SUPPLEMENTARY INFORMATION

Silica-supported chlorometallate(III) ionic liquids as recyclable catalysts for Diels-Alder reaction under solventless conditions

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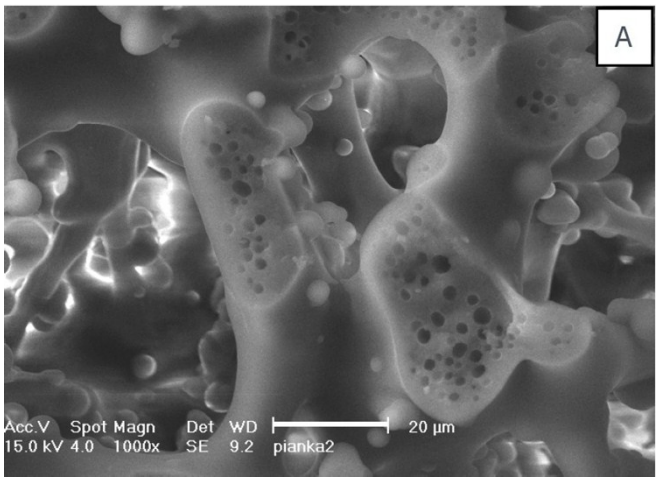


Fig. 1. Scanning electron microscopy micrograph of hierarchical porosity silica monolith.

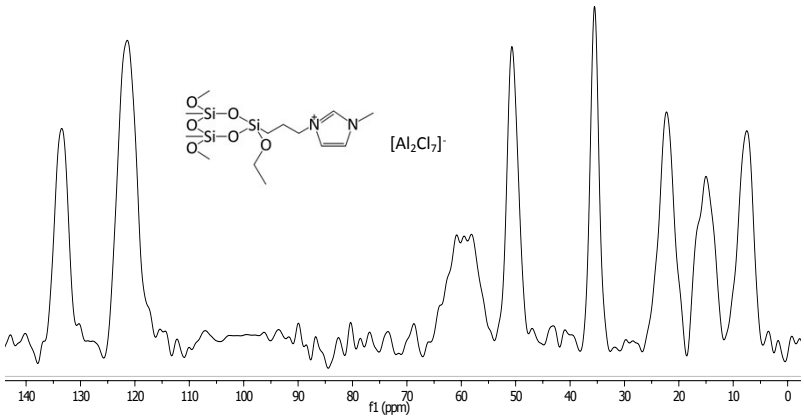


Fig. 2. ^{13}C CP MASS NMR of SiO_2-[tespmim][Al_2Cl_7] (Solid state ^{13}C NMR experiments were performed using a Bruker 500 MHz NMR spectrometer).

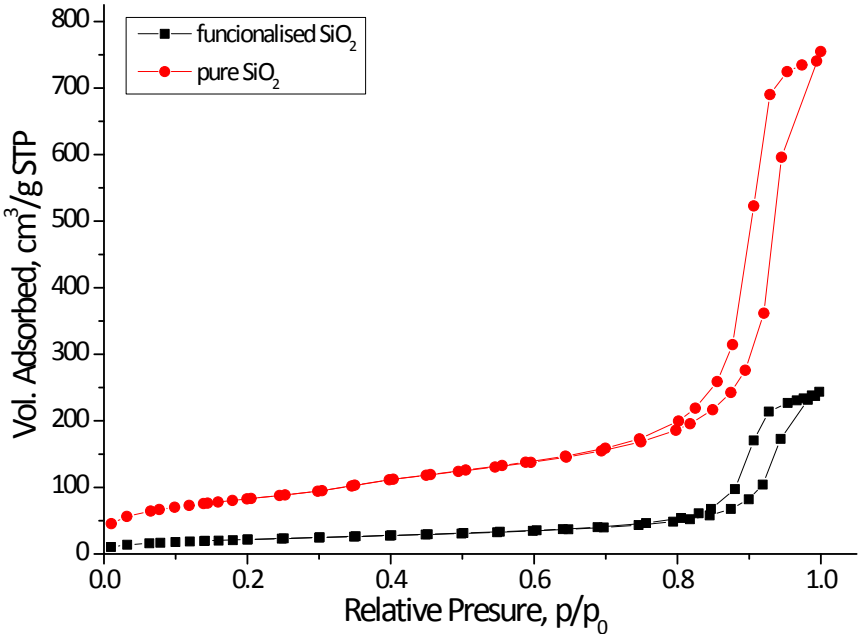


Fig. 3. Nitrogen adsorption isotherms of pure SiO_2 and after functionalisation.

Obtained silica monoliths are characterised by Type IV of isotherm, which is typical for porous materials. After functionalisation, decrease in adsorbed volume of nitrogen and specific surface area was observed, but not in the type of isotherm. It is mean that the functionalisation did not change the structure of support.

Table 1. Data concerning pure silica and after functionalisation.

Parameter	**Pure SiO_2**	**Functionalised SiO_2**
S_{BET}, m^2/g	300.25	78.29
Pore volume, cm^3/g	1.17	0.38

Synthesis of SiO_2-[tespmim][Al_2Cl_7] (alternative method):

SiO_2 (2 g) was suspended in dry toluene (10 cm^3). Next, 1 g of [tespmim][Cl] was added. Two-necked round-bottomed flask was equipped with a nitrogen-filled balloon, closed with a septum and stirred at 90 °C for 16 h. Subsequently, toluene and ethanol created in the grafting step were removed under vacuum and the catalyst was dried for 4 h at 80 °C under reduced pressure. The excess of 1-(triethoxysilyl)propyl-3-methylimidazolium was removed by 24 h extraction with boiling dichloromethane. The dried support was then mixed with $AlCl_3$ in toluene and left stirring for 3 hours at room temperature. After filtration, the excess of $AlCl_3$ was removed by extraction with boiling dry dichloromethane in an Soxhlet apparatus and the material was dried under reduced pressure.

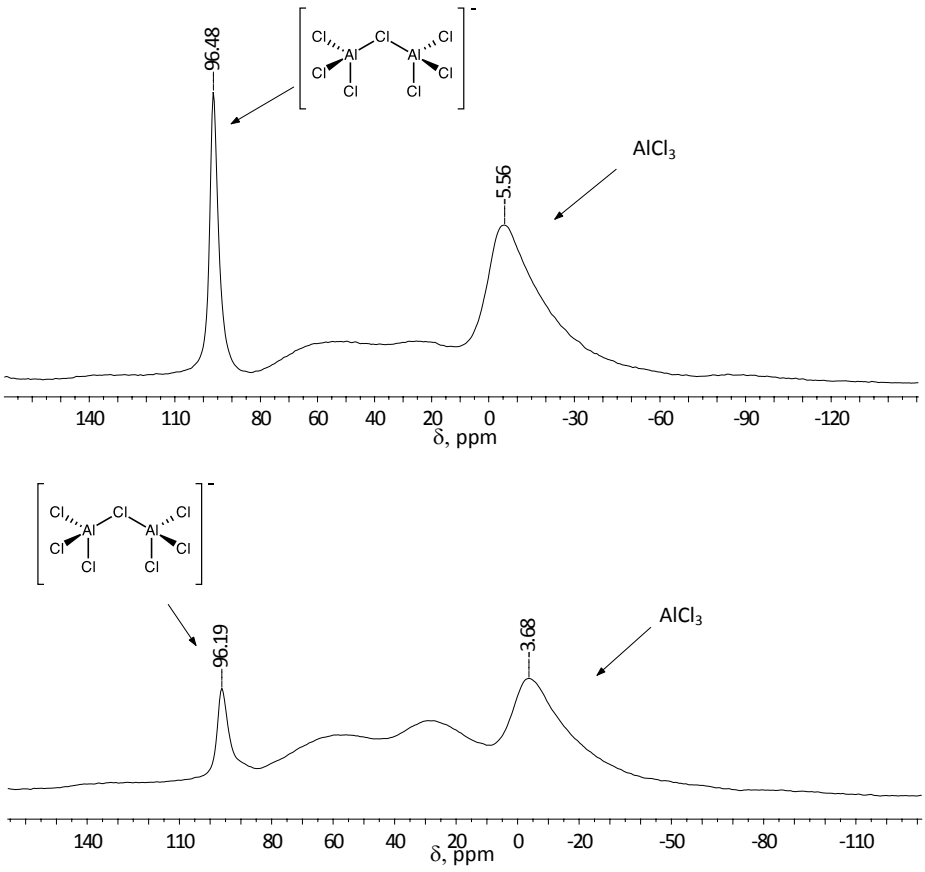
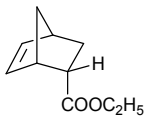


Fig. 4. ^{27}Al MAS NMR of SiO_2-[tespmim][Al_2Cl_7] obtained with the alternative method (before Soxhlet extraction (top) and after (bottom).

Analysis of Diels-Alder cycloadducts

^{1}H and ^{13}C NMR spectra of Diels-Alder cycloadducts were recorded at 599.829 and 150,827 MHz using Varian spectrometer with TMS as internal standard. GC–MS analysis was performed using an Agilent gas chromatograph 7890C (HP-5 MS capillary column, 30 m x 0.25 mm x 0.25 μm, helium 1 mL/min) conjugated with an Agilent mass spectrometer 5975C with EI ionization (70 eV). Products were identified using the NIST/EPA/NIH Mass Spectral Library.

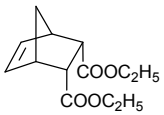


Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, ethyl ester:

^{1}H NMR (600MHz, $CDCl_3$, TMS) δ: 1.22 (t, 3H, J=5.4Hz), 1,24-1,27 (m, 1H), 1.42-1.44 (m, 2H), 1.87-1.92 (ddd, 1H, J=12.1, 9.4, 3.7Hz), 2.88-2.91 (brs, 1H), 2.92-2.95 (dt, 1H, J=9.4, 3.9 Hz), 3.19-3.21 (brs, 1H), 4.04-4.11 (m, 2H), 5.92-5.94 (dd, 1H, J=5.7, 2.8Hz), 6.17-6.19 (dd, 1H, J=5.7, 3.1Hz);

^{13}C NMR (600MHz, $CDCl_3$ δ): 14.26, 29,22, 42.53, 43.36, 45.67, 49.60, 60,14, 132.33 137.69, 174.85;

MS (EI) m/z (%) 166 (5, $M^{+\cdot}$), 121 (7) 101 (17), 93 (7), 91 (10), 77 (7), 73 (8), 66 (100), 65 (10), 55 (15), 39 (13).

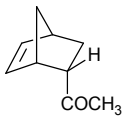


Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, 2,3-diethyl ester:

^{1}H NMR (600MHz, $CDCl_3$ δ): 1.22 (t, 6H, J=7.2Hz), 1.32-1.34 (m, 1H), 1.46-1.48 (dt, 1H, J= 2.0, 1.4Hz), 3.15-3.17 (m, 2H), 3.27-3.28 (dd, 2H J=1.9, 1.3Hz), 4.03-4.11 (m, 4H), 6.26 (t, 2H, J=1.8Hz);

^{13}C NMR (600MHz, $CDCl_3$ δ): 16.78, 48.95, 50.93, 51.29, 62.87, 137.47, 175.03;

MS (EI) m/z (%) 193 (9, $M^{+\cdot}$), 173 (17), 165 (13), 145 (4), 128 (3), 127 (37), 119 (23), 100 (2), 99 (35), 91 (23), 77 (6), 67 (7), 66 (100), 65 (15), 53 (4), 39 (13).

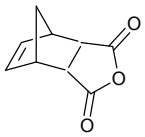


1-(Bicyclo[2.2.1]hept-5-en-2-yl)ethanone:

^{1}H NMR (600MHz, $CDCl_3$ δ): 1.33-1.35 (m, 1H), 1.46-1.52 (m, 2H), 1.74-1.79 (ddd, 1H, J=8.7, 3.3Hz), 2.13-2.15 (s, 3H), 2.90-2.93 (brs, 1H), 3.00-3.03 (dt, 1H J=8.7, 3.9Hz), 3.24-3.26 (brs, 1H), 5.86-5.88 (dd, 1H, J=5.7, 2.8Hz), 6.16-6.18 (dd, 1H, J=5.6, 3.1Hz);

^{13}C NMR (600MHz, $CDCl_3$ δ): 30.08, 31.83, 45.32, 48.50, 52.59, 55.01, 133.86, 140.51, 211.61;

MS (EI) m/z (%) 136 (6, $M^{+\cdot}$), 117 (1), 94 (1), 92 (2), 91 (10), 79 (2), 77 (11), 72 (1), 71 (14), 67 (6), 66 (100), 65 (12), 63 (3), 58 (8), 51 (5), 43 (31), 41 (6), 39 (21).

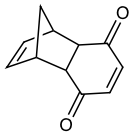


Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride:

^{1}H NMR (600MHz, $CDCl_3$ δ): 1.57-1.59 (dt, 1H, J=9.1, 1.5Hz), 1.78-1.79 (dt, 1H, J=9.0, 1.7Hz), 3.50-3.52 (m, 2H), 3.57-3.59 (dd, 2H, J=3.0, 1.6Hz), 6.29-6.30 (t, 2H, J=1.9Hz);

^{13}C NMR (600MHz, $CDCl_3$ δ): 48.75, 49.72, 55.39, 138.16, 173.94;

MS (EI) m/z (%) 164 (1, M+·), 120 (3), 99 (2), 92 (13), 91 (39), 89 (1), 77 (2), 67 (5), 66 (100), 65 (16), 63 (7), 51 (8), 40 (9), 39 (30), 38 (8).

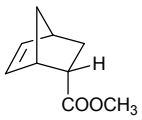


Tricyclo[6.2.1.0]undeca-4,9-diene-3,6-dione:

^{1}H NMR (600MHz, CDCl3 δ): 1.41-1.44 (dt, 1H, J=8.7, 1.7Hz), 1.52-1.55 (dt, 1H, J=8.7, 1.7Hz), 3.20-3.22 (brs, 2H), 3.52-3.55 (brs, 2H), 6.05-6.06 (m, 2H), 6.56-6.57 (m, 2H);

^{13}C NMR (600MHz, CDCl3 δ): 50.98, 51.33, 51.39, 137.91, 144.66, 202.01;

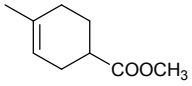
MS (EI) m/z (%) 174 (14, $M^{+\cdot}$), 91 (11), 82 (6), 67 (6), 66 (100), 65 (18), 63 (6), 54 (15), 53 (5), 40 (14).



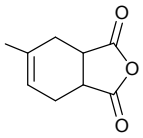
5-(Methoxycarbonyl)bicyclo[2.2.1]hept-2-ene:

^{1}H NMR (600MHz, $CDCl_3$ δ): 1.27-1.29 (d, 1H, J=8.1Hz), 1.41-1.45 (m, 2H), 1.89-1.93 (ddd, 1H, J=11.8, 9.4, 3.7Hz), 2.89-2.92 (brs, 1H), 2.93-2.96 (dt, 1H, J=9.2, 3.9Hz), 3.19-

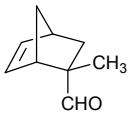
3.21 (brs, 1H), 3.62 (s, 3H), 5.92-5.94 (dd, 1H, J=5.7, 2.8 Hz), 6.18-6.20 (dd, 1H, J=5.7, 3.1Hz);
^{13}C NMR (600MHz, $CDCl_3$ δ): 31.91, 45.16, 45.82, 48.30, 52.26, 54.10, 135.01, 140.38, 177.89;
MS (EI) m/z (%) 154 (21, $M^{+\cdot}$), 95 (49), 94 (100), 93 (19), 79 (73), 77 (23), 67 (36), 55 (25), 41 (25), 39 (33).



4-Methoxycarbonyl-1-methylcyclohexene:
^{1}H NMR (600MHz, CDCl3 δ): 1.65 (brs, 3H), 1.68-1.72 (m, 2H), 1.98-2.02 (m, 2H), 2.20-2.24 (m, 2H), 2.47-2.52 (ddd, 1H, J=11.5, 9.2, 2.8Hz), 3.68 (s, 3H), 5.36-5.38 (m, 1H);
^{13}C NMR (600MHz, CDCl3 δ): 26.07, 28.11, 30.31, 31.91, 41.79, 54.18, 121.84, 136.33, 179.08;
MS (EI) m/z (%) 155 (34, $M^{+\cdot}$), 153 (13), 139 (6), 123 (27), 121 (12), 96 (11), 95 (100), 94 (40), 81 (11), 79 (21), 77 (7), 67 (31), 55 (19), 41 (25), 40 (6).



1,2,3,6-Tetrahydro-4-methylphthalic anhydride:
^{1}H NMR (600MHz, CDCl3 δ): 1.76-1.78 (brs, 3H), 2.25-2.28 (m, 2H), 2.48-2.52 (dd, 1H, J=15.6, 2.9Hz), 2.55-2.60 (ddd, 1H, J=15.6, 6.4, 2.7Hz), 3.31-3.42 (m, 2H), 5.61-5.64 (m, 1H);
^{13}C NMR (600MHz, CDCl3 δ): 26.10, 26.70, 31.04, 42.08, 42.72, 122.78, 139.20, 176.88, 177.03;
MS (EI) m/z (%) 166 (3, $M^{+\cdot}$), 139 (2), 138 (27), 123 (4), 93 (89), 78 (11), 65 (9), 51 (17), 41 (11), 39 (41), 40 (7).



Bicyclo[2.2.1]hept-5-ene-2-methyl-2-carboxaldehyde, ^{1}H NMR (600MHz, $CDCl_3$, TMS) δ: 0.76-0.78 (dt, 1H, J=9.1, 1.4Hz), 1.02 (s, 3H), 1.39-1.41 (m, 2H), 2.24-2.28 (dd, 1H, J=12.0, 3.8Hz), 2.82-2.84 (m, 1H), 2.89-2.92 (brs, 1H), 6.11-6.13 (m, 1H), 6.29-6.31 (m, 1H), 9.40 (s, 1H, *endo*) 9.70 (s, 1H, *exo*); ^{13}C NMR (600MHz, CDCl3 δ): 22.67, 37.24, 45.85, 50.24, 51.10, 56.52, 135.72, 142.17, 208.42; MS (EI) m/z (%) 136 (4, $M^{+\cdot}$), 107 (2), 92 (1), 91 (7), 80 (1), 79 (9), 78 (2), 67 (7), 66 (100), 65 (12), 63 (3), 51 (5), 43 (3), 41 (12), 40 (7), 39 (25), 37 (1).