane.

4. Catalyst Characterisation Data

Figure S1a: S-1 BET Isotherm

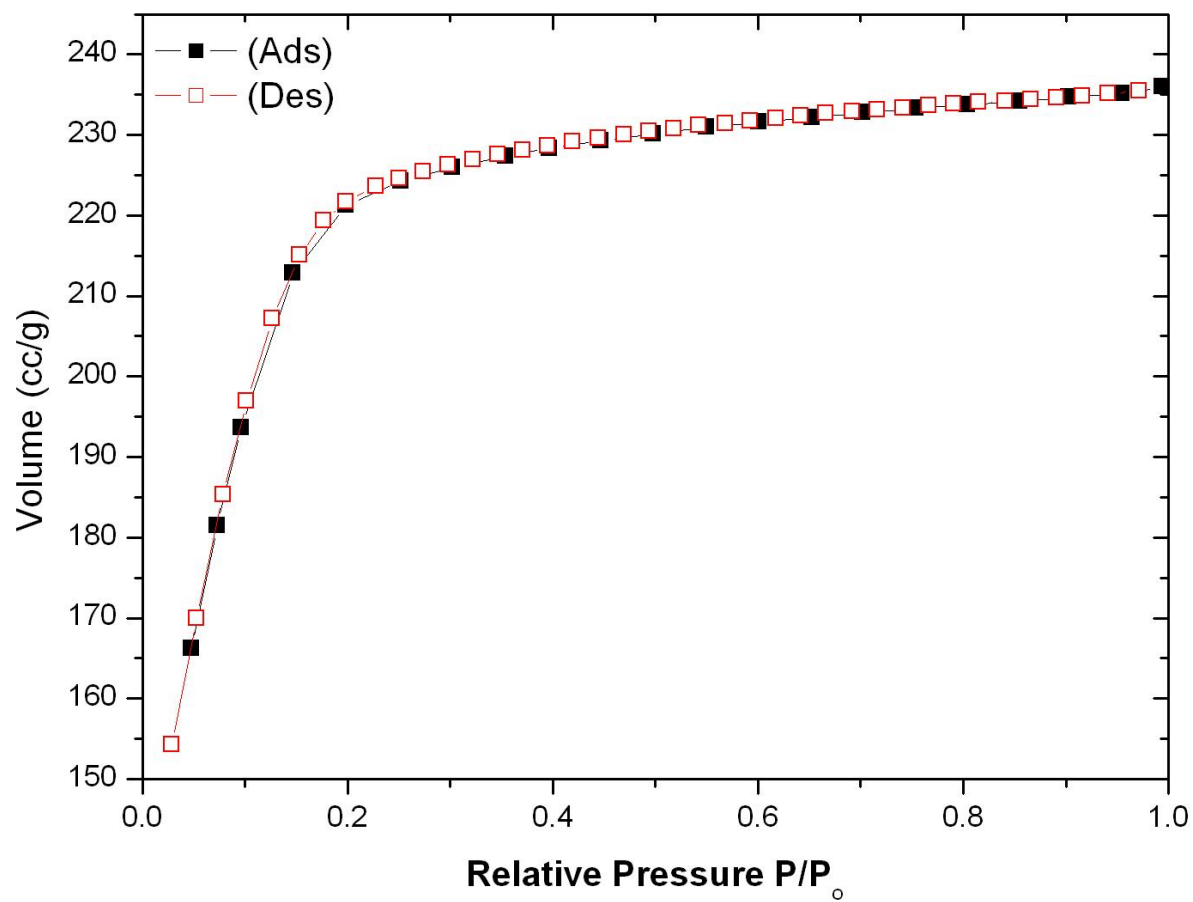


Figure S1b: S-1 NLDFIT Pore Size Distribution

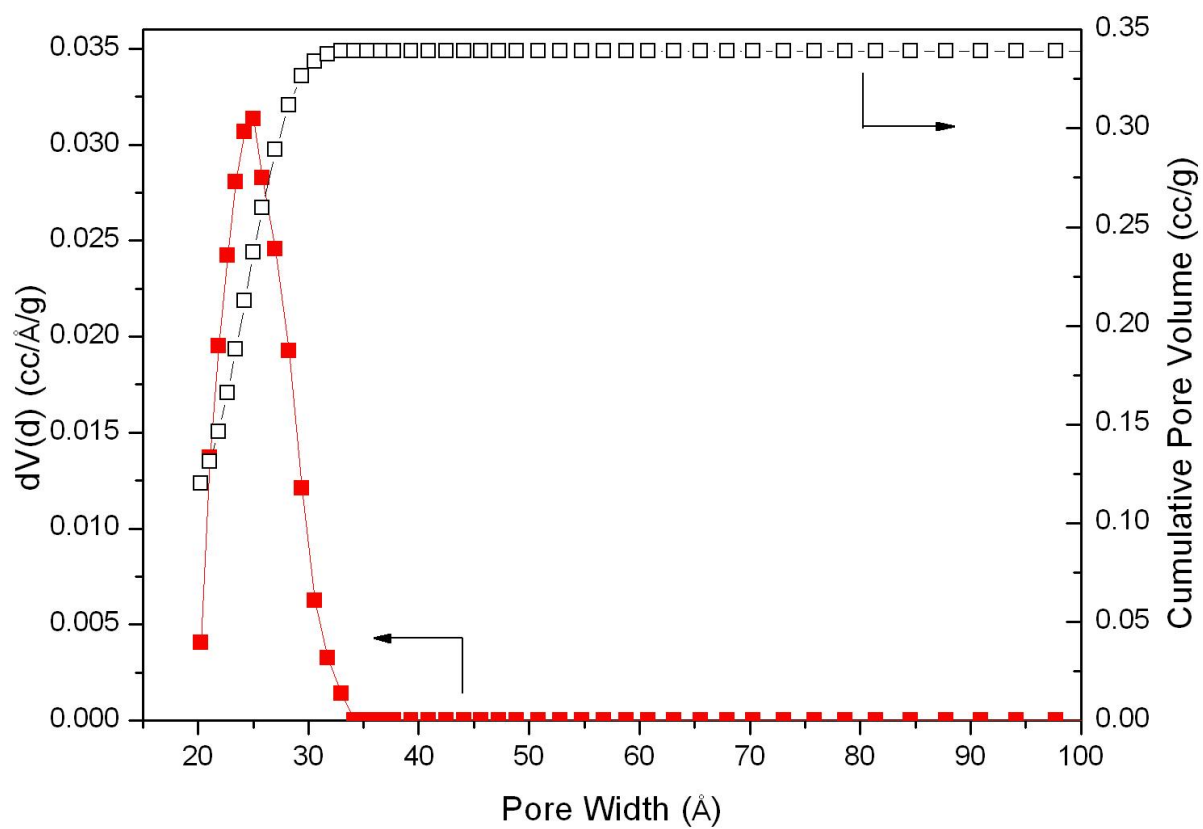


Figure S1c: Al-14-(2.42) BET Isotherm

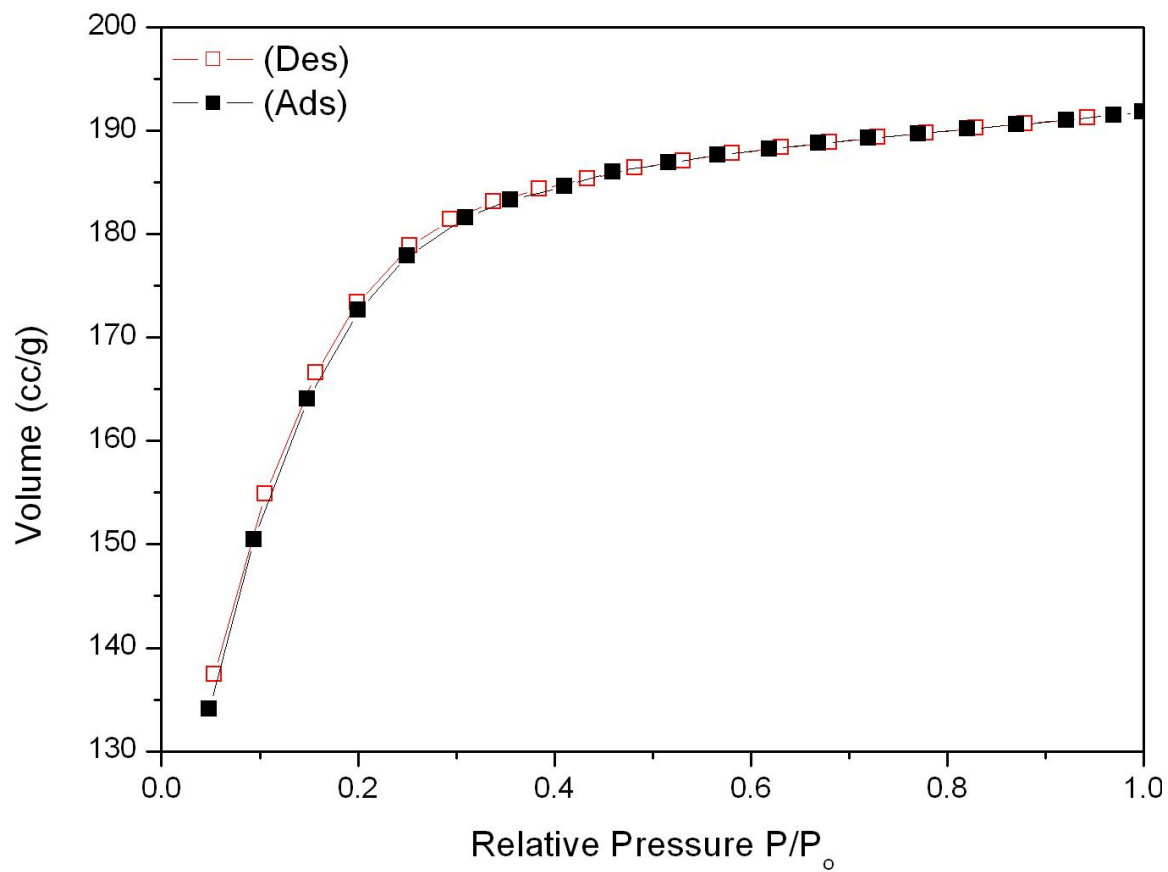


Figure S1d: Al-14-(2.42) NLDFT Pore Size Distribution

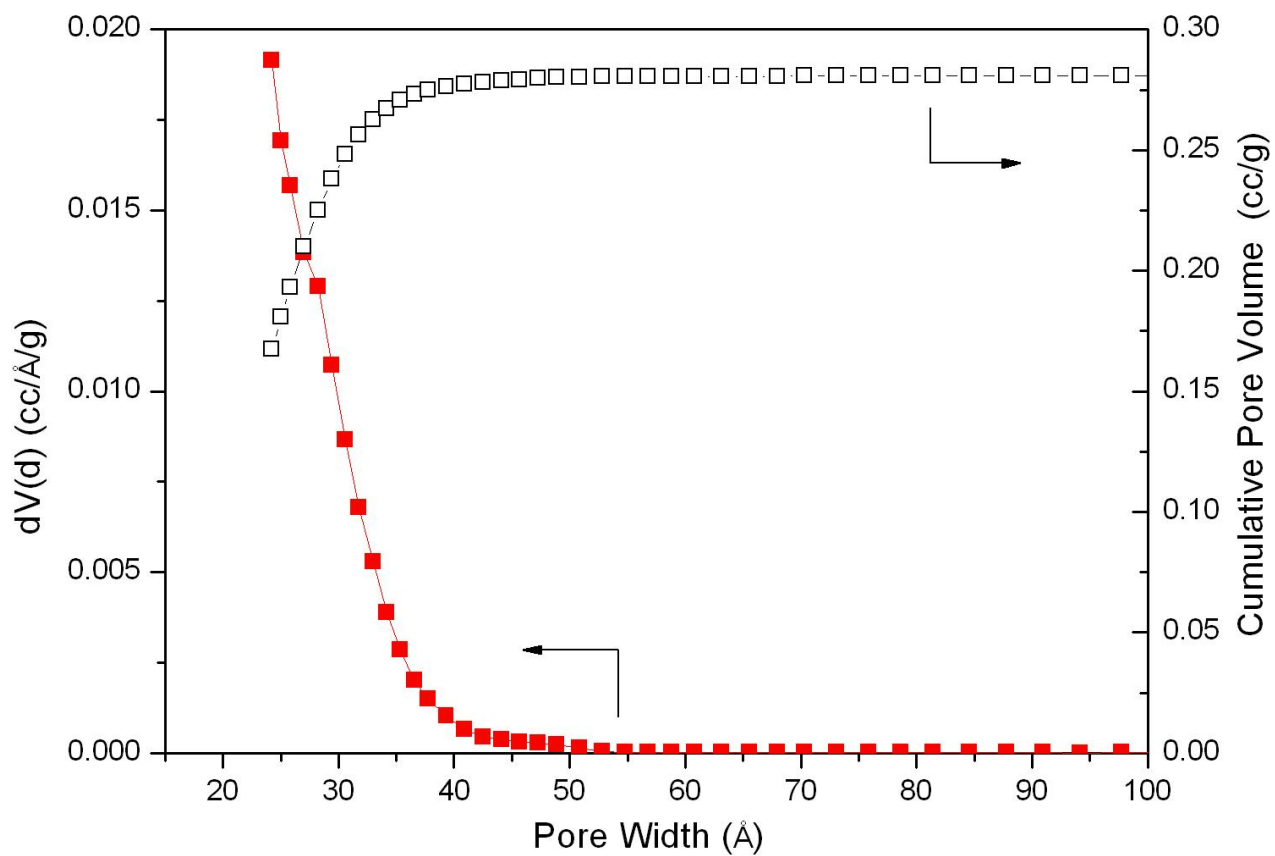


Figure S1e: Al-14-(3.18) BET Isotherm

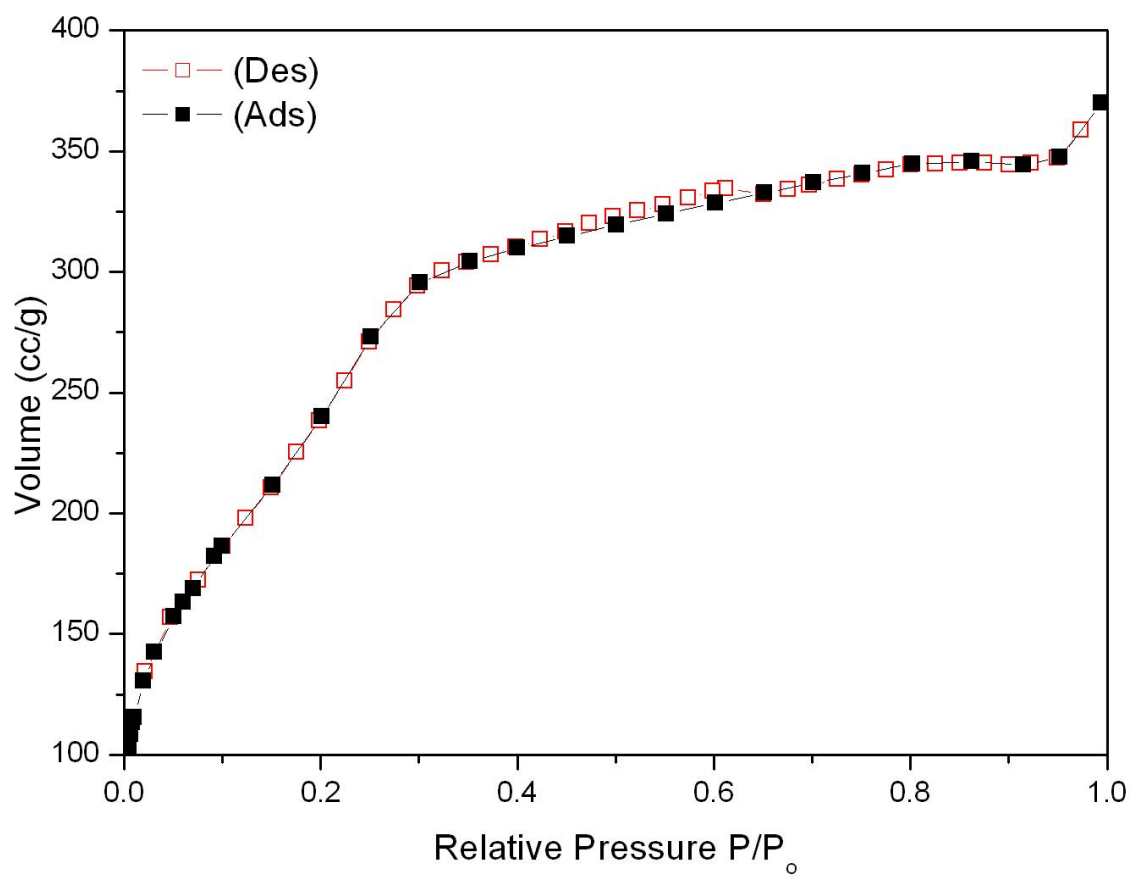


Figure S1f: Al-14-(3.18) NLDFT Pore Size Distribution

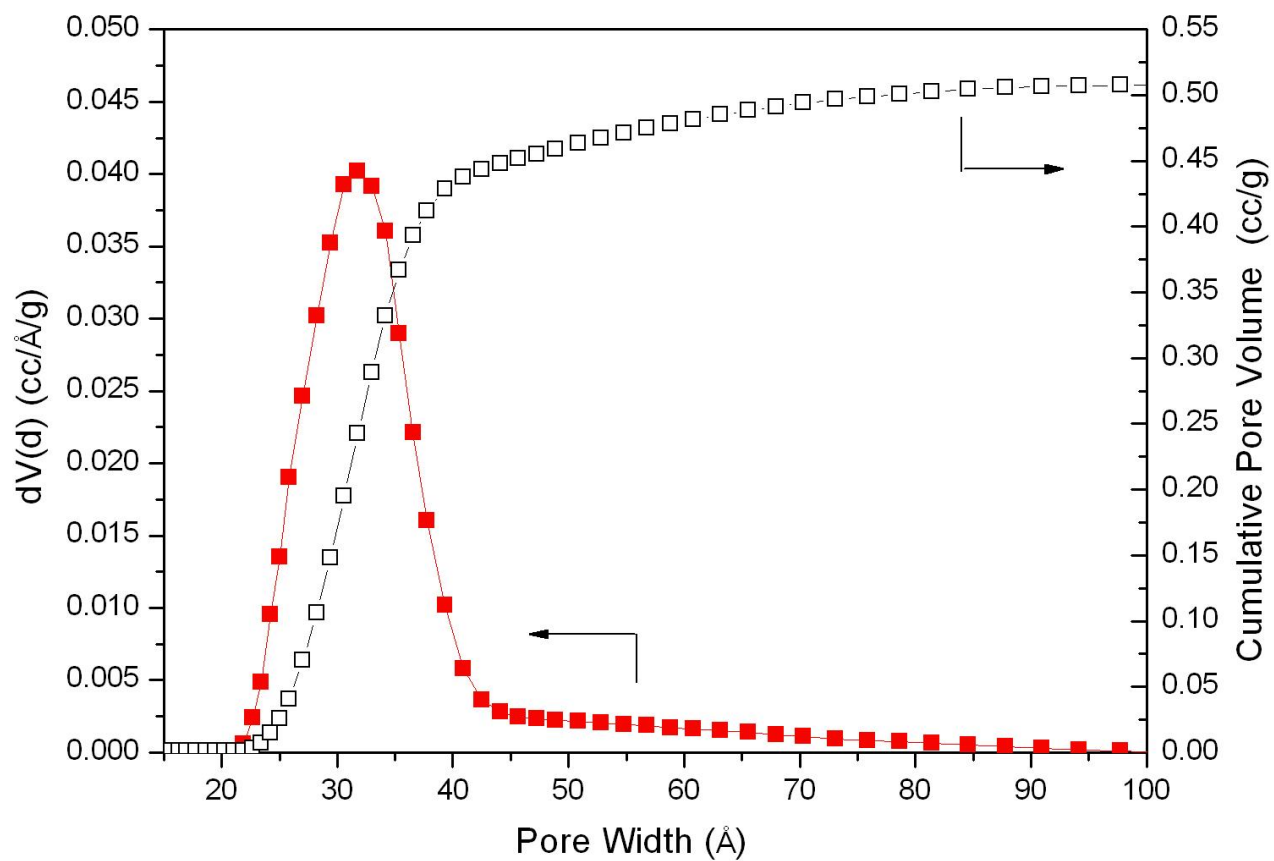


Figure S2a: ^{27}Al MAS NMR Al-14-(2.42)

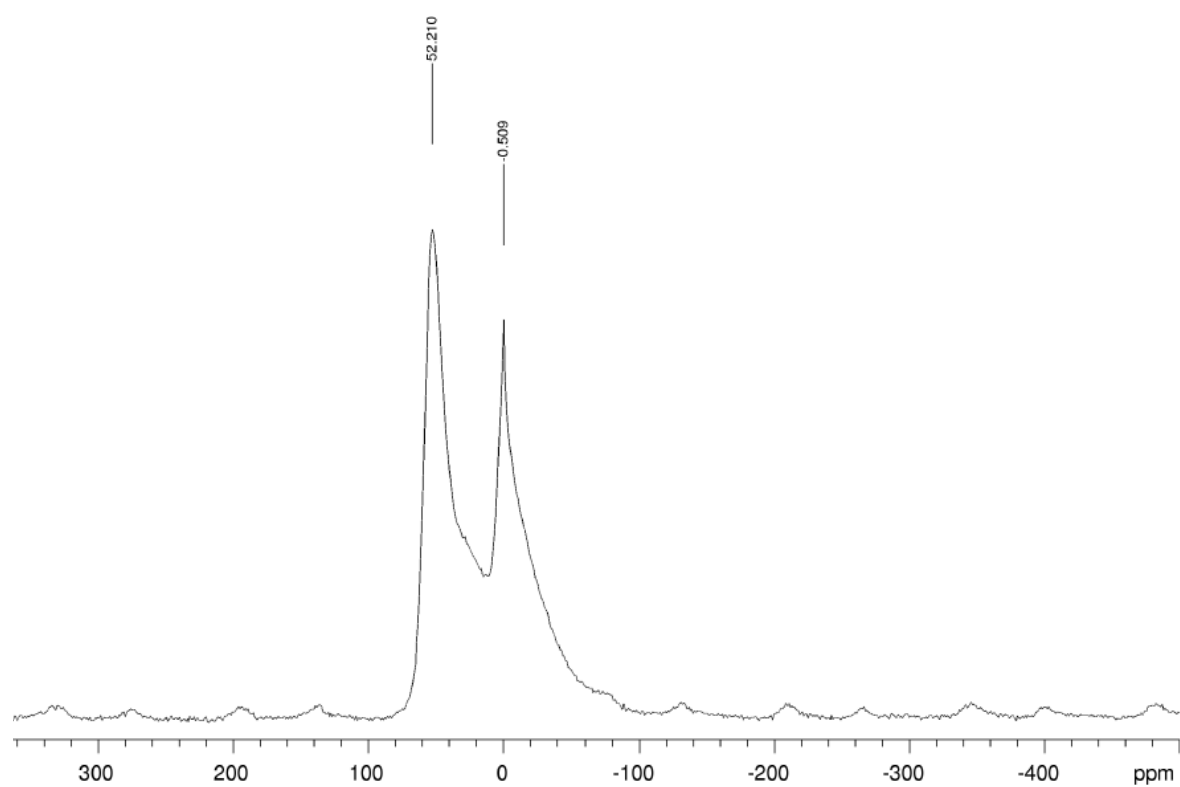


Figure S2b: ^{28}Si MAS NMR Al-14-(2.42)

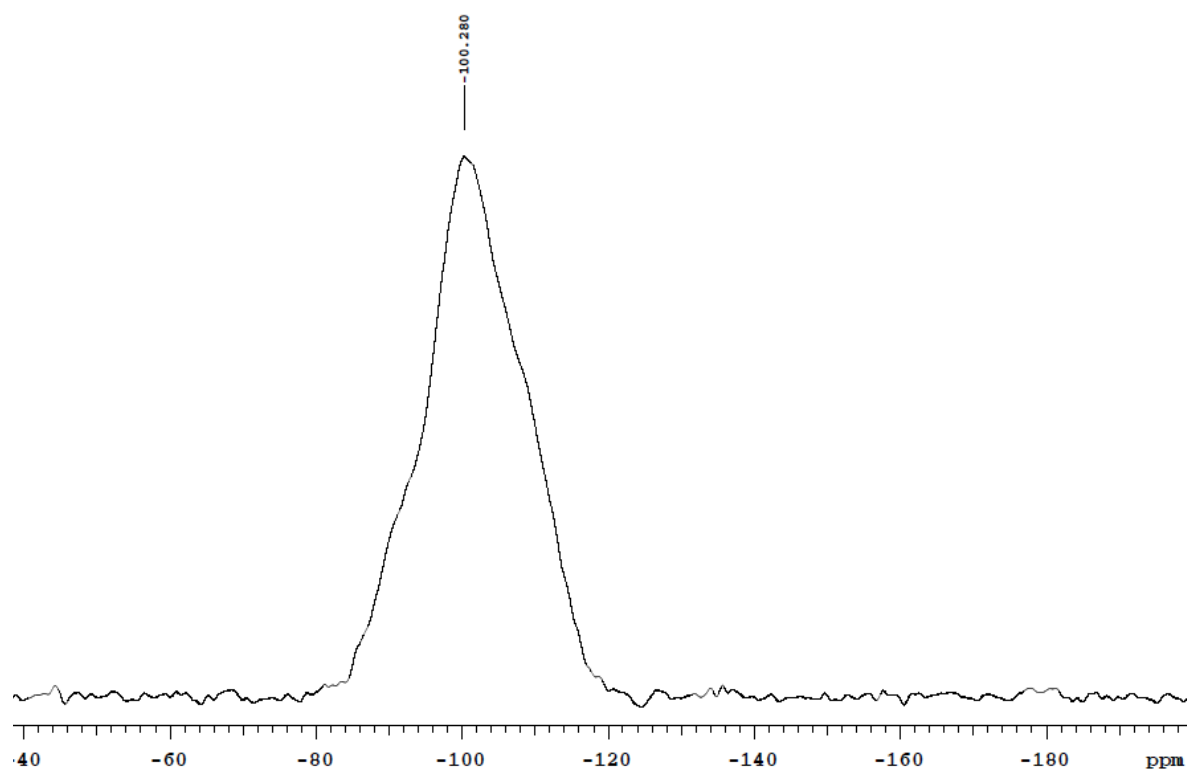


Figure S2c: ^{27}Al MAS NMR Al-14-(3.18)

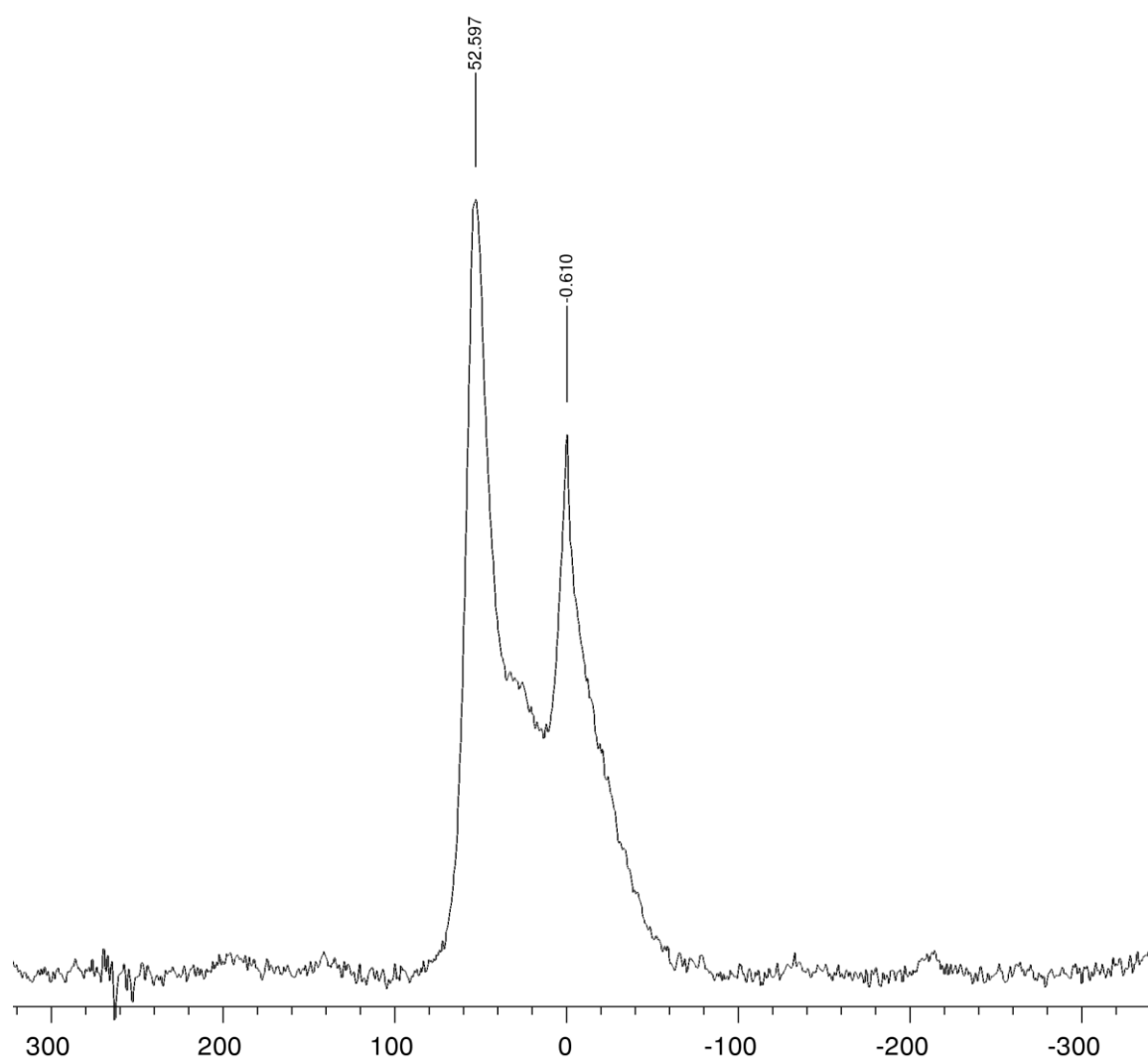


Figure S2d: ^{28}Si MAS NMR Al-14-(3.18)

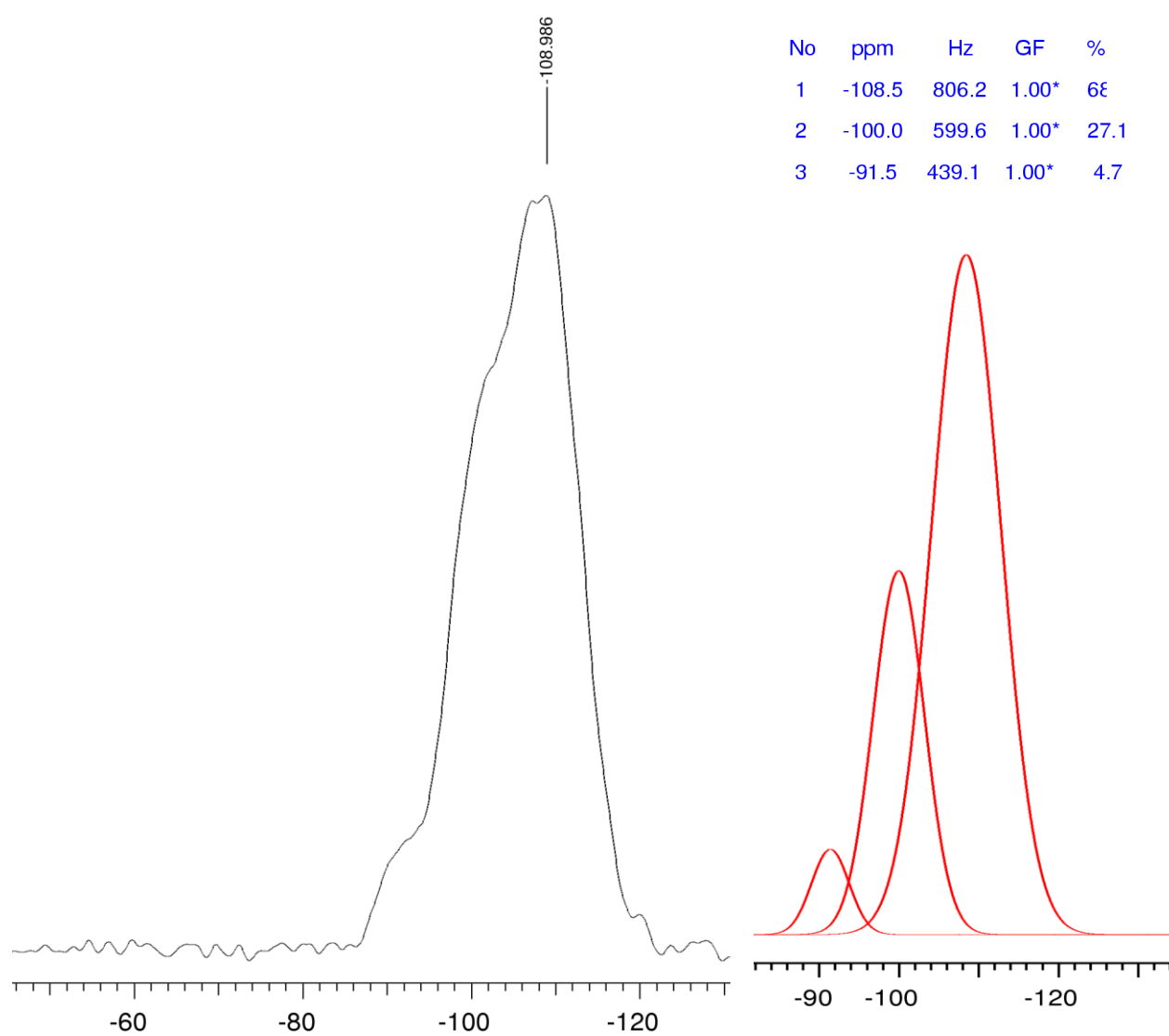


Figure S3a: XRD Data for calcined Al-14-(2.42)

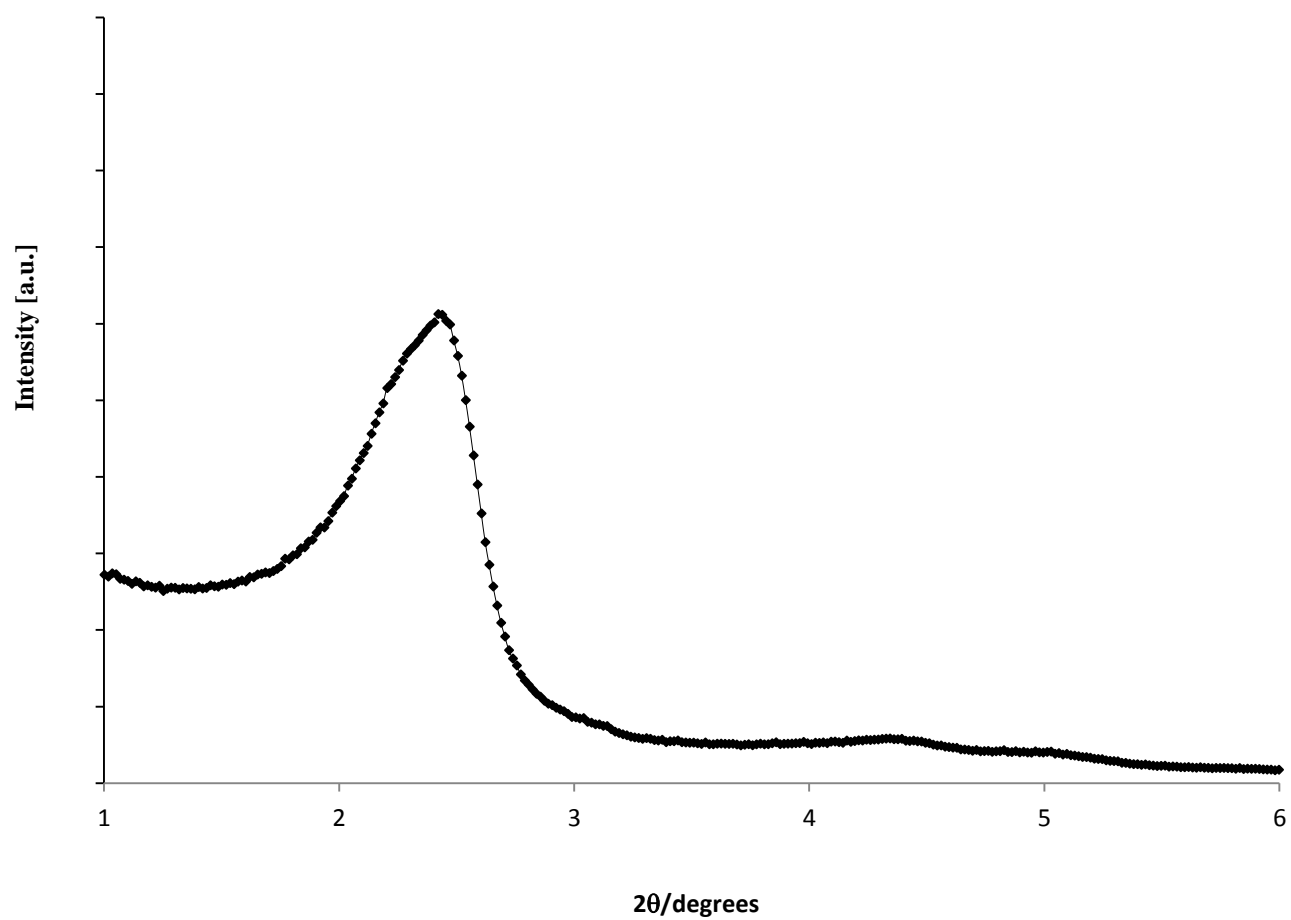


Figure S3b: XRD Data for calcined Al-14-(3.18)

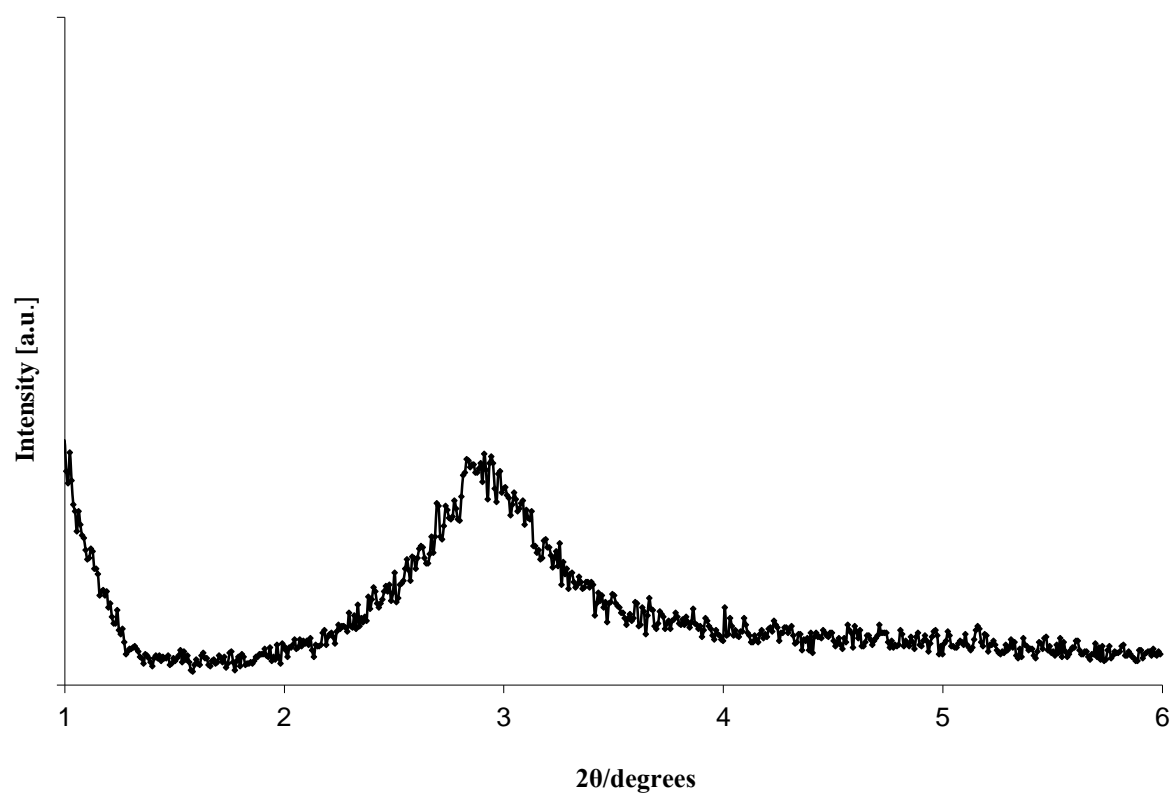
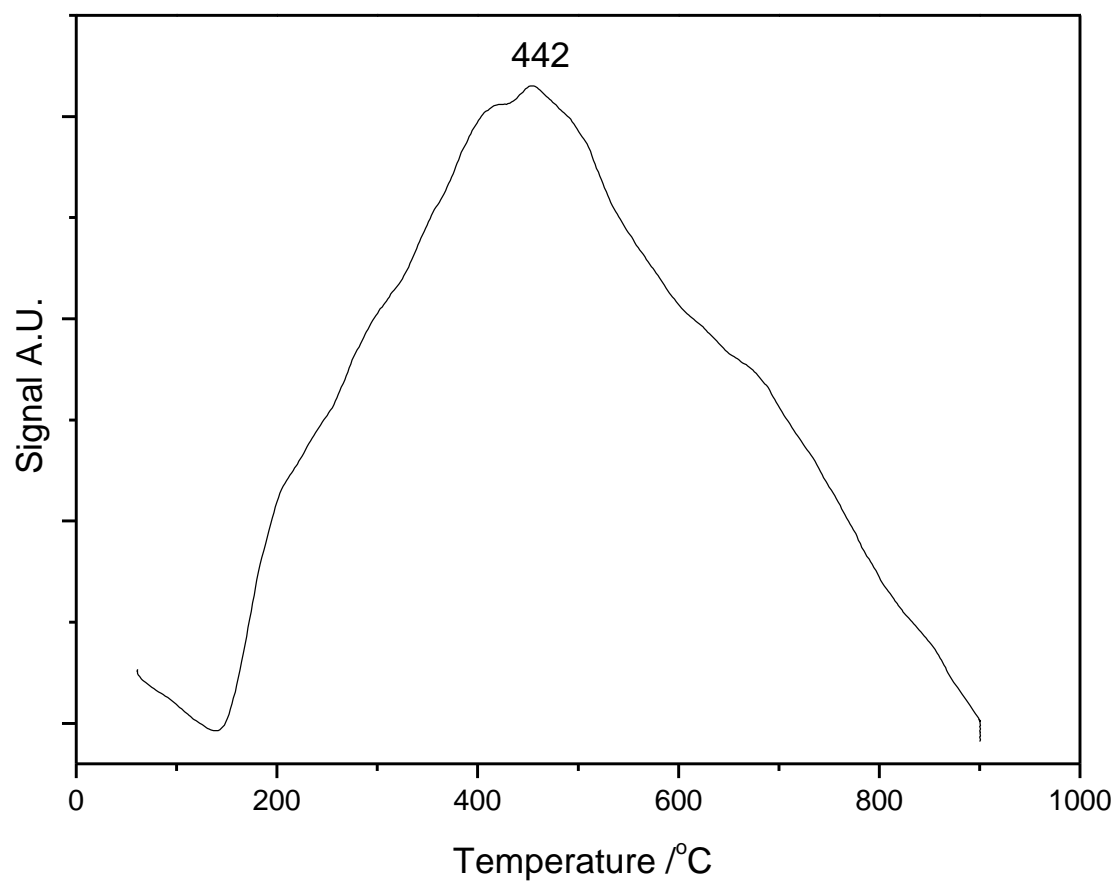


Figure S4a: TPD data for calcined Al-14-(3.18)



5. Experimental Procedures

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 removed under reduced pressure to give the product.

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, 2mmol) 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 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 drop-wise over 30 minutes 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.

6. Recalcined Catalyst Data

Cycle	Si/Al Gel Composition	Si/Al (EDX) ^a	BET Surface Area (m ² g ⁻¹) ^b	Conversion ^{c,d} (%)	Selectivity ^{d,e} (%)
1 st Use	13	14	774	66	66
1 st Re-use	13	16	666	66	56
2 nd Re-use	13	14	628	67	65

^a Determined by EDX analysis. ^b Obtained by the BET method. ^c The catalyst (50 mg) was added to a solution of PMBA (2 mmol) and benzyl alcohol (1 mmol) in DMC (2 mL) and heated to 80 °C for 1 hr. On completion of the reaction, the catalyst was recovered by filtration, washed with additional DMC (2 × 2mL) and recalcined in air at 550 °C for 1 hr before re-use. ^d Percentage unsymmetrical ether product to dimer **3**. ^e Determined by ¹H NMR analysis of the crude reaction mixture.

7. Spectroscopic Data for Ether Products

4-Methoxybenzyl *n*-butyl ether²: (Table 3: entry 1): ¹H NMR (400 MHz; CDCl₃) δ = 0.95 (3H, t, *J* = 7.0 Hz), 1.40-1.50 (2H, m), 1.60-1.70 (2H, m), 3.50 (2H, t, *J* = 7.0 Hz), 3.80 (3H, s), 4.45 (2H, s), 6.90 (2H, d, *J* = 9.0 Hz), 7.30 (2H, d, *J* = 9.0 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 158.9, 130.6, 129.0, 113.5, 72.3, 69.7, 54.9, 31.7, 19.2, 13.7; MS (EI) *m/z* 194 (M)⁺; *v*_{max}/cm⁻¹ (neat) 2958, 1613, 1514, 1361, 1247, 1172, 1096.

4-Methoxybenzyl *n*-propyl ether³: (Table 3: entry 2): ¹H NMR (400 MHz; CDCl₃) δ = 0.85 (3H, t, *J* = 7.0 Hz), 1.15 (2H, hex, *J* = 7.0 Hz), 3.30 (2H, q, *J* = 7.0 Hz), 3.65 (3H, s), 4.35 (2H, s), 6.75 (2H, d, *J* = 9.0 Hz), 7.15 (2H, d, *J* = 9.0 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 158.9, 130.6, 129.0, 113.8, 72.2, 71.6, 55.0, 22.8, 10.4; MS (EI) *m/z* 180 (M)⁺; *v*_{max}/cm⁻¹ (neat) 2970, 1613, 1513, 1379, 1247, 1172, 1036.

4-Methoxybenzyl iso-propyl ether³: (Table 3: entry 3): ¹H NMR (400 MHz; CDCl₃) δ = 1.25 (6H, d, *J* = 7.0 Hz), 3.75 (1H, hept, *J* = 7.0 Hz), 3.80 (3H, s), 4.50 (2H, s), 6.95 (2H, d, *J* = 9.0 Hz), 7.30 (2H, d, *J* = 9.0 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 158.8, 131.0, 128.9, 113.5, 70.4, 69.5, 55.0, 21.9; MS (EI) *m/z* 180 (M)⁺; *v*_{max}/cm⁻¹ (neat) 2960, 1613, 1513, 1361, 1247, 1172, 1095.

4-Methoxybenzyl ethyl ether³: (Table 3: entry 5): ¹H NMR (400 MHz; CDCl₃) δ = 1.10 (3H, t, *J* = 7.0 Hz), 3.35 (2H, q, *J* = 7.0 Hz), 3.65 (3H, s), 4.30 (2H, s), 6.75 (2H, d, *J* = 9.0 Hz), 7.15 (2H, d, *J* = 9.0 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 158.9, 130.1, 129.1, 113.5, 72.1, 65.2, 55.0, 15.0; MS (EI) *m/z* 166 (M)⁺; *v*_{max}/cm⁻¹ (neat) 2973, 1612, 1513, 1301, 1246, 1172, 1095.

4-Methoxybenzyl methyl ether³: (Table 3: entry 6): ¹H NMR (400 MHz; CDCl₃) δ = 3.50 (3H, s), 3.85 (3H, s), 4.40 (2H, s), 6.95 (2H, d, *J* = 9.0 Hz), 7.30 (2H, d, *J* = 9.0 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 159.0, 130.1, 129.1, 74.1, 57.5, 55.0; MS (EI) *m/z* 152 (M)⁺; *v*_{max}/cm⁻¹ (neat) 2932, 1612, 1513, 1380, 1247, 1173, 1095.

4-Methoxybenzyl *tert*-butyl ether³: (Table 3: entry 7): ¹H NMR (400 MHz; CDCl₃) δ = 1.35 (9H, s), 3.85 (3H, s), 4.45 (2H, s), 6.95 (2H, d, *J* = 9.0 Hz), 7.30 (2H, d, *J* = 9.0 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 158.6, 131.9, 128.7, 113.5, 73.0, 63.3, 55.1, 27.5; MS (EI) *m/z* 194 (M)⁺; *v*_{max}/cm⁻¹ (neat) 2970, 1613, 1513, 1389, 1245, 1171, 1035.

Cinnamyl *n*-butyl ether²: (Table 3: entry 8): ¹H NMR (400 MHz; CDCl₃) δ = 0.85 (3H, t, *J* = 7.0 Hz), 1.30-1.35 (2H, m), 1.50-1.55 (2H, m), 3.40 (2H, t, *J* = 7.0 Hz), 4.00 (2H, d, *J* = 6.0 Hz), 6.15

(1H, dt, $J = 6$ and 16.0 Hz), 6.50 (1H, d, $J = 16.0$ Hz), 7.15 - 7.30 (5H, m); ^{13}C NMR (100 MHz; CDCl_3) $\delta = 136.6, 131.9, 128.4, 127.4, 126.3, 71.2, 70.0, 31.7, 19.2, 13.8$; MS (EI) m/z 190 (M) $^+$; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) $2958, 1659, 1495, 1361, 1109, 965$.

Diphenylmethyl *n*-butyl ether²: (Table 3: entry 10): ^1H NMR (400 MHz; CDCl_3) $\delta = 1.05$ (3H, t, $J = 7.0$ Hz), 1.45 - 1.55 (2H, m), 1.60 - 1.80 (2H, m), 3.60 (2H, t, $J = 7.0$ Hz), 5.45 (1H, s), 7.25 - 7.50 (10H, m); ^{13}C NMR (100 MHz; CDCl_3) $\delta = 142.6, 128.2, 127.2, 126.9, 83.5, 68.8, 31.9, 19.4, 13.9$; MS (EI) m/z 240 (M) $^+$; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) $2869, 1493, 1303, 1185, 1095, 910$.

Cinammyl PMB ether⁴: (Table 5: entry 7): ^1H NMR (400 MHz; CDCl_3) $\delta = 3.70$ (3H, s), 4.00 (2H, d, $J = 7.0$ Hz), 4.45 (2H, s), 6.25 (1H, dt, $J = 6$ and 16.0 Hz), 6.55 (1H, d, $J = 16.0$ Hz), 6.85 (2H, d, $J = 9.0$ Hz) 7.15 - 7.30 (7H, m); ^{13}C NMR (100 MHz; CDCl_3) $\delta = 159.2, 136.7, 132.4, 130.4, 129.5, 128.6, 127.7, 126.5, 126.2, 113.7, 71.9, 70.5, 55.3$; MS (EI) m/z 190 (M) $^+$; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) $3027, 1614, 1514, 1455, 1360, 1246, 1173, 965$.

4-Methoxybenzyl benzyl ether: (Table 6: entry 2): ^1H NMR (400 MHz; CDCl_3) $\delta = 3.65$ (3H, s), 4.35 (2H, s), 4.40 (2H, s) 6.75 (2H, d, $J = 9.0$ Hz), 7.15 - 7.25 (7H, m); ^{13}C NMR (100 MHz; CDCl_3) $\delta = 159.1, 138.3, 130.2, 129.6, 129.3, 128.2, 127.6, 127.4, 113.7, 71.7, 71.6, 55.1$; MS (EI) m/z 228 (M) $^+$; HRMS (EI) calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2$ (M) $^+$ 228.1142 , found 228.1145 ; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) $2834, 1612, 1512, 1453, 1359, 1246, 1172, 1034$.

4-Methoxybenzyl-(4-methylbenzyl) ether: (Table 6: entry 3): ^1H NMR (400 MHz; CDCl_3) $\delta = 2.42$ (3H, s), 3.85 (3H, s), 4.55 (2H, s), 4.60 (2H, s) 6.95 (2H, d, $J = 9.0$ Hz), 7.25 (2H, d, $J = 9.0$ Hz), 7.30 - 7.40 (4H, m); ^{13}C NMR (100 MHz; CDCl_3) $\delta = 159.0, 137.1, 135.2, 130.3, 129.2, 128.9, 127.7, 113.6, 71.5, 71.4, 55.1, 21.0$; MS (EI) m/z 242 (M) $^+$; HRMS (EI) calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2$ (M) $^+$ 242.1301 , found 242.1302 ; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) $2854, 1612, 1513, 1463, 1358, 1247, 1172, 1083$.

Cyclohexyl 4-methoxybenzyl ether: (Table 6: entry 4): ^1H NMR (400 MHz; CDCl_3) $\delta = 1.25$ - 1.60 (6H, m), 1.75 - 1.80 (2H, m), 1.95 - 2.00 (2H, m), 3.35 (1H, m), 3.80 (3H, s), 4.50 (2H, s), 6.90 (2H, d, $J = 9.0$ Hz), 7.30 (2H, d, $J = 9.0$ Hz); ^{13}C NMR (100 MHz; CDCl_3) $\delta = 159.1, 131.3, 129.0, 113.6, 69.2, 55.2, 32.2, 25.8, 24.1$; MS (EI) m/z 220 (M) $^+$; HRMS (EI) calculated for $\text{C}_{14}\text{H}_{20}\text{O}_2$ (M) $^+$ 220.1458 , found 220.1458 ; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) $2931, 1613, 1513, 1452, 1361, 1246, 1172, 1087$.

***p*-Methoxybenzyl-2-hydroxyethylether:** (Table 6: entry 5): ^1H NMR (400 MHz; CDCl_3) $\delta = 2.60$ (1H, br s), 3.45 (2H, t, $J = 7.0$ Hz), 3.60 (2H, t, $J = 7.0$ Hz), 3.70 (3H, s), 4.35 (2H, s), 6.75 (2H, d, J

= 9.0 Hz), 7.15 (2H, d, J = 9.0 Hz); ^{13}C NMR (100 MHz; CDCl_3) δ = 159.0, 129.8, 129.3, 113.6, 72.7, 71.0, 61.5, 55.0; MS (EI) m/z 182 (M^+); HRMS (EI) calculated for $\text{C}_{10}\text{H}_{14}\text{O}_3$ (M^+) 182.0937, found 182.0937; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3418, 2862, 1613, 1514, 1463, 1358, 1247, 1175, 1033.

***p*-Methoxybenzyl-6-hydroxyhexylether: (Table 6: entry 6):** ^1H NMR (400 MHz; CDCl_3) δ = 1.35–1.40 (4H, m), 1.55–1.65 (4H, m), 1.85 (1H br s), 3.45 (2H, t, J = 7.0 Hz), 3.60 (2H, t, J = 7.0 Hz), 3.80 (3H, s), 4.45 (2H, s), 6.85 (2H, d, J = 9.0 Hz), 7.25 (2H, d, J = 9.0 Hz); ^{13}C NMR (100 MHz; CDCl_3) δ = 159.0, 130.6, 129.2, 113.7, 72.4, 69.9, 62.7, 55.2, 32.6, 29.6, 25.9, 25.5; MS (EI) m/z 182 (M^+); HRMS (EI) calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3$ (M^+) 238.1563, found 238.1565; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3400, 2858, 1652, 1613, 1514, 1463, 1361, 1248, 1173, 1035.

Diphenylmethyl benzyl ether⁵: (Table 6: entry 8): ^1H NMR (400 MHz; CDCl_3) δ = 4.45 (2H, s), 5.35 (1H, s), 7.15–7.30 (15H, m); ^{13}C NMR (100 MHz; CDCl_3) δ = 142.1, 138.4, 128.4, 128.3, 127.7, 127.5, 127.4, 127.2, 127.1, 82.4, 70.5; MS (EI) m/z 274 (M^+); $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 2863, 1599, 1494, 1454, 1301, 1185, 1091.

***p*-Methoxybenzyl bis-ether⁶(3):** ^1H NMR (400 MHz; CDCl_3) δ = 3.85 (6H, s), 4.55 (4H, s), 6.95 (4H, d, J = 9.0 Hz), 7.35 (4H, d, J = 9.0 Hz); ^{13}C NMR (100 MHz; CDCl_3) δ = 159.0, 130.4, 129.2, 113.6, 71.3, 55.1; MS (EI) m/z 258 (M^+); $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 2837, 1614, 1514, 1302, 1246, 1173, 1034.

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