Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Friedel-Crafts alkylation catalysed by $GaCl_3$-based liquid coordination complexes

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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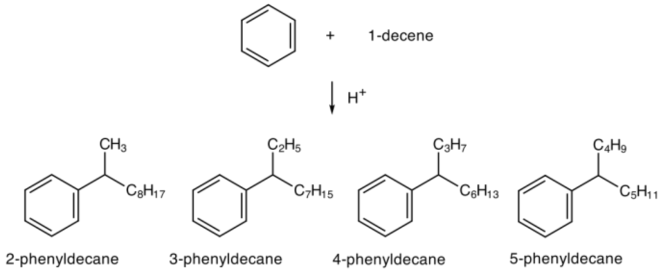
Friedel-Crafts alkylation of benzene with 1-decene was catalysed by a new family of liquid Lewis acids: liquid coordination complexes (LCCs). LCCs are prepared by mixing a metal halide (*e.g.* $GaCl_3$) and a donor molecule (*e.g.* N,N-dimethylacetamide, urea, or trioctylphosphine oxide), with metal halide typically used in excess. This leads to the formation of a eutectic mixture comprised of charged and neutral species in a dynamic equilibrium. $GaCl_3$-based LCCs were used in catalytic amounts, giving high reaction rates at ambient conditions, with selectivities to 2-phenyldecane superior to those previously reported in the literature. The influence of reaction conditions and catalyst composition on reaction rate and selectivity was investigated. Optimised reaction conditions were suggested. This exploratory study offers promise with regards to the development of safer, LCC-based alternatives to HF in industrial alkylations.

Introduction

Linear monoalkylbenzenes (LABs) with alkyl chains comprising 10-14 carbons are important intermediates for the production of alkylbenzenesulfonates, which are biodegradable anionic detergents. In 2011, world LAB capacity was estimated at 3.6 mt *per annum*.[1] LABs are produced *via* acid-catalysed Friedel-Crafts alkylation of benzene with linear alphaolefins. The first step is the formation of a carbocation at the C2 position of the olefin chain. Then, two competing reactions occur: carbocation migration to the chain centre, and attack of the carbocation on the aromatic ring, leading to a distribution of phenylalkanes, as shown in Scheme 1. Minor side-products include di- and trialkylated benzenes, as well as dimers and trimers of the olefin. It is desirable to limit carbocation migration, as the desired product is the most biodegradable 2-phenylalkane.[2]



Scheme 1 Alkylation reaction of benzene with 1-decene.

There are three industrial catalysts for LAB production: HF gas (64% of worldwide capacity), fluoride silica-alumina catalyst (UOP Detal^{TM} process, 35% of worldwide capacity) and now obsolete homogenous $AlCl_3$.[1,3] Each of these catalysts leads to a mixture of products containing all isomers of LABs (Scheme 1), albeit with varying distributions. The selectivity to the 2-phenylalkane product in industrial processes (using internal olefins) is 26-33% for the $AlCl_3$-catalysed reaction, 14-20% for HF,[4] and around 25% for solid bed catalyst in Detal^{TM} process. Demonstrably, there is a need for a catalyst offering greater selectivity towards 2-phenylakanes and devoid of drawbacks of the extant catalytic systems. The main driver is replacing HF, which is highly toxic, volatile, and corrosive.[5]

Chloroaluminate(III) ionic liquids in homogenous biphasic regime were used as a more sustainable alternative.[6,7,8,9] Reported reactions benefitted from high selectivity, easy separation and recycle of the catalyst, and mild operational conditions (30-50 °C). The molar excess of benzene to 1-decene (6 to 14) was used to avoid side reactions. Nearly full conversion of 1-decene (92-100%) was achieved in each case, with the selectivity to 2-phenyldecene at 36-42%.

Although Lewis acidic chlorometallate ionic liquids are the most studied catalysts used in homogenous biphasic systems,[10] and chloroaluminate(III) catalysts have found industrial applications,[11] they too suffer from certain drawbacks. Despite decreasing prices, the cost of the most common 1-alkyl-3-methylimidazolium-based ionic liquids is often prohibitive for large-scale applications: even if recycling of the catalyst is implemented, gradual decomposition and leaching-incurred costs are higher for a more expensive compound.[12]

Less investigated alternatives are liquid Lewis acids based on eutectic mixtures of a metal halide (typically $AlCl_3$) and an organic donor molecule (*e.g.* dimethylformamide, dimethylacetamide or dimethylsulfoxide). Applications of such mixtures in organic chemistry, *e.g.* for Friedel-Crafts acylations,[13,14,15,16,17,18] have been reported since the 1990s, but no alkylations have been described to date. It has been postulated that by coordinating to the aluminium centre, *O*-donors modulate its acidity,[13] but no mechanistic insight beyond this has been offered until recently.

Coleman *et al.*[19] studied mixtures of MCl_3 (M = Al or Ga) and donor molecules, prepared under anhydrous, solventless conditions, with various mol ratios of metal chloride, χ_{MCl3}. Based on Raman and multi-nuclear NMR spectroscopies, the neat liquids were shown to contain equilibrated cationic, anionic and neutral coordination complexes of aluminium or gallium (Scheme 2). Such liquid Lewis acids were collectively named liquid coordination complexes (LCCs).

$$\begin{array}{lll} & & 2MCl_3 + 2L \\ & & \downarrow \\ (a) & \chi_{MCl3} = \mathbf{0.50} & [MCl_2L_2][MCl_4] \rightleftharpoons 2[MCl_3L] \\ & & \downarrow + MCl_3 \\ (b) & \chi_{MCl3} = \mathbf{0.60} & [MCl_2L_2][M_2Cl_7] \rightleftharpoons [MCl_3L] + [M_2Cl_6L] \\ & & \downarrow + MCl_3 \\ (c) & \chi_{MCl3} = \mathbf{0.67} & [MCl_2L_2][M_3Cl_{10}] \rightleftharpoons 2[M_2Cl_6L] \end{array}$$

Scheme 2 Speciation of LCCs as a function of molar ratios of metal chloride (χ_{MCl3}); L = dimethylacetamide, acetamide, thiourea, urea, trioctylphosphine or trioctylphosphine oxide; M = Al(III) or Ga(III).[19]

LCCs containing binuclear complexes ($\chi_{MCl3} > 0.50$) were inferred to be Lewis acidic, which corroborated with the reported Lewis acid catalytic activity of such mixtures.[13,14,15,16,17,18] Measurements of Lewis acidity, performed for DMA-$AlCl_3$ and DMA-$GaCl_3$, $\chi_{MCl3} = 0.60$, revealed high Lewis acidity, expressed as Gutmann Acceptor Number,[20] AN. For LCCs, Acceptor Number was found to be AN = 96-103,[19] slightly higher than that of corresponding chlorometallate ionic liquids (AN = 93-95).[21] Moreover, LCCs were found to be superior in terms of cost and ease of preparation. Recently, LCCs were used, as safer and greener alternatives to BF_3 gas, to catalyse oligomerisation of 1-decene to polyalphaolefins, in a sustainable and economically-attractive process.[22]

To further explore applications of LCCs as inexpensive and sustainable Lewis acid catalysts, herein we investigate the alkylation of benzene with 1-decene. Several $GaCl_3$-based LCCs were used as catalysts, their performances were compared to those of $GaCl_3$ and chlorogallate(III) ionic liquids, and the influence of a range of variables on the catalytic process was investigated.

Experimental

Materials

Dimethylacetamide, (DMA), urea (Ur), trioctylphosphine oxide ($P_{888}O$), 1-ethyl-3-methylimidazolium chloride ([emim]Cl), gallium chloride(III) and 1-decene were purchased from Sigma-Aldrich and dried over molecular sieves. Benzene was purchased from Avantor Performance Materials Poland S.A and dried over sodium.

Synthesis

LCCs were prepared in the glovebox, according to the literature procedure in 2 g scale.[19] Neutral donor ligand (0.25 - 1.00 mol eq.) was added dropwise over 2 minutes with stirring (700 rpm), to gallium(III) chloride, to achieve molar ratio of $GaCl_3$ in the product between $\chi_{GaCl3} = 0.50$ and 0.75. Heat was evolved. Afterwards, the mixture was stirred (0.5-24 h, 30-80 °C) to obtain homogenous mixture and complete the reaction. All LCCs were stored in the glovebox until used.

Friedel-Crafts alkylation

All reactions were carried out under dry nitrogen, in a computer-controlled METTLER TOLEDO RTCal™ glass reactor, equipped with a mechanical stirrer, a thermocouple, a cooling mantle and an *in situ* FT-IR probe.

In a typical procedure, the reaction mixture, comprising benzene, 70 g and 1-decene, 18 g (at 7:1 molar ratio) was placed in the reactor, stirred vigorously with mechanical stirrer (800 rpm) and purged with nitrogen. Subsequently, a mixture of LCC 0.19-0.90 g (0.25-2.00 mol % per 1-decene) and 0.6 g of benzene was added, via syringe, with stirring. Reaction progress was monitored by FT-IR spectroscopy, using an *in situ* probe, typically until conversion of 1-decene was complete. Afterwards, the reaction was quenched with a small amount of water, and the product mixture was analysed using GC-MS.

Analyses

GC-MS analysis was performed using an Agilent Gas Chromatograph 7890C equipped with a HP-5 MS column (30 m × 0.25 mm × 0.25 µm), MS Agilent 5975C, EI ionization 70 eV, and the results were compared to NIST/EPA/NIH Mass Spectral Library.

Results and discussion

Selection of LCCs for the study

As reported by Coleman *et al.*,[19] LCCs based on $AlCl_3$ were found to form liquid mixtures around $\chi_{AlCl3} = 0.60$, where binuclear species are predominant (see Scheme 2). Mononuclear complexes which formed around $\chi_{AlCl3} = 0.50$ were more prone to crystallisation, and for $\chi_{AlCl3} > 0.60$, excess of $AlCl_3$ was typically precipitated.[23] In contrast, $GaCl_3$-based LCCs were liquid for all $\chi_{GaCl3} \geq 0.60$ compositions, and in some cases even for $\chi_{GaCl3} \geq 0.50$. This can be justified by drawing analogies with chlorometallate ionic liquids: melting points of chlorogallate(III) systems are in general lower than those of chloroaluminate(III) analogues. Furthermore, chlorogallate(III) anions have a strong tendency to form oligomeric clusters, such as $[Ga_3Cl_{10}]^-$ and $[Ga_4Cl_{13}]^-$, instead of precipitating solid $GaCl_3$.[24] Using $GaCl_3$-based LCCs in this screening study gave the opportunity to investigate the effect of the catalyst composition, expressed as χ_{GaCl3} value, on the catalytic process.

Reactants ratio

In the Friedel-Crafts alkylation of aromatics by olefins, a large excess of the aromatic reactant is typically used to minimise the side-reaction of olefin polymerisation. A commonly reported benzene to 1-decene ratio is 6-14:1.[4,5,6,7] At the same time, lowering the excess of benzene is beneficial from economic and sustainability standpoints (smaller plant size, less energy to recover and recycle benzene). Benzene : 1-decene ratios from 12:1 to 5:1 were investigated to find the chemical (yield) and economical (process efficiency) optimum (Table 1). For a very high dilution of 1-decene (12:1 benzene:1-decene ratio) the reaction did not occur, and for 10:1 ratio long reaction times were required to achieve full conversion of 1-decene. For 7:1 reactants ratio, the reaction time was only 17 min, and increased to 23 min when 5:1 ratio was used. The existence of optimum benzene:1-decene ratio is in agreement with the literature.[25] In summary, if less benzene was used, more polyalkylated products and polyolefins would be produced, which are essentially a waste. As shown in the Table 1, and stated in the introduction, it is industrial standard to use excess benzene, because it is more sustainable and economically viable to recycle benzene, rather than dispose of waste by-product. In consequence, 7:1 benzene to 1-decene ratio was used throughout this work.

Table 1. The influence of reactant molar ratio on the results of alkylation of benzene with 1-decene, catalysed with GaCl3-based LCCs.[a]

Benzene : 1-decene	Time /min	Selectivity to PDs	Selectivity to 2PD
5 : 1	23	85	47
7 : 1	17	89	48
10 : 1	35	89	48
12 : 1	50	0	0

[a] reaction conditions: T = 20 °C; r = 800 rpm; catalyst: Ur-$GaCl_3$, (χ_{GaCl3} = 0.75), 0.40 mol % per 1-decene.

Catalyst structure and loading

The influence of LCC loading, composition (expressed as χ_{GaCl3}), and ligand structure on the reaction were investigated, and compared to results obtained using $GaCl_3$, and chlorogallate(III) ionic liquid, $[emim][Ga_2Cl_7]$. The results of a range of reactions, carried out at 20 °C, with 7:1 benzene : 1-decene molar ratio, are presented in Table 2; selected entries are compared in graphical form.

Table 2. The influence of ligand, LCC composition (expressed as χ_{GaCl3}) and catalyst amount on reaction rate and selectivity.[a]

Entry	Ligand	χ_{GaCl3}	Catalyst loading, mol %	Reaction time needed for full 1-decene conversion, min	Selectivity %[b]		Yield %[b]		TOF, h^{-1}
					PDs	2-PD	PDs	2PD	
1	$P_{888}O$	0.50	2.00	50[c]	0	0	0	0	-
2	$P_{888}O$	0.60	0.75	50[c]	86	46	52	4	-
3	$P_{888}O$	0.60	1.50	38	84	46	84	39	8842
4	$P_{888}O$	0.60	1.75	25	85	47	85	40	11657
5	$P_{888}O$	0.60	2.00	18	83	47	83	39	13833
6	$P_{888}O$	0.67	1.00	10	83	47	83	39	49800
7	$P_{888}O$	0.67	0.75	25	82	48	82	39	26240
8	$P_{888}O$	0.75	0.35	50	83	48	83	40	28457
9	$P_{888}O$	0.75	0.40	23	84	48	84	40	54783
10	$P_{888}O$	0.75	0.50	12	84	47	84	40	84000
11	$P_{888}O$	0.75	0.75	4	84	47	84	40	168000
12	Ur	0.60	1.00	50[c]	88	48	63	8	-
13	Ur	0.60	1.50	13	86	47	86	40	26462
14	Ur	0.60	1.75	7	87	46	87	40	42612
15	Ur	0.60	2.00	5	87	46	87	40	52200
18	Ur	0.67	0.75	12	86	47	86	40	57333
19	Ur	0.67	1.00	5	85	47	85	40	102000
20	Ur	0.75	0.35	36	86	48	86	41	41905
21	Ur	0.75	0.40	17	89	48	89	43	78529
22	Ur	0.75	0.50	10	85	47	85	40	102000
23	Ur	0.75	1.00	2	86	44	86	38	258000
24	DMA	0.60	1.50	6	86	47	86	40	57333
25	DMA	0.60	2.00	3	86	46	86	40	86000
26	-	1.00	0.50	50[c]	100	53	20	40	-
27	-	1.00	1.00	30	85	49	85	42	17000
28	-	1.00	3.00	1	86	46	86	40	172000
29	$[emim][Ga_2Cl_7]$	0.67	1.00	90	91	40	91	36	6067
30	$[emim][Ga_2Cl_7]$	0.67	2.00	18	90	39	90	35	15000

[a] reaction conditions: T = 20 °C; r = 800 rpm; feedstock: 18 g of 1-decene, molar ratio of benzene : 1-decene = 7:1; χ_{GaCl3} – gallium chloride molar ratio, dimethylacetamide, (DMA), urea (Ur), trioctylphosphine oxide ($P_{888}O$), 1-ethyl-3-methylimidazolium cation ([emim]),

[b] determined by GC/MS analysis;

[c] the reaction has been stopped after 50 min, without achieving complete 1-decene conversion;
[d] TOF (Turn Over Number) calculated for conversion of 1-decene to PDs (sum of 2,3,4,5-phenyldecanes).

CATALYST LOADING. The reaction conditions and catalyst loadings were selected to achieve full conversion of 1-decene in less than 30 min. This time allowed to appreciate differences in kinetic curves recorded for different catalysts. However, in some cases, for very low catalyst loadings (entries 2, 8 and 12, Table 2), the reactions were terminated after 50 min without achieving full conversion. It was observed by online analysis of declining of double bond in 1-decene using FT-IR spectra. TOF values were calculated for experiments with full conversion, and compared to benchmark experiments, where an ionic liquid, [emim][Ga_2Cl_7], or neat $GaCl_3$, were used as catalysts.

As expected, increase in catalyst loading led to shorter reaction times (Table 2); TOF numbers also increased for higher catalyst loadings. The relationship between catalyst loading and time required to reach complete conversion was non-linear, as shown in Figure 1. For each LCC, a loading could be found where the reaction reached completion within 5 min, and past this amount, increase in the loading did not result in a substantial increase in reaction rate. In general, LCC loadings are low compared to the literature; reported alkylations with chlorometallate ionic liquids and $AlCl_3$-based reactants require 1-6 mol % of the catalyst (per 1-decene), 4 mol % being the typical loading.[26]

In comparison to benchmark reactions, TOF for the ionic liquid catalyst was an order of magnitude lower than that recorded for LCCs. The highest TOFs were achieved using $P_{888}O$-$GaCl_3$, χ_{GaCl3} = 0.75 (168000 h^{-1}), which was on par with neat $GaCl_3$ (172000 h^{-1}), but was surpassed by the performance of Ur-$GaCl_3$, χ_{GaCl3} = 0.75 (258000 h^{-1}). This compares favourably to the literature, with recalculated TOF for $AlCl_3$[6,27] vary from 2771 h^{-1} to 12146 h^{-1} and for chloroaluminate ionic liquids [5,6,7] vary from 2771 h^{-1} to 45238 h^{-1}.

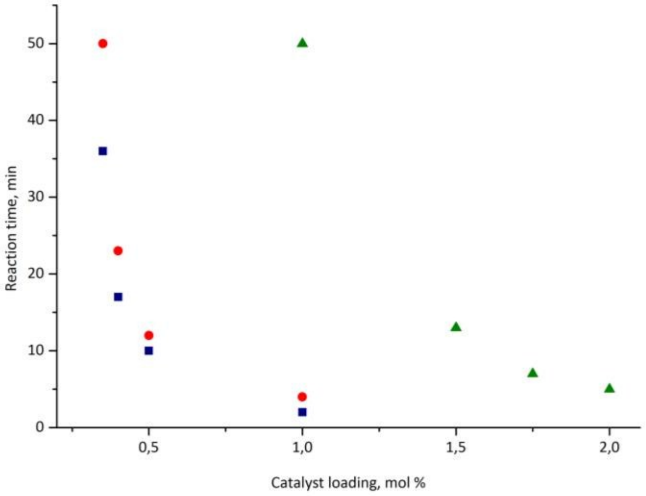


Figure 1. Reaction time required to reach full conversion of 1-decene, plotted as a function of catalyst loading for three LCCs: Ur-$GaCl_3$, χ_{GaCl3} = 0.60 (green), Ur-$GaCl_3$, χ_{GaCl3} = 0.75 (blue) and $P_{888}O$-$GaCl_3$, χ_{GaCl3} = 0.75 (red). Reaction conditions: T = 20 °C; r = 800 rpm; molar ratio of benzene : 1- decene = 7:1.

Change in 1-decene concentration in the reaction mixture was followed, as a function of time, by *in situ* FT-IR spectroscopy. All curves recorded for LCC-catalysed reactions showed an induction period, significantly shortened for higher catalyst loadings and high χ_{GaCl3} values of the catalyst (see example in Figure 2). The presence of an induction period may indicate either an autocatalytic process, or competitive reactions with different kinetic profile.

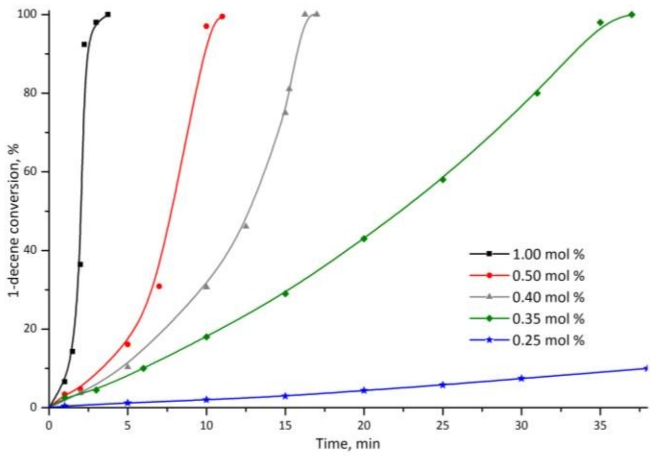


Figure 2. Influence of the catalyst loading on the reaction rate; reaction conditions: T = 20 °C; r = 800 rpm; molar ratio of benzene : 1-decene = 7:1 catalyst: Ur-$GaCl_3$, χ_{GaCl3} = 0.75.

In conclusion, catalytic performance of LCCs appears to be far superior to that of ionic liquids, but similar to that of neat $GaCl_3$, both in terms of conversion and selectivity (see Table 2). This is reflected also in the shape of corresponding kinetic curves (Figure 3). For reactions catalysed by either LCCs or homogenous $GaCl_3$, there is induction period, absent from the profile of the ionic liquid-catalysed reaction.

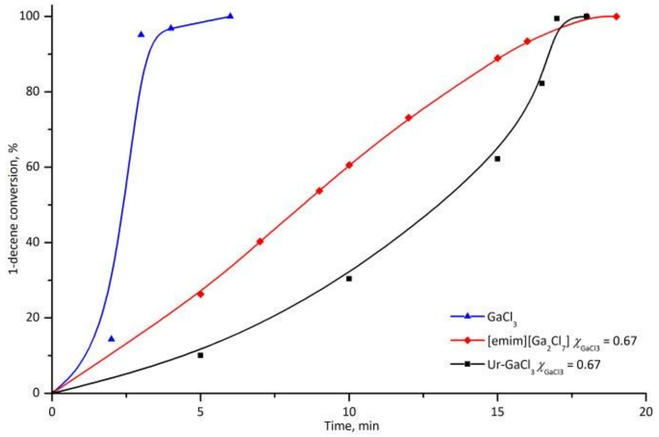


Figure 3. Conversion of 1-decene against reaction time for three types of catalyst: homogenous $GaCl_3$, ionic liquid and LCC; reaction conditions: T = 20 °C; r

= 800 rpm; molar ratio of benzene : 1-decene = 7:1; catalyst loadings were adjusted to achieve comparable reaction times.

CATALYST COMPOSITION AND MECHANISTIC CONSIDETATIONS. Composition of an LCC catalyst (χ_{GaCl3}) is directly related to its speciation (Scheme 2), which in turn is crucial for the catalytic performance. From research on halometallate ionic liquids[10] it is known that only bi- and polynuclear complexes of chlorogallate(III) systems are Lewis acidic. In the Friedel-Crafts alkylation of benzene with 1-decene, the first step is the reaction of Lewis acidic complexes with adventitious water, generating a Brønsted superacidic proton (Eqn 1), which then reacts with 1-decene to form a carbocation (see Scheme 1).

$$[Ga_2Cl_7]^- + H_2O \longrightarrow [GaCl_4]^- + [GaCl_3OH] + H^+ \qquad (1)$$

Indeed, in experiments catalysed with LCCs used at equal loadings, but with different χ_{GaCl3} values (Table 2), the complete conversion of 1-decene was achieved in a shorter time for higher χ_{GaCl3} values. This was particularly emphasised for lower catalyst loadings, as shown in Figure 1. Considering the speciation of LCCs (Scheme 2), reaction rate increased with the number of bi- and trinuclear complexes in the LCC, which impart Lewis acidity to the system, and consequently - generate more superacidic protons. In the control experiment, performed using an LCC containing only mononuclear complexes ($P_{888}O$-$GaCl_3$, χ_{GaCl3} = 0.50, entry 1 in Table 2) was not Lewis acidic and, as expected, displayed no catalytic activity.

After the generation of a carbocation from 1-decene, it attacks benzene to form 2-phenelydecene (desired product), or undergoes undesired side-reactions. These include: isomerisation of double bond in 1-decene (carbocation migration towards the middle of the chain), oligomerisation of 1-decene and polyalkylation of benzene. Although oligomerisation is kinetically favoured, in this work it was reduced to a minimum by dilution of 1-decene with benzene. The by-products were mainly polyalkylated benzenes. Migration of the double bond decreased selectivity to 2-PD, but not to PDs.

Irrespective of the catalyst loading, selectivities to phenyldecanes (PD) in general, and to the desired 2-phenyldecane (2-PD), were very similar for all LCCs for $GaCl_3$. Selectivity to PD was *ca*. (84±1)% for the $P_{888}O$-$GaCl_3$ family, and (86±1)% for DMA-$GaCl_3$, Ur-$GaCl_3$, or $GaCl_3$. Selectivity to the desired product, 2-PD, was virtually the same for all LCCs and $GaCl_3$, around 46-48%. In comparison, although ionic liquids gave higher selectivity to PD in general (90-91%), selectivity to 2-PD was only *ca*. 39-40%, in agreement with literature data for Lewis acidic ionic liquids.[4,5,6,7] In conclusion, ionic liquids were more active in promoting isomerisation, whereas LCCs and homogenous $GaCl_3$ were more active in promoting polyalkylation. It can be an outcome of lower Lewis acidity of ionic liquids what causes lowering of global reaction rate and at the same time promoting of monoalkylbenzenes creation.

In chlorogallate(III) ionic liquids, the only Lewis acidic species are chlorogallate(III) anions, $[Ga_xCl_y]^-$.[24] In contrast, in LCCs, these are in equilibrium with neutral $[Ga_xCl_{(y-1)}L]$ complexes, containing *O*-donors.[19] Neat $GaCl_3$ was used as a homogenous catalyst dissolved in benzene. Benzene dissolves very high (up to equimolar) quantities of $GaCl_3$, forming organometallic complexes: $[GaCl_3$(benzene)] and $[Ga_2Cl_6$[(benzene)],[28] not dissimilar to complexes in LCCs. It appears that the change from chloride-only coordination around gallium to mixed ligands slows down at least one of the reaction steps, as visible from the induction period, found consistently for both homogenous $GaCl_3$ and for LCCs, but not for ionic liquids (Figure 3). We are currently working on computational models of these complex mixtures, to elucidate how differences in speciation affect the kinetics of different steps in Friedel-Crafts alkylation.

LIGANDS ON LCC AND PHASE BEHAVIOUR. Considering the mechanism of Friedel-Crafts alkylation, involving proton generation (Eqn 1), subsequent carbocation formation (Scheme 1) and the following carbocationic process, there is no direct coordination of substrates to the metal centre. In this sense, a change in ligand is not expected to affect selectivity or conversion. However, ligands on LCCs control their phase behaviour, which is a key parameter in the process. Whereas $P_{888}O$-based LCCs and ionic liquids were phase-separated from the reactants (the reaction mixture was an emulsion), LCCs based on Ur and DMA, as well as neat $GaCl_3$, were fully soluble in the reaction mixture.

Reaction times required to achieve full conversion of 1-decene were compared for two loadings of LCCs, based on three different ligands ($P_{888}O$, Ur or DMA), but of the same composition (χ_{GaCl3} = 0.60). As shown in Figure 4, for both LCC loadings, the reaction rate followed the order: DMA>Ur>$P_{888}O$. The reaction using $GaCl_3$ (homogenous) was faster than for any LCC, but reactions using chlorogallate(III) ionic liquids (see Table 2) were slower than for any tested LCC. The reaction rate appears to be influenced by the catalyst accessibility: homogenous $GaCl_3$ and LCCs were more efficient than the biphasic systems. Nevertheless, it must be noted that the $[emim]^+$ cation (6 carbons and two heteroatoms) is significantly smaller than the $P_{888}O$ ligand (24 carbons and two heteroatoms), and yet the ionic liquid had much lower catalytic activity than $P_{888}O$-$GaCl_3$. This points to other important factors that may be playing a role, such as interactions between carbocations and ions of the catalytic system, and differences in speciation of chlorogallate(III) complexes in ionic liquid and LCCs. A similar conclusion has been reached in our previous work on oligomerisation of 1-decene, and in-depth computational studies are currently being carried out in our group to understand this interplay between phase behaviour, catalyst speciation, and kinetics of different carbocationic processes.

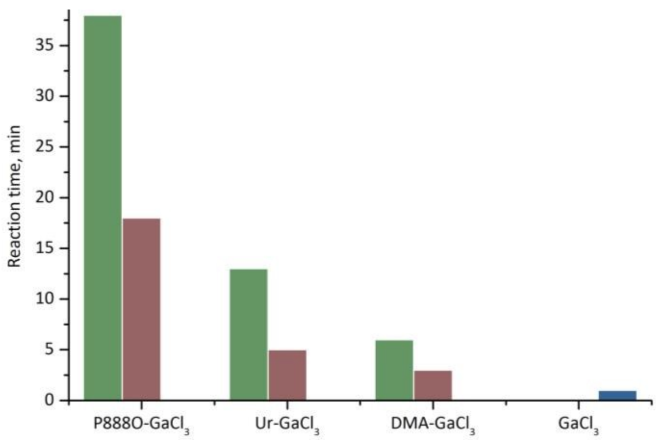


Figure 4. Reaction time required to reach full conversion of 1-decene, for a series of LCCs of general formula L-GaCl$_3$, χ_{GaCl3} = 0.60, where L = $P_{888}O$, Ur or DMA; catalyst loading was 1.50 mol % per 1-decene (green) or 2.00 mol % per 1-decene containing 0.68 g GaCl$_3$ (red), compared to results obtained with GaCl$_3$ (navy, loading 3.00 mol % per 1-decene, 0.68 g). Reaction conditions: T = 20 °C; r = 800 rpm; molar ratio of benzene : 1-decene = 7 : 1.

Reaction temperature

The influence of reaction temperature on the reaction time required for full 1-decene conversion and on selectivity was tested using Ur-GaCl$_3$, χ_{GaCl3} = 0.75 (0.40 mol % per 1-decene). Reactions were carried out at a range of temperatures from 10 to 40 °C, in 10 °C intervals. Reaction rate increased with temperature as expected, to reach full conversion in 17 min at 20 °C and only 4 min at 40 °C. Induction periods were observed in all reactions (Figure 5). No significant changes in selectivity, either to PDs or 2-PD, were observed with changing reaction temperature. In conclusion, temperature can be used to achieve faster reaction rates, but not to improve selectivity.

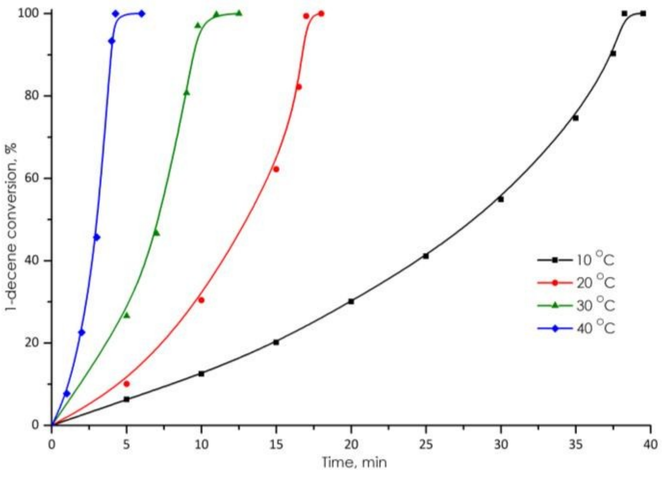


Figure 5. Influence of temperature on reaction time. Reaction conditions: r = 800 rpm; molar ratio of benzene : 1-decene = 7:1; catalyst: Ur-GaCl$_3$ χ_{GaCl3} = 0.75, 0.40 mol % per 1-decene.

Conversion *vs.* selectivity

In order to validate that the induction period observed by FT-IR is also detected by GC-MS, and to monitor changes of both selectivity and conversion *vs.* reaction time, reaction was sampled in regular intervals and the samples tested by GC-MS. Results obtained from GC-MS, shown in Table 3, were in agreement with those from FT-IR.

Table 3. The influence of reaction time on conversion of 1-decene and selectivity.[a]

Entry	Reaction time, min	Conversion, %	Selectivity, %[b]	
			PDs	2-PD
1	5	8	100	50
2	10	26	100	50
3	15	41	100	50
4	20	55	89	50
5	25	65	89	49
6	29	81	87	49
7	31	97	86	48
8	33	99	85	48
9	36	100	86	48

[a] reaction conditions: T = 20 °C; r = 800 rpm; molar ratio of benzene : 1-decene = 7:1; catalyst: Ur-GaCl$_3$, χ_{GaCl3} = 0.75, 0.35 mol % per 1-decene.
[b] determined by GC/MS analysis.

To facilitate interpretation of the results, selectivity towards both PDs and 2-PD was plotted as a function of conversion (Figure 6). Demonstrably, with conversion no higher than 55%, it is possible to entirely avoid polyalkylation, and to maintain selectivity to 2-PD at a very high level of 50%.

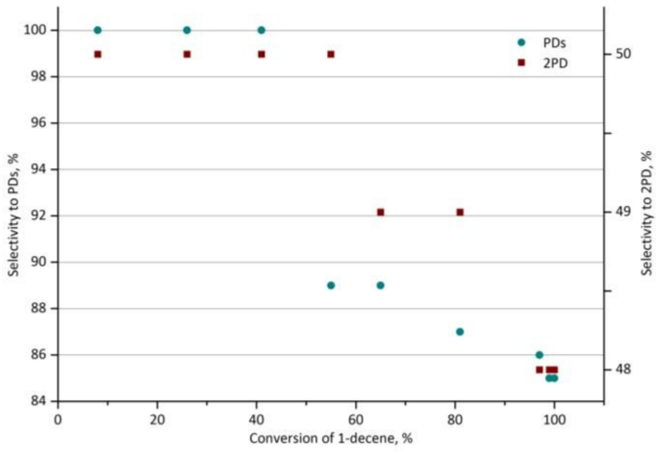


Figure 6. Influence of the catalyst type on the reaction kinetic pathway; reaction conditions: 20 °C, 800 rpm, benzene : 1-decene = 7:1; catalyst: Ur-GaCl$_3$, χ_{GaCl3} = 0.75, catalyst loadings were adjusted to achieve comparable reaction times.

Future outlook

The conclusive finding of this study is that LCC-catalysed alkylation of benzene with 1-decene should be carried out using an LCC with a lipophilic ligand (*e.g.* $P_{888}O$) to induce phase-separation of the catalyst from the reaction mixture, retaining selectivity as good as that obtained with neat GaCl$_3$. To further increase high selectivity to 2-PD, it would be desirable to maintain conversion around 50%, and recycle products. In order to enhance reaction rate, high χ_{GaCl3} value and elevated reaction temperature are preferred. In order to translate these findings to an industrially viable proposition, GaCl$_3$ would need to be replaced with less costly AlCl$_3$. Ideally, both feedstock and catalyst would be recycled, especially if operating at low (*ca*. 50%) conversion. This stage of research is currently under investigation in our group.

Conclusions

LCCs are very active catalysts in Friedel-Crafts alkylation of aromatics with alphaolefins. Small amounts of LCC catalysts (0.35 - 2.00 mol % per 1-decene) at ambient temperatures gave full conversions and high selectivities to 2-phenyldecene (46-47%) in short reaction time (2-25 min). The composition (χ_{GaCl3}) and ligand on the Ga^{III} centre, as well as reaction temperature, influenced the reaction rate (*i.e*. the time in which full olefin conversion is achieved), but not the selectivities. Higher reaction rates were achieved with small ligands (Ur, DMA) and high χ_{GaCl3} values. However, phase-separation of the catalyst was only observed for a bulkier, lipophilic ligand ($P_{888}O$). Selectivities are related to conversion, and working at lower conversions (*ca*. 50%) may lead to very high selectivity to 2-phenyldecane (even 50%).

Kinetic curves and selectivities in LCC-catalysed reactions differ from ionic liquid-catalysed reactions, but are very similar to results obtained with homogenous $GaCl_3$. Although homogenous $GaCl_3$ gives higher reaction rate, LCCs based on $P_{888}O$ have the advantage of phase-separating from the reaction mixture and facilitating separation.

Problem of corrosiveness of $GaCl_3$ derives from its hydrolysis and HCl release would be similar like in industrial Al-based catalyst. On the other hand, $GaCl_3$-based catalysts are far safer and less corrosive than HF. Other possibilities, like gallium triflates are more expensive than halides, and contain fluorine, which is normally avoided when possible from industrial processes, therefore we have focused on $GaCl_3$-based systems, as a greener option. In Table 4 the comparison of reaction conditions for LCC *vs.* industrial processes was demonstrated.

In summary, LCCs can be safer and more sustainable alternatives to HF in Friedel-Crafts alkylation. In contrast to HF, they are fluorine-free liquids of very low volatility, which makes them easier and cheaper to contain. Furthermore, LCCs are prepared at ambient temperature, solventless, with 100% atom economy, and from potentially bio-derived and biodegradable ligands, such as urea. Replacing $GaCl_3$ with less expensive (although less versatile in terms of composition) $AlCl_3$ may lead to an economically viable process.

Table 4. Comparison of reaction conditions for LCCs *vs.* industrial processes.

Patent	Catalyst	T, °C	Molar ratio benzene: olefin	Selectivity to 2-phenylalkyl-benzenes
US 3494971	UOP/HF	50 [a]	8 : 1	16 [b]
US 5344997	UOP Detal^{TM,}	150 [a]	30 : 1	25 [b]
reference 28	$AlCl_3$	70	8 : 1	32
this work	LCC	20	7 : 1	40

[a] pressure 3.5 MPa.
[b] alkylation with industrial olefins (mixture of internal olefins)

Acknowledgements

This work was financed by the Ministry of Science and Higher Education, National Science Centre (grant no. UMO-2012/06/M/ST8/00030).

Notes and references

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1 A. Aitani, J. B. Wang, I. Wang, S. Al-Khattaf, T. Tsai, *Catal Surv Asia*, 2014, **18**, 1.

2 G. D. Yadav, N. S. Doshi, *Org. Process Res. Dev.*, 2002, **6**, 263

3 J. A. Kocal, *Alkylation of aromatics using a fluorided silica-alumina catalyst*, US 5344997, 1994.

4 J. A. Kocal, *Process for the production of a monoalkylated aromatic hydrocarbon*, US 3494971, 1970.

5 J. A. Kocal, B. V. Vora, T. Imai, *Appl. Catal., A: Gen.*, 2001, **221**, 295.

6 C. Qiao, C. Li, *Front. Chem. Eng. China* 2008, **2** 69.

7 C. Qiao, Y. Zhang, J. Zhang, C. Li, *Appl. Catal. A: Gen*., 2004, **276**, 61.

8 K. Qiao, Y. Deng, *J. Mol. Catal. A: Chem.*, 2001, **171**, 81.

9 H. Xin, Q. Wu, M. Han, D. Wang, Y. Jin, *Appl. Catal. A: Gen*., 2005, **292,** 354.

10 J. Estager, J. D. Holbrey and M. Swadźba-Kwaśny, *Chem. Soc. Rev.*, 2014, **43**, 847.

11 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.

12 a) D. R. MacFarlane and K.R. Seddon, *Aust. J. Chem.*, 2007, **60**, 3; b) N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; c) L. Andreani and J. D. Rocha, *Braz. J. Chem. Eng.*, 2012, **29**, 1.

13 S. Yous, J. H. Poupaert, I. Lesieur, P. Depreux, D. Lesieurt, J. *Org. Chem.*, 1994, **59**, 1574.

14 E. G. Mata, A. G. Suarez, *Synth. Commun.*, 1988, **27**, 1291.

15 A. G. Suarez, *Tetrahedron Lett.*, 1999, **40**, 3523.

16 F. Guenadil; H. Aichaoui, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2002, **177**, 2633.

17 H. A. Derbala, *J. Heterocyclic Chem.*, 2012, **49**, 700.

18 L. Messaoud, Y. Wassila, S. Khemissi, A. Yasmina, C. Hanane, *J. Chem. Res.*, 2014, **38**, 331.

19 F. Coleman, G. Srinivasan, M. Swadźba-Kwaśny, *Angew. Chem. Int. Ed.*, 2013, **52**, 12582.

20 V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978.

21 J. Estager, A. A. Oliferenko, K. R. Seddon and M. Swadźba-Kwaśny, *Dalton Trans*, 2010, **39**, 11375.

22 J. Hogg, A. Ferrer Ugalde, M.P. Atkins, F. Coleman and M. Swadźba-Kwaśny, *Green Chem.*, 2015, DOI: 10.1039/C4GC02080D

23 H. A. Øye, M. Jagtoyen, T. Oksefjell, and J. S. Wilkes, *Mat Sci Forum*, 1991, **73**, 183.

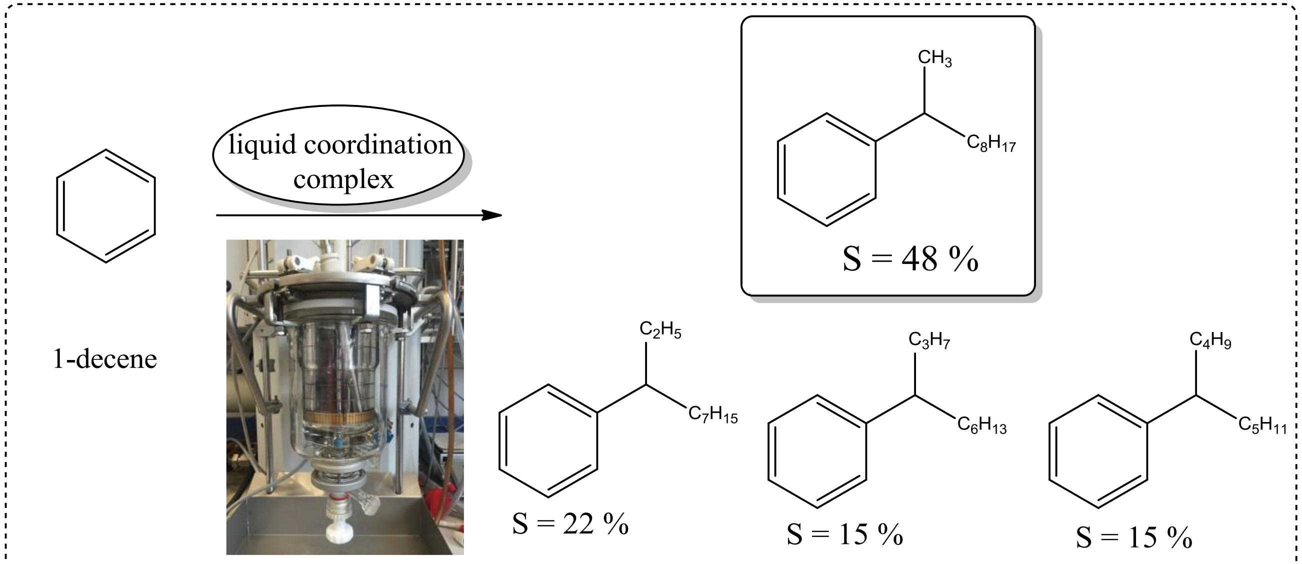
24 (a) S. P. Wicelinski, R. J. Gale, S. D. Williams, and G. Mamantov, *Spectrochim. Acta A*, 1989, **45**, 759; (b) C. Hardacre, R. W. Murphy, K. R. Seddon, G. Srinivasan and M. Swadźba-Kwaśny, *Aust. J. Chem.*, 2010, **63**, 845.

25 (a) H. Xin, Q. Wu, M. Han, D. Wang and Y. Jin, *Appl. Catal. A*, 2005, **292**, 354; (b) Y. Yi, F. Ding, W. Li, M. Ge, G. Jin and J. Gao, *Electrochem.*, 2009, **77**, 591.

26 M. Röper, E. Gehrer, T. Narbeshuber and W. Siegel, *Acylation and Alkylation*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

27 X. Hu, M. L. Foo, G. K. Chuah, and S. Jaenicke, *J. Catal.*, 2000, **195**, 412.

28 S. Ulvenlund, A. Wheatley and L.A. Bengtsson, *J. Chem. Soc., Dalton Trans.*, 1995, 255.



The high activity and selectivity of liquid coordination complexes as catalyst in Friedel-Crafts alkylation of aromatics at ambient temperature with alphaolefins is demonstrated.