Nanoporous Aluminoilicate Mediated Transacetalization Reactions: Application in Glycerol Valorization

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1. General Methods
Commercially available reagents were used without further purification. Ethane-1,2-diol and propane-1,3-diol were stored over activated 4Å molecular sieves prior to use. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Merk Kieselgel neutral alumina. 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 on a Bruker 400 MHz or a Jeol 270 MHz spectrometer in CDCl₃ 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 using the ionization technique stated. ES refers to electrospray ionization, CI refers to chemical ionization using ammonia and EI refers to electron impact ionization. High resolution mass spectra (HRMS) were obtained courtesy of the EPSRC Mass Spectrometry Service, Swansea University, UK using the ionization method specified. GC-MS analysis was performed using a Varian 450GC and Varian 300MS employing a VF-5ms capillary column (30m, 0.25mm i.d. and 0.25µm) 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.

2. Catalyst Characterisation Data
Figure 1a: BET Isotherm Data for S-1
Figure 1b: BET Isotherm Data for AS-(14)

Figure 1c: BET Isotherm Data for AS-(56)
Figure 2a: $^{27}\text{Al MAS NMR AS-}(14)$.

Figure 2b: $^{28}\text{Si MAS NMR AS-}(14)$.
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Figure 3b: $^{28}\text{Si}$ MAS NMR AS-(56).
Figure 4a: Pore Size Distribution S-1.

Figure 4b: Pore Size Distribution AS-(14).
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Figure 5b: XRD Data for calcined AS-(54)
4. Spectroscopic data for acetal products from acetal exchange reactions of dimethyl- and diethylacetals.

2-Phenyl-[1,3]-dioxane\(^1\) (Table 3; entry 1): \(^{1}\text{H} NMR (\text{CDCl}_3; 400 MHz) \delta = 1.45-1.45 (1\text{H}, m), 2.20-2.30 (1\text{H}, m), 3.95-4.05 (2\text{H}, m), 4.25-4.35 (2\text{H}, m), 5.55 (1\text{H}, s), 7.35-7.55 (5\text{H}, m); ^{13}\text{C} NMR (\text{CDCl}_3; 100 MHz) \delta = 138.7, 128.8, 128.2, 126.0, 101.7, 67.4, 25.8; \nu_{\text{max}} \text{(film)/cm}^{-1} \text{(neat)} 2852, 1377, 1237, 1101, 988, 746 and 696; MS (EI) \text{m/z} 164; \text{HRMS (ES) calculated for } C_{10}H_{13}O_2 (M - H)^{+} 163.0754, \text{found (M - H)}^{+} 163.0755.

5,5-Dimethyl-2-phenyl-[1,3]-dioxane\(^2\) (Table 3; entry 2): \(^{1}\text{H} NMR (\text{CDCl}_3; 400 MHz) \delta = 0.75 (3\text{H}, s), 1.25 (3\text{H}, s), 3.55 (2\text{H}, d, J = 11.0 \text{ Hz}), 3.70 (2\text{H}, d, J = 11.0 \text{ Hz}), 5.30 (1\text{H}, s), 7.25-7.35 (3\text{H}, m), 7.40-7.45 (2\text{H}, m); ^{13}\text{C} NMR (\text{CDCl}_3; 100 MHz) \delta = 138.4, 128.8, 128.2, 126.1, 101.7, 30.2, 23.0, 21.8; \nu_{\text{max}} \text{(film)/cm}^{-1} \text{(neat)} 2846, 1388, 1215, 1101, 1017, 745 and 696; MS (EI) \text{m/z} 192; \text{HRMS (ES) calculated for } C_{12}H_{17}O_2 (M + NH}_4^{+} 193.1223, \text{found (M + NH}_4^{+} 193.1224.

2-Phenyl-[1,3]-dioxane\(^3\) (Table 3; entry 3): \(^{1}\text{H} NMR (\text{CDCl}_3; 400 MHz) \delta = 3.95-4.05 (2\text{H}, m), 4.10-4.15 (2\text{H}, m), 5.80 (1\text{H}, s), 7.35-7.40 (3\text{H}, m), 7.45-7.50 (2\text{H}, m); ^{13}\text{C} NMR (\text{CDCl}_3; 100 MHz) \delta = 137.8, 129.1, 128.2, 126.3, 103.6, 65.2; \nu_{\text{max}} \text{(film)/cm}^{-1} \text{(neat)} 2887, 1456, 1392, 1204, 1096, 968, 746 and 699; MS (EI) \text{m/z} 150.

2-(4-Methoxyphenyl)-5,5-dimethyl-[1,3]-dioxane\(^4\) (Table 3; entry 5): \(^{1}\text{H} NMR (\text{CDCl}_3; 400 MHz) \delta = 0.75 (3\text{H}, s), 1.25 (3\text{H}, s), 3.60 (2\text{H}, d, J = 11.0 \text{ Hz}), 3.65 (2\text{H}, d, J = 11.0 \text{ Hz}), 3.75 (3\text{H}, s), 5.30 (1\text{H}, s), 6.80 (2\text{H}, d, J = 9.0 \text{ Hz}), 7.35 (2\text{H}, d, J = 9.0 \text{ Hz}); ^{13}\text{C} NMR (\text{CDCl}_3; 100 MHz) \delta = 160.0, 131.1, 127.4, 113.7, 101.7, 55.3, 30.2, 23.1, 21.9; \nu_{\text{max}} \text{(film)/cm}^{-1} \text{(neat)} 2947, 2867, 1613, 1519, 1301, 1250, 1097 and 830; MS (EI) \text{m/z} 222; \text{HRMS (ES) calculated for } C_{13}H_{19}O_3 (M + H)^{+} 223.1329, \text{found (M + H)}^{+} 223.1327.

2-(4-Bromophenyl)-[1,3]-dioxane\(^4\) (Table 3; entry 6): \(^{1}\text{H} NMR (\text{CDCl}_3; 400 MHz) \delta = 1.35-1.45 (1\text{H}, m), 2.00-2.20 (1\text{H}, m), 3.85-3.95 (2\text{H}, m), 4.15-4.20 (2\text{H}, m), 5.40 (1\text{H}, s), 7.30-7.35 (2\text{H}, d, J = 9.0 \text{ Hz}), 7.45-7.50 (2\text{H}, d, J = 9.0 \text{ Hz}); ^{13}\text{C} NMR (\text{CDCl}_3; 100 MHz) \delta = 137.7, 131.1, 127.6, 122.5, 100.5, 67.1, 25.5; \nu_{\text{max}} \text{(film)/cm}^{-1} \text{(neat)} 2857, 1378, 1491, 1277, 1106, 1013, 912 and 648; MS (EI) \text{m/z} 243.

2-(4-Nitrophenyl)-5,5-dimethyl-[1,3]-dioxane\(^5\) (Table 3; entry 7): \(^{1}\text{H} NMR (\text{CDCl}_3; 400 MHz) \delta = 0.75 (3\text{H}, s), 1.25 (3\text{H}, s), 3.60 (2\text{H}, d, J = 11.0 \text{ Hz}), 3.75 (2\text{H}, d, J = 11.0 \text{ Hz}), 5.40 (1\text{H}, s), 7.60
(2H, d, $J = 9.0$ Hz), 8.20 (2H, d, $J = 9.0$ Hz); $^{13}$C NMR (CDCl$_3$; 100 MHz) $\delta = 147.9, 145.0, 127.1, 123.1, 99.8, 77.8, 30.0, 22.8, 21.5$; $\nu_{\text{max}}$ (film)/cm$^{-1}$ (neat) 2857, 1519, 1346, 1216, 1102 and 1017; MS (EI) $m/z$ 237.

1,4-Dioxaspiro[4.5]decane$^6$ (Table 3; entry 8): $^1$H NMR (CDCl$_3$; 400 MHz) $\delta = 1.30$-1.70 (10H, m), 3.85 (4H, s); $^{13}$C NMR (CDCl$_3$; 100 MHz) $\delta = 109.0, 64.1, 35.1, 25.1, 23.9$; $\nu_{\text{max}}$ (film)/cm$^{-1}$ (neat) 1316, 1231, 1163, 1102 and 1038; MS (EI) $m/z$ 142.

1,5-Dioxaspiro[5.5]undecane$^7$ (Table 3; entry 9): $^1$H NMR (CDCl$_3$; 400 MHz) $\delta = 1.25$-1.90 (12H, m), 3.75-3.85 (4H, m); $^{13}$C NMR (CDCl$_3$; 100 MHz) $\delta = 97.8, 58.9, 32.9, 25.6, 22.3$; $\nu_{\text{max}}$ (film)/cm$^{-1}$ (neat) 1277, 1255, 1158, 1142, 1109 and 1052; MS (EI) $m/z$ 156.

3,3-Dimethyl-1,5-dioxaspiro[5.5]undecane$^8$ (Table 3; entry 10): $^1$H NMR (CDCl$_3$; 400 MHz) $\delta = 0.90$ (6H, s), 1.30-1.75 (10H, m), 3.45 (4H, s); $^{13}$C NMR (CDCl$_3$; 100 MHz) $\delta = 97.7, 69.8, 32.6, 30.2, 25.8, 22.8, 22.6$; $\nu_{\text{max}}$ (film)/cm$^{-1}$ (neat) 2936, 2858, 1364, 1284, 1104, 914, and 733; MS (EI) $m/z$ 184; HRMS (ESI) calculated for C$_{11}$H$_{21}$O$_2$ (M + H)$^+$ 185.1536, found (M + H)$^+$ 185.1537.

5. Spectroscopic data for acetal products from acetal exchange reactions of dimethyl- and diethylacetals with glycerol.

2,2-Dimethyl-[1,3]-dioxolan-4-yl)methanol$^9$ (Table 4; entry 3): $^1$H NMR (CDCl$_3$; 270 MHz) $\delta = 1.35$ (3H, s), 1.40 (3H, s), 2.60 (1H, br s), 3.55-3.75 (3H, m), 3.90-4.00 (1H, m), 4.10-4.20 (1H, m); $^{13}$C NMR (CDCl$_3$; 67.5 MHz) $\delta = 109.3, 76.2, 65.8, 62.9, 26.6, 25.1$; $\nu_{\text{max}}$ (film)/cm$^{-1}$ (neat) 3390, 1417, 1260, 1110, 1035 and 853; MS (EI) $m/z$ 132.

1,4-dioxaspiro[4.5]decane-2-methanol$^9$ (Table 4; entry 4): $^1$H NMR (CDCl$_3$; 270 MHz) $\delta = 1.25$-1.75 (10H, m), 2.40 (1H, br s), 3.55 (1H, dd, $J = 5.0$ and 11.0 Hz), 3.65 (1H, dd $J = 5.0$ and 11.0 Hz), 3.75 (1H, dd $J = 6.0$ and 8.0 Hz), 3.95 (1H, dd, $J = 6.0$ and 8.0 Hz), 4.10-4.20 (1H, m); $^{13}$C NMR (CDCl$_3$; 67.5 MHz) $\delta = 110.0, 75.8, 65.5, 63.2, 36.4, 34.8, 25.0, 24.0, 23.8$; $\nu_{\text{max}}$ (film)/cm$^{-1}$ (neat) 3448, 1366, 1281, 1163, 1099, 911, and 735; MS (EI) $m/z$ 172.

References


