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

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A range of Lewis acidic metal chlorides were tested as homogenous catalysts in a model Diels-Alder reaction; $AlCl_3$ and $GaCl_3$ performed best in terms of conversion and *endo*:*exo* selectivity. Based on this outcome, corresponding chlorometallate(III) ionic liquids were tested as homogenous catalysts, without decrease in perfomrance compared to the chlorides. Finally, these ionic liquids were heterogenised by covalent tethering of the cation onto a multimodal porous silica support; such supported chlorogallate(III) ionic liquids are reported for the first time. Supported chlorometallate(III) ionic liquids were used as recyclable, heterogeneous catalysts for Diels-Alder reaction under solventless conditions. High yields (99% and and high *endo*-selectivities (95%) were obtained after very short reaction times (5 min), at near-ambient temperature (25 °C).

Introduction

The Diels–Alder reaction is a powerful transformation, allowing for the construction of six-membered carbocycles (Scheme 1).
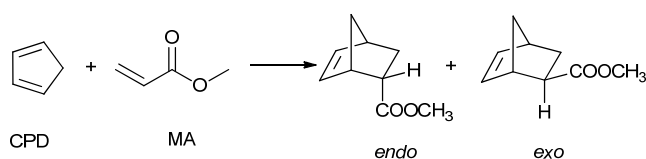
Scheme 1. Diels-Alder cycloaddition of cyclopentadiene to methyl acrylate

The Diels-Alder reaction is the key step in the syntheses of pharmacologically active ingredients, agrochemicals, flavors and fragrances.[1] Although it can proceed without a catalyst, enhanced reaction rates and selectivities were reported when a catalyst was used.[2] Lewis acidic catalysts coordinate to the dienophile, influencing both the reaction rate and the selectivity to *endo:exo* or *ortho/para* isomers (Scheme 1).[3] Zinc(II) chloride, boron(III) fluoride, tin(IV) chloride, aluminium(III) chloride, *etc*. have all been used as catalysts. A range of ionic liquids have also been tested as catalysts for Diels-Alder reaction;[4] the most active were Lewis acidic chloroaluminate(III) systems.[5,6,7]

Chlorometallate ionic liquids are synthesised by the reaction of a metal halide with an organic halide salt, at various molar ratios, typically reported as molar ratio of the metal halide component, χ_{MClx}. When metal halide is used in excess ($\chi_{MClx} > 0.50$), oligonuclear, Lewis acidic anions are formed.[8]

An ionic liquid based on 1-ethyl-3-methylimidazolium chloride and a slight excess of aluminium chloride(III), $[C_2mim]Cl-AlCl_3$; $\chi_{AlCl3}= 0.51$ was used as both solvent and catalyst for cycloaddition of cyclopentadiene to methyl acrylate. The reaction rate was 10 times higher than in water, which is one of the most effective solvents for this reaction, and a good *endo:exo* ratio was obtained (95:5). However, the chloroaluminate(III) ionic liquid was used in a large excess.[5] In addition, chloroindate(III)[9] chlorozincate(II) and chlorostannate(II) ionic liquids were found to be active catalyst for the Diels-Alder reaction.[10,11] There are still some challenges to achieve, like application of catalytic amounts of ionic liquids and lowering reaction times.

Heterogenisation of catalysts can offer advantages in handling, separation and recycling.[12] By supporting ionic liquids, the required amount of ionic phase can be significantly reduced. In addition, it enables the use of fixed-bed reactor systems.[11] Three main methods of immobilisation of ionic liquid on silica support: *via* anion, *via* cation and physically supported liquid phase (SILP) were described. Hölderich[13] postulated that for chloroaluminate(III) ionic liquids, immobilisation *via* cation is the most efficient. Leaching of the active phase is limited compared to the SILP approach due to covalent binding, and the Lewis acidic anion retains its full activity.

Supported chlorometallate ionic liquids, such as chloroaluminates(III),[13] chloroindates(III),[14] chloroferrates(III) and chlorostannates(II)[15] were extensively studied as catalysts in Friedel–Crafts alkylation and acylation. In all cases, high

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efficiency, good stability and the possibility of recycling were demonstrated. The performance of SILPs was typically better, and sometimes on par with that of free ionic liquids. Surprisingly, there is only a single report on the application of chlorometallate SILPs for the Diels-Alder. Lewis acidic chloroaluminate(III) ionic, synthesised from poly(4-vinylpyridine) or poly(1-vinylimidazole) polymers, exhibited similar activity and selectivity to the homogeneous analogue.[16] The reaction was carried out in toluene and the selectivity *endo:exo* product was 61:39. The polymer-supported chloroaluminate(III) catalysts was recycled five times, with a 20% loss of initial activity.

In this work, we explored the catalytic potential of chlorogallate(III) and chloroaluminate(III) ionic liquids supported on silica by covalently bound cations, under solventless conditions.

Experimental

Materials and methods

All reactants were purchased from Sigma-Aldrich and used as received, unless otherwise stated. Dichloromethane was distilled from P_2O_5 and stored over activated 3Å molecular sieves. All metal chlorides were anhydrous, 99.99% purity, packed in ampules under inert gas. MH-type silica material and 1-methyl-3(triethoxysilylpropyl)imidazolium chloride were prepared according to the literature.

Synthesis of 1-methyl-3-(triethoxysilyl-propyl)imidazolium chloride, [tespmim]Cl

The mixture of 0.12 mol (3-chloropropyl)triethoxysilane and 0.12 mol of 1-methylimidazole (freshly distilled) was refluxed at 78 °C for 24 h under nitrogen atmosphere. The reaction mixture was cooled down and any remaining volatile substances were removed by rotary evaporation. The crude product was additionally washed with Et_2O (5x5 ml) and dried under vacuum. The product (slightly yellow viscous oil) was obtained with 98% yield.

1H NMR (600 MHz, CDCl3, TMS): d = 10.66 (s, 1H), 7.36 (m, 1H), 7.59 (m, 1H), 4.34 (t, 2H, J = 7.40 Hz), 4.14 (s, 3H), 3.82 (4, 6H, J = 7.40 Hz), 2.05 (m, 2H), 1.20 (t, 9H, J = 7.80 Hz), 0.61 (m, 2H); 13C NMR (300 MHz, CDCl3, TMS): d = 138.13, 123.34, 121.58, 58.53, 51.66, 36.51, 24.32, 18.2, 7.03. Anal. Calcd.: C, 48.45; H, 8.39; N, 8.69. Found: C, 48.34; H, 8.30; N, 8.77.

General procedure for synthesis of silica support (MH) with the extensive system of meso- and macropores

The synthesis of support using porogenes of different sizes (polyethylene glycol and cetyltrimethylammonium bromide), together with the induction and freezing of the transition structures originating from the phase separation process, led to the formation of a macroporous, interconnected, open network with bimodal system of macropores of micrometer size. In a typical procedure 8.7 g of polyethylene glycol (PEG) with molecular weight of 35.000 g/mol was dissolvedin 100 ml of 1M HNO_3 Sol was stirred until a clear solution was obtained. Then

83 ml tetraethoxysilane was added slowly and after that 3.84 g of cetylotrimethylammonium bromide. This solution was left to gel at 40 °C and aged for 10 days at the same temperature Next the white alcogels obtained were impregnated in a 1 M NH_4OH solution for 9 h at 90 °C, washed with deionised water, dried for 4 days at room temperature and then calcined at 550 °C for 8 h under air (heating ramp 0.5 K/min). The size and shape of the monoliths were determined by the size and shape of the vessel used. Composition led to the formation of a macroporous, interconnected, open network with bimodal system of macropores of micrometer size. Apart from the macropores, the material also exhibited textural mesopores, with BET surface area of 300 m^2/g, total pore volume – 3.5-4 cm^3/g and mean mesopore diameter of about 20 nm (determined by nitrogen adsorption), macropore diameter 30-50 μm. The SEM picture of silica support MH is presented in ESI.

Synthesis of 1-methyl-3-(triethoxysilyl-propyl)imidazolium chlorometallate(III) ionic liquids, [tespmim][$M_nCl_{(3n+1)}$]

All chlorometallate ionic were prepared according to the general procedure, at a 1 g scale.[17] Appropriate amounts of dry [tespmim]Cl were placed in a round bottom flask equipped with a stirring bar. Then metal chloride MCl_3 (where M = Al or Ga) was added slowly, with stirring to achieve the desired composition, and then allowed to fully react (1000 rpm, 3 h, 60 °C). All reactions were carried out under dry inert gas. Exact amounts of reactants are listed in Table 1.

Synthesis of 1-methyl-3-(triethoxysilyl-propyl)imidazolium chlorometallate(III) ionic liquids anchored on the silica support, MH-[tespmim][$M_nCl_{(3n+1)}$]

MH (1 g) was suspended in dry toluene (5 cm^3). Next, 1.55 mmol of ionic liquid: [tespmim][Al_2Cl_7] or [tespmim][Ga_3Cl_{10}], was added. Two-necked round-bottomed flask was equipped with a nitrogen-filled balloon, closed with a septum and stirred at 80 °C for 3 h. Subsequently, toluene was removed under vacuum and the catalyst was dried for 4 h at 80 °C under reduced pressure. To verify ionic liquids immobilisation efficiency ICP, solid state ^{1}H, ^{13}C, ^{29}Si and ^{27}Al NMR were performed.

Table 1. The amounts of reactants used for the synthesis of chlorometallate ionic liquids

Chlorometallate ionic liquid	χ_{MCl3}[a]	[tespmim]Cl, mmol	MCl_3, mmol
[tespmim][$AlCl_4$]	0.50	2.19	2.19
[tespmim][Al_2Cl_7]	0.67	1.70	3.39
[tespmim][$GaCl_4$]	0.50	2.00	2.00
[tespmim][Ga_2Cl_7]	0.67	1.48	2.96
[tespmim][Ga_3Cl_{10}]	0.75	1.17	3.52

[a] χ_{MCl3}-molar ratio of metal chloride in ionic liquids

Diels-Alder reaction catalysed with homogenous catalysts

The dienophile (4 mmol) and the catalyst, containing 5 mol% of MCl_3 per dienophile were placed in a two-necked round-bottomed flask equipped with septum, the balloon with argon and stirring bar. Then the diene (6 mmol) was added dropwise to the vigorously stirred (1500 rpm) reaction mixture. The reaction was carried out at room temperature for 5 – 120 min, and monitored by gas chromatography.

The Diels-Alder reaction catalysed with supported ionic liquids

The dienophile (4 mmol) and the catalyst, containing 5 mol% of MCl_3 per dienophile (0.1235 g of MH-[tespmim][Al_2Cl_7] or 0.0998 g of MH-[tespmim][Ga_3Cl_{10}]), were placed in a two-necked round-bottomed flask equipped with septum, the balloon with argon and stirring bar. Then the diene (6 mmol) was added dropwise to the vigorously stirred (1500 rpm) reaction mixture. The reaction was carried out at room temperature for 5 – 120 min, and monitored by gas chromatography. Afterwards, 1 ml of dichloromethane was added to the mixture, and the catalyst was filtered off. The solvent was removed, and the products were purified by column chromatography (100 % chloroform) or crystallisation, as necessary. All Diels-Alder adducts were characterised by NMR spectroscopy and ESI-MS.

Recycling of MH-[tespmim][Ga_3Cl_{10}]

For the recycling experiment, amounts of reactants were doubled: dienophile (8 mmol), diene (12 mmol), and 0.1996 g of MH-[tespmim][Ga_3Cl_{10}]. After the reaction, the product and unreacted starting materials were separated by distillation. Next, the catalyst was dried (4 h in 80 °C under reduced pressure) and reused.

Analyses

Gas chromatography was performed using a Perkin Elmer Clarus 500 gas chromatograph equipped with an SPB™-5 column (30 m x 0.2 mm x 0.2 μm) with *n*-decane as internal standard.
GC–MS was performed using an Agilent gas chromatograph 7890C (HP-5 MS capillary column, 30 m x 0.25 mm x 0.25 μm, conjugated with an Agilent mass spectrometer 5975C with EI ionization (70 eV). Products were identified using the NIST/EPA/NIH Mass Spectral Library.
The morphology of silica support was determined with scanning electron microscopy (SEM) using a Philips XL30 apparatus.
^{29}Si MAS NMR spectra were measured at 59.517 MHz using a Bruker HP-WB high-speed MAS probe equipped with a 4mm zirconia rotor to record the NMR spectra at a spinning speed of 8 kHz. Solid state ^{13}C NMR experiments were performed using a Bruker 500 MHz NMR spectrometer. For ^{27}Al NMR solid state measurements a Bruker Avance III 400 MHz WB spectrometer using 4 mm probe MAS was used (calibration with Al_2O_3 as external standard).
Inductively coupled plasma (ICP) measurements were performed on Optical Emission Spectrometer ICP-OES Varian 710-ES.

Results and discussion

Homogenous Diels-Alder reaction catalysed with metal chlorides

Although Lewis acidic metal chlorides are the most common catalysts for the Diels-Alder reaction,[2] the literature lacks comparative studies of the activity different metal chlorides, which could guide the selection of best chlorometallate ionic liquids. In the preliminary screening, a range of metal chlorides ($AlCl_3$, $GaCl_3$, $InCl_3$, $FeCl_3$, $SnCl_4$, $SnCl_2$, $TiCl_4$) were tested as Lewis acidic catalysts in a model cycloaddition of methyl acrylate (MA) to cyclopentadiene (CPD), shown in Scheme 1. The influence of the catalyst on conversion and selectivity is shown in Figure 1.

Aluminium(III) chloride and gallium(III) chloride performed best, with high conversion and high *endo*-selectivity (94 %), achieved after only 5 minutes. Reaction catalysed with tin(IV) chloride also proceeded at a very high rate, but the *endo*-selectivity was lower (91%). Conversely, catalysis with iron(III) chloride led to good *endo*-stereoselectivity (94%), but with lower conversion of dienophile (α_{MA} = 65%), caused by competitive polymerisation of cyclopentadiene. Other metal chlorides ($TiCl_3$, $InCl_3$ and $SnCl_2$) performed poorer, both in terms of conversion and selectivity. Consequently, chlorometallate ionic liquids based on $AlCl_3$ and $GaCl_3$ were selected for further study.

Homogenous Diels-Alder reaction catalysed with chlorometallate(III) ionic liquids

Lewis acidity of chlorometallate ionic liquids depends on both metal electrophilicity and the mole fraction of metal
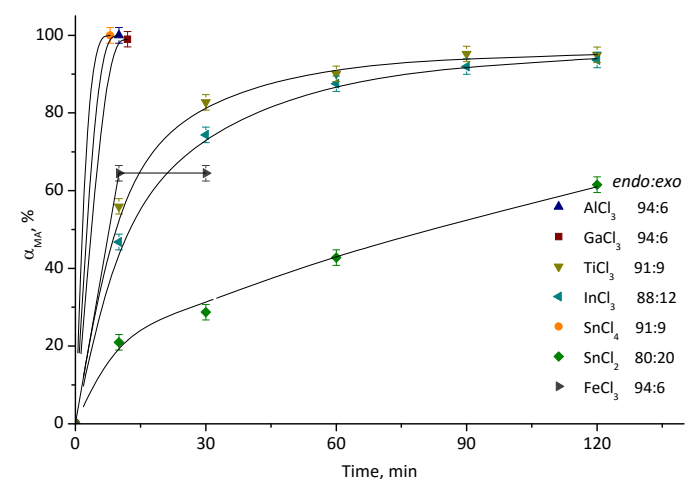

Fig. 1 The influence of the metal chloride catalyst on the conversion of methyl acrylate (α_{MA}) and the stereoselectivity in Diels-Alder reaction.
Reaction conditions: T = 25 °C; r = 1500 rpm; CPD (4 mmol); MA (6 mmol); catalyst loading 5 mol % per MA.

chloride, χ_{MCl3}. For chloroaluminate(III) and chlorogallate(III) systems, compositions of χ_{MCl3} = 0.50 are neutral (and typically not catalytically active), and χ_{MCl3} > 0.50 are Lewis acidic. Whereas chloroaluminates(III) form homogenous ionic liquids up to χ_{AlCl3} = 0.67,[18] chlorogallate(III) ionic liquids remain homogenous within a wide range of compositions, with GaCl$_3$ contents up to χ_{GaCl3} = 0.75 reported.[19]

Firstly, chlorometallate(III) ionic liquids were tested as homogenous catalysts. The catalytic activity of metal chlorides and corresponding chlorometallate(III) ionic liquids, in homogenous mode, is compared in Table 2. For meaningful comparison, in all cases there is 5 mol% of nominal metal(III) chloride content per dienophile. Two ionic liquids were used: one build of the most popular cation used to form ionic liquids, 1-ethyl-3-methylimidazolium, [C$_2$mim]$^+$, and second with silyl-functionalised cation 1-methyl-3-(triethoxysilylpropyl) imidazolium, [tespmim]$^+$, which enables covalent tethering on silica support.

As expected, a Lewis-basic ionic liquid, [C$_2$mim]Cl, and neutral chlorometallate systems (χ_{MCl3} = 0.50) do not exhibit catalytic properties. Discrepancy between the activity of chloroaluminate(III) ionic liquids containing different cations, [C$_2$mim]$^+$ and [tespmim]$^+$, and of same composition (χ_{AlCl3} = 0.67) are negligible, with high methyl acrylate conversion (99% after 5 min) and high stereoselectivity (endo:exo = 95:5). Although chlorogallate(III) ionic liquid with χ_{GaCl3} = 0.67 had inferior performance, the system with increased GaCl$_3$ content, χ_{GaCl3} = 0.75, performed on par with chloroaluminate(III) systems. This is in agreement with literature report on higher Lewis acidity of the χ_{GaCl3} = 0.75 composition, compared to the χ_{GaCl3} = 0.67 one.

Demonstrably, with both AlCl$_3$ and GaCl$_3$, and the corresponding chlorometallate ionic liquids, it is possible to achieve full methyl acrylate conversions and very high stereoselectivities (endo:exo = 95:5) in short reaction times (5 min) and under solventless conditions. This is in stark contrast to the only prior report on the cyclopentadiene cycloaddition to methyl acrylate catalysed with a chloroaluminate(III) ionic liquid, where very long reaction time (72 h) was reported, along with high catalyst loading and the presence use of solvent.[4]

Table 2 Chlorometallate(III) ionic liquids as catalyst in Diels-Alder reaction

| Catalyst	χ_{MCl3}	Time, min	α_{MA}, %	endo:exo
[C$_2$mim]Cl	0.00	10	2	75:25
[C$_2$mim][AlCl$_4$]	0.50	5	2	75:25
[C$_2$mim][Al$_2$Cl$_7$]	0.67	5	99	95:5
[tespmim][AlCl$_4$]	0.50	5	9	75:25
[tespmim][Al$_2$Cl$_7$]	0.67	5	99	95:5
[tespmim][GaCl$_4$]	0.50	5	6	80:20
[tespmim][Ga$_2$Cl$_7$]	0.67	5	73	95:5
[tespmim][Ga$_3$Cl$_{10}$]	0.75	5	98	95:5

Reaction conditions: T = 25 °C; r = 1500 rpm; CPD (4 mmol); MA (6 mmol); catalyst contains 5 mol % of MCl$_3$ per MA

Preparation of the heterogeneous catalyst, MH-[tespmim][M$_n$Cl$_{(3n+1)}$]

Compared to extensively studied chloroaluminate(III) ionic liquids, chlorogallate(III) systems offer equal or even slightly higher Lewis acidity[17] and superior moisture stability.[20] Despite some reports on their superior performance,[7,21,22] applications of chlorogallate(III) systems in Lewis acid catalysis are relatively poorly explored - arguably due to their much higher price compared to the chloroaluminate(III) counterparts. Immobilisation and recycling could aid to overcome the cost issue; surprisingly, there were no literature reports on the immobilisation of chlorogallate ionic liquids. Therefore, it was considered valuable to carry out a comparative study of the catalytic performance of both chloroaluminate(III) and chlorogallate(III) systems, immobilised on a silica support.

Multimodal porous silica (MH) was chosen as a support.[23,24] Materials with a multimodal hierarchical pore structure, containing micro-, meso- and macropores, benefit from decreased limitations to mass transport to and from the active sites due to their unique structure. Interconnected macropores are the main transport arteries to the smaller micro/mesopores, which in turn are responsible for the activity and selectivity of a chemical reaction.[25] MH-type silica materials have been successfully used in our group as carriers for various catalysts, including lipase[26] and Brønsted acidic ionic liquids,[27] which led us to select them also for this work. The material prepared for this work contained macropores, as well as textural mesopores, with BET surface area of 300 m^2/g, total pore volume – 3.5-4 cm^3/g and mean pore mesopore diameter of about 20 nm (determined by nitrogen adsorption), macropore diameter 30-50 μm. (ESI).[25,26]

Immobilisation of chlorometallate ionic liquids on silica, reported by Hölderich,[15] included binding of the cation (in the chloride salt form) on silica, via triethoxysilyl functionality on the cation, and subsequent addition of aluminium(III) chloride to form chloroaluminate(III) ionic liquids. This, however, could result in some metal chloride being deposited directly on the silica surface, and in its pores. To avoid this unfavorable phenomenon, Yin et al. proposed a modified procedure, whereby a silyl-functionalised cation was firstly reacted with metal chloride, to form a chlorometallate ionic liquid, and the resulting product was bound onto silica.[11] This synthetic route was used in this work (Scheme 1). In the first step, (3-chloropropyl)triethoxysilane was treated with 1-methylimidazole to yield 1-methyl-3-(triethoxysilylpropyl) imidazolium chloride, [tespmim]Cl. Then, a metal chloride was added to [tespmim]Cl to form chlorometallate ionic liquids of desired composition: [tespmim][M$_n$Cl$_{(3n+1)}$], χ_{MCl3} = 0.67 or 0.75, where M = Al or Ga. Then, the ionic liquids were covalently tethered onto the silica.
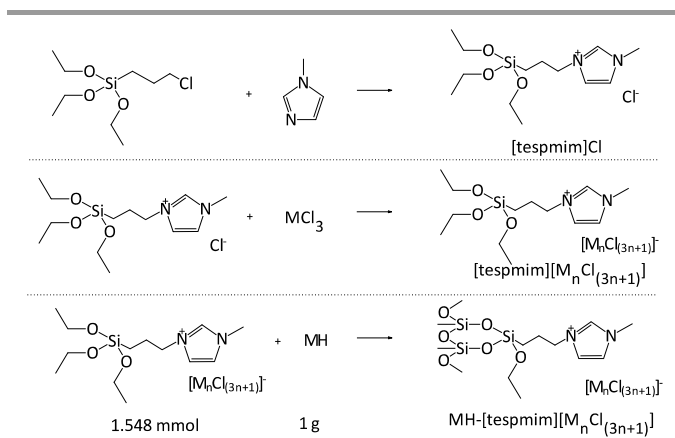
Scheme 1 Immobilisation of chlorometallate ionic liquids onto silica

The atomic absorption (ICP OES) analysis, performed for selected catalysts, have shown high efficiency of the immobilisation method (Table 3). The differences between the measured and calculated amount of the metal content in the catalyst were within the standard error of the method.

Table 3 ICP analysis of catalysts

Catalyst	Measured content of metal in catalyst, mass %	Theoretical content of metal in catalyst, mass %
MH-[tespmim][Al$_2$Cl$_7$]	4.52	5.24
MH-[tespmim][Ga$_3$Cl$_{10}$]	13.92	14.45

Cross-polarised ^{29}Si MAS-NMR was performed to confirm the covalent binding of the ionic liquid to the silica support. The ^{29}Si CP-MAS NMR spectrum of MH-[tespmim][Al$_2$Cl$_7$], is shown in Figure 2. The strong signal at –111 ppm is assigned to the (SiO)$_3$Si-OSi group, indicating that the ionic liquid is attached to the silica surface. Peak at -69 ppm corresponds to the (Si-O)$_2$-SiR-OEt group (where R is the rest of ionic liquid, Fig. 2).
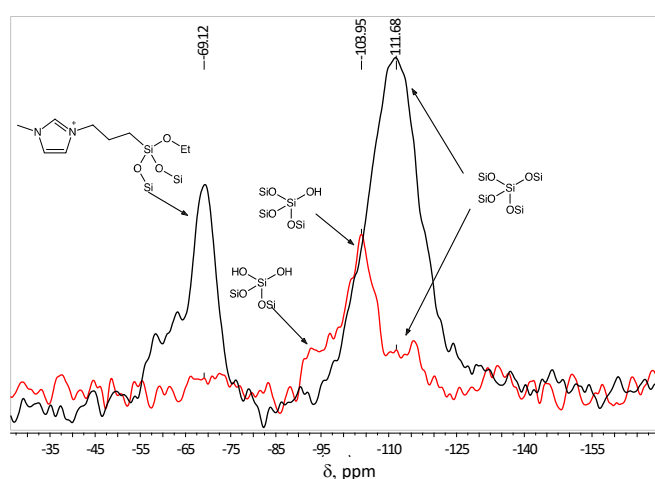
Fig. 2 ^{29}Si MAS NMR of MH (red) and MH-[tespmim][Al$_2$Cl$_7$] (black)

This confirms that the condensation reaction between the surface Si-OH groups of the support and Si-OEt groups of the ionic liquid cation occurred. The cations are tethered to the surface mainly *via* two Si-O-Si bonds (larger signal at -69 ppm), as opposed to one Si-O-Si bond (weaker signal at -60 ppm).

The corresponding ^{13}C MAS NMR spectrum, despite significant line broadening, features all signals originating from the ionic liquid cation (ESI).

^{27}Al MAS NMR spectrum of MH-[tespmim][Al$_2$Cl$_7$](Figure 3) was recorded to confirm the anionic speciation, and to check for the presence of unsupported AlCl$_3$. A single signal at 102 ppm is consistent with ^{27}Al nuclei surrounded by four chlorines. Signal broadening indicates the presence of [Al$_2$Cl$_7$]$^-$, rather than more symmetrical [AlCl$_4$]$^-$.[28] Signal from free AlCl$_3$, expected at -1.2 ppm, was not observed.[15]
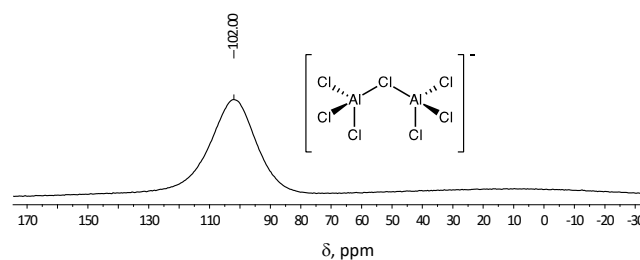

Fig. 3 ^{27}Al MAS NMR of MH-[tespmim][Al$_2$Cl$_7$]

Diels-Alder reaction catalysed with supported chlorometallate(III) ionic liquids, MH-[tespmim][M$_n$Cl$_{(3n+1)}$]

To harness numerous benefits of heterogenisation of ionic liquid catalysts,[12] two best-performing systems: [tespmim][Al$_2$Cl$_7$] and [tespmim][Ga$_3$Cl$_{10}$], were immobilised on the support and used as catalysts (Table 4). Both systems had similar performance in terms of conversions and selectivities, on par with that of homogenous systems (viz. Table 2). Isolated yields were also very high. Considering postulated superior moisture stability of chlorogallate(III) ionic liquids,[20] the MH-[tespmim][Ga$_3$Cl$_{10}$] was selected for further investigations.

Table 4 Immobilised ionic liquids as catalysts of Diels-Alder reaction

Catalyst	α_{MA}, %	Isolated yield, %	*endo:exo*
MH-[tespmim][Al$_2$Cl$_7$]	100	97	95:5
MH-[tespmim][Ga$_3$Cl$_{10}$]	100	97	95:5

Reaction conditions: T = 25 °C; r = 1500 rpm; CPD (4 mmol); MA (6 mmol); catalyst contains 5 mol % of MCl$_3$ per MA (0.1235 g of MH-[tespmim][Al$_2$Cl$_7$]; 0.0998 g of MH-[tespmim][Ga$_3$Cl$_{10}$]), reaction time 5 min.

The studies on the influence of the catalyst loading on methyl acrylate conversion (α_{MA}) and stereoselectivity showed that the nominal loading of 5 mol % of GaCl$_3$ per methyl acrylate (0.0998 g of the catalyst) is sufficient to obtain full conversion in 5 min (Figure 4). Decreased quantities of the catalyst resulted in major decrease in methyl acrylate conversion and minor drop in stereoselectivity.
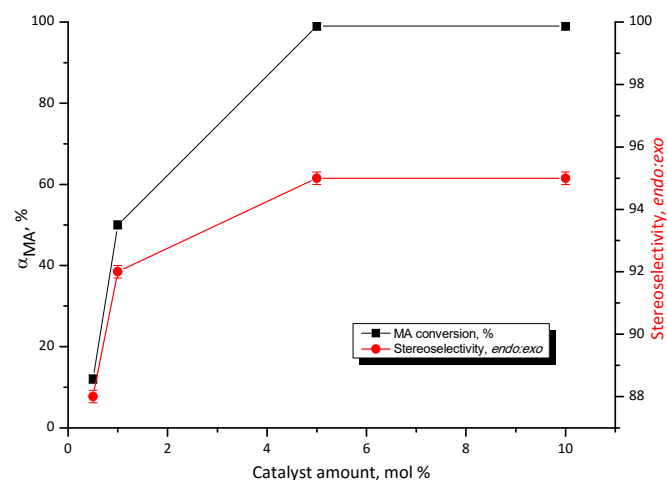
Fig. 4 The influence of catalyst loading on the conversion of methyl acrylate (α_{MA}) and the stereoselectivity of Diels-Alder reaction.
Reaction conditions: T = 25 °C; r = 1500 rpm; CPD (4 mmol); MA (6 mmol); catalyst MH-[tespmim][Ga$_3$Cl$_{10}$] contains from 1-10 mol % of MCl$_3$ per MA, reaction time 5 min.

Fig. 5 The influence of temperature on the conversion methyl acrylate (α_{MA}) and the stereoselectivity of Diels-Alder reaction.
Reaction conditions: T = 25 °C; r = 1500 rpm; CPD (4 mmol); MA (6 mmol); catalyst contains 5 mol % of MCl$_3$ per MA (0.0998 g of MH-[tespmim][Ga$_3$Cl$_{10}$]), reaction time 5 min.

Influence of the reaction temperature on both selectivity and conversion of the cycloaddition is shown in Figure 5. Decreasing the temperature from 22 to -10 °C did not affect either conversion or stereoselectivity of the reaction. At -15 °C, a slight increase in selectivity (96 %) was accompanied by significant decrease in conversion of methyl acrylate (α_{MA} = 84%). Further decrease in temperature to -94 °C resulted in further minor increase in selectivity (97%), but major drop in conversion (α_{MA} = 69%). Considering nearly negligible improvements in selectivity, it was established that it is most energy-efficient to maintain the reaction temperature at near-ambient (25 °C).

Under these optimised conditions, supported catalysts perform very well compared to other Lewis acids reported in the literature (Table 5). Reaction time was reduced to 5 min, compared to hours in other reports, with conversions higher than in all but one report, and the catalyst loading on the low end of the reported spectrum. Moreover, endo-selectivity was at a very good level of 95%, without the need to cool the reaction below ambient temperature.

Recycling of the immobilised catalyst, MH-[tespmim][Ga$_3$Cl$_{10}$] was studied over ten consecutive runs (Figure 6). After each run, the product and unreacted starting materials were distilled off from the catalyst, using Schlenk line to protect it from moisture. Then, the catalyst was charged with fresh starting material, and next catalytic run was commenced. Over four consecutive runs, no changes in conversion and selectivity were observed. After the fourth cycle, the conversion of methyl acrylate started to drop, and selectivity was decreasing from the seventh cycle.
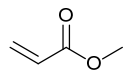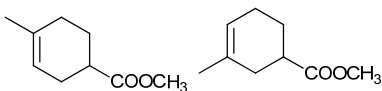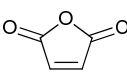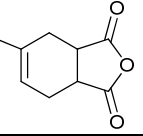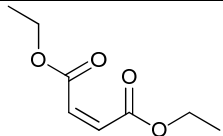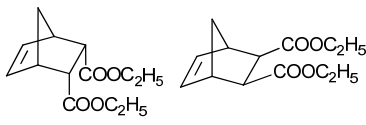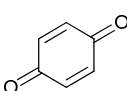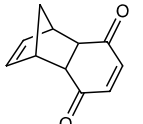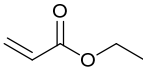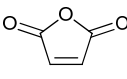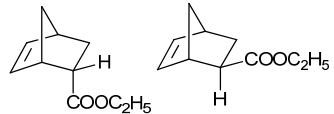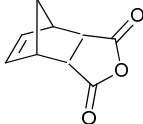
Working under inert conditions, and considering reasonably good moisture stability of chlorogallate(III) systems, deactivation of the catalyst by hydrolysis appears to be unlikely. Since products were removed by distillation, and the ionic liquid was covalently tethered to the support, washing off the catalyst is also improbable.

However, it is known that gallium(III) chloride sublimes easily. It is suspected that, whilst removing the product mixture under reduced pressure, some gallium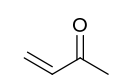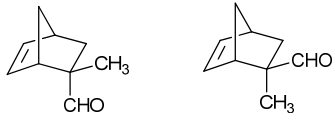(III) chloride was removed from the ionic liquid, decreasing the χ_{GaCl3} value, and consequently the catalytic performance.

Table 5 Comparison of catalysts activity used in the reaction of cyclopentadiene with methyl acrylate

Catalyst	Catalyst amount, mol %	Solvent	T, °C	t, h	α_{MA}, %	endo:exo
AlCl$_3$[29]	10	DCM	0	4	87	95:5
Cu(OTf)$_2$[29]	10	DCM	0	4	35	98:2
ZnI$_2$[29]	10	DCM	rt	20	16	92:8
Ce(IV)-SiO$_2$[30]	20	-	-20	2	99	98:2
UI$_3$(THF)$_4$[31]	5	DCM	rt	1	77	95:5
Al-HMS[32]	150mg/1mmol	hexane	-1	18	94	97:3
[C$_2$mim]Cl- AlCl$_3$ χ = 0.51[5]	0.2ml/1mmol	-	rt	72	79	95:5
[C$_2$mim][Al$_2$Cl$_7$] (this work)	5	-	25	5 min	99	95:5
MH-[tespmim][Al$_2$Cl$_7$](this work)	5	-	25	5 min	99	95:5

Table 6 Diels-Alder reaction of various dienophiles with cyclopentadiene and isoprene in the presence of MH-[tespmim][Ga$_3$Cl$_{10}$] as catalyst.

Diene	Dienophile	Product	Time, min	$\alpha_{dienophile}$, %	Yield, %	Isomer ratio[a]
isoprene	methyl acrylate	COOCH$_3$ isomers	10	100	97	94:6
	maleic anhydride	anhydride product	180	100	93	-
cyclopentadiene	diethyl maleate	COOC$_2$H$_5$ products	30	100	96	97:3
	p-benzoquinone	diketone product	10	75	-	-
			30	83	79	-
	ethyl acrylate	COOC$_2$H$_5$ products	5	100	97	93:7
	maleic anhydride	anhydride product	30	89	83	-
	methacrolein	CH$_3$/CHO products	5	100	97	80:20
	methyl vinyl ketone	COCH$_3$ products	5	100	96	92:8

[a] The ratios of 1,4-/1,3-substitiuted isomers or *endo:exo* isomers.
Reaction conditions: T = 25 °C; r = 1500 rpm; diene (8 mmol); dienophile (12 mmol); catalyst contains 5 mol % of MCl$_3$ per MA (0.1996 g of MH-[tespmim][Ga$_3$Cl$_{10}$])
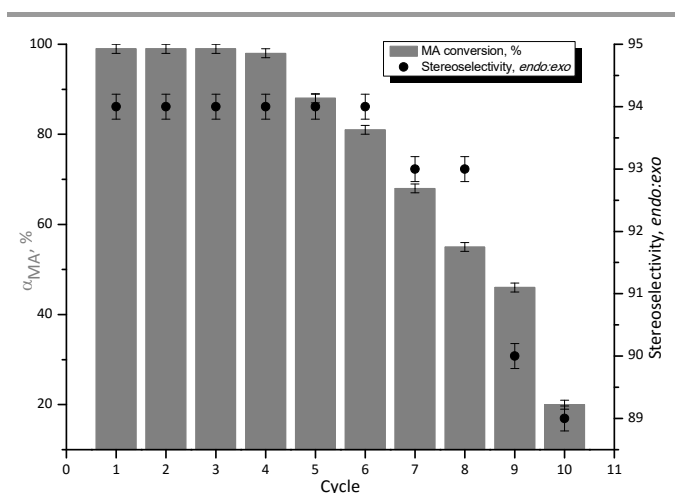
Fig. 6 Recycling of the MH-[tespmim][Ga₃Cl₁₀] catalyst in Diels-Alder reaction. Reaction conditions: T = 25 °C; r = 1500 rpm; CPD (8 mmol); MA (12 mmol); catalyst contains 5 mol % of MCl₃ per MA (0.1996 g of MH-[tespmim][Ga₃Cl₁₀]), reaction time 5 min.

Moving onto the continuous flow system could significantly prolong the life of the catalyst, but such experiments are beyond the scope of this paper.

Finally, in order to test robustness of the new catalytic system, the Diels-Alder reactions with a wide range of dienes and dienophiles were tested, using the MH-[tespmim][Ga₃Cl₁₀] catalyst. Results for two dienes: cyclopentadiene and isoprene, and six dienophiles: ethyl acrylate, diethyl maleate, methacrolein, methyl-vinyl ketone, benzoquinone and maleic anhydride, are shown in Table 5. It was demonstrated that the catalyst was active for all studied reactant combinations, and cycloadducts were formed with high yields and selectivities where applicable), within reaction times typically not exceeding 30 min.

Conclusions

Lewis acidic metal chlorides were compared as homogenous catalysts in a model Diels-Alder reaction, with AlCl₃ and GaCl₃ giving highest conversions and *endo:exo* selectivities. Catalytic performance of the corresponding chlorometallate(III) ionic liquids was on par with metal chlorides.

Chloroaluminate(III) and chlorogallate(III) systems were heterogenised, by covalently binding cations of these ionic liquids onto multimodal porosity silica support. These supported catalysts performed at ambient temperature (25 °C), under solventless conditions, and produced results superior to those reported in the literature. Reaction time was reduced to 5 min, compared to hours in other reports,[5] with conversions higher than in all but one report,[30] and low catalyst loading (5%). *Endo*-selectivity was at a very good level of 95%, without the need to cool the reaction below ambient temperature.

Supported chlorogallate(III) ionic liquids were demonstrated to be recyclable, and very robust in terms of substrate scope.

Acknowledgements

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