Environmentally Friendly Catalysis using Supported Reagents: Evolution of a Highly Active Form of Immobilised Aluminium Chloride[1]

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An entirely heterogeneous form of aluminium chloride that is highly active in the liquid-phase alkylation of aromatics using alkenes and chloroalkanes is prepared by treating porous support materials with $AlCl_3$ in solution.

The heterogenisation of inorganic reagents and catalysts that are useful in organic reactions is an important goal in clean technology.[2] Aluminium chloride is one of the most widely used inorganic reagents in organic chemistry and its many drawbacks, such as its corrosive nature, difficulties in separation and recovery, and the large volumes of environmentally hazardous waste associated with its use, make it a prime target for heterogenisation.[3] There have been several attempts to achieve this goal but with limited success especially for liquid-phase applications. Immobilisation of aluminium chloride onto inorganic support materials has been achieved both in the vapour phase[4,5] and using chlorinated solvents[6] but the successful applications of the resulting supported reagents have been largely limited to gas-phase reactions including alkane isomerisations and cracking reactions with the activity in liquid-phase Friedel–Crafts alkylations being disappointing and considerably less than that of aluminium chloride itself.[7] As part of our programme of research into the development of supported reagent catalysts as replacements for environmentally unacceptable reagents we have sought replacements for established Friedel–Crafts catalysts such as aluminium chloride. Acid-treated montmorillonite supported zinc chloride ('clayzic')[8] has proven to be a popular Friedel–Crafts catalyst and forms the basis of a new industrial catalyst,[9] but its usefulness is limited and it is generally much less active than aluminium chloride (though offering many advantages such as excellent stability and minimal waste on use).[3] We now wish to report the first preparation of a supported form of aluminium chloride which shows comparable activity to the parent reagent in liquid-phase Friedel–Crafts alkylations.[1]

We have prepared supported aluminium chloride catalysts, that are active in the room temperature octylation of benzene using oct-1-ene, by refluxing a well-stirred slurry of anhydrous aluminium chloride, pre-dried support (typically 300 °C for 18 h) and benzene for 1 h under dry nitrogen. Diffuse reflectance FTIR analysis of pyridine adsorbed on the catalysts[10] reveals the presence of both strong Lewis acid sites (1615 cm^{-1}) and strong Brønsted acid sites (1540 and 1637 cm^{-1}). This can be contrasted with the analysis of the active sites in acid-treated clays, which reveal essentially Brønsted acid character, and those in 'clayzic' which reveals essentially Lewis acid sites.[8] The presence of both strong Lewis and Brønsted acid activity is consistent with the presence of surface-bound sites such as $-O-AlCl_2$ (as suggested in earlier work on immobilised aluminium chloride),[6] and the polarisation of surface hydroxys by coordinatively unsaturated aluminium centres. The combination of such sites might also justify the use of the term 'solid superacid' as has been used to describe another earlier form of immobilised aluminium chloride.[5]

The choice of solvent used in the preparation of the catalyst is important—use of acetonitrile gave an inactive material (presumably due to complexation of the aluminium chloride by the Lewis basic solvent) while use of *iso*-octane gave a purple solid (reminiscent of that reported in experiments involving $AlCl_3$ and chlorinated solvents)[11] which was inactive unless first washed with hot benzene (apparently removing a polymeric coating MS; of the initial solid showing repeating CH_2 units to $m/z > 500$) after which it was capable of catalysing the model reaction but only at reflux temperatures. The loading of aluminium chloride and the choice of support material are also critical factors (see below). The mixture is then cooled to room temperature and, for the model reaction described here, the oct-1-ene is added dropwise over a period of 1–2 h after which time the reaction is normally complete. There is usually a small exotherm on adding the octene (8 °C with a cold water bath). The results from several experiments are summarised in Table 1. It is also possible to recover a dry catalyst by filtering and washing with benzene under dry nitrogen. The powdered catalyst can then be stored under dry, inert conditions with minimal loss in activity over a period of several months. It is important to note that no aluminium leaching occurs from catalysts that are not overloaded (see below) and these 'optimised' catalysts can be reused several times with little loss in activity (see Table 1). Reactions with the best catalysts occur rapidly at room temperature and, under these conditions, there is no change in the isomer ratios of the monoalkylated products over prolonged reaction periods suggesting that the catalysts are not capable of promoting dealkylations/isomerisations at room temperature. The activity of these heterogeneous catalysts is remarkable, being comparable to that of $AlCl_3$ itself and considerably surpassing that of acid treated clays and clayzic (Table 1), Al^{3+} exchanged clays, zeolites and pillared clays (typically requiring temperatures > 100 °C for the reaction of the more reactive dodecene with benzene)[12,13] and indeed any heterogeneous catalyst we are aware of.[2,14–16]

The choice of support material is important both in terms of obtaining an active, truly heterogeneous catalyst and achieving a significant improvement in selectivity towards mono-alkylation compared to $AlCl_3$. Mesoporous silica, acid treated montmorillonite and acidic alumina are effective supports, while neutral alumina gives a low-activity catalyst and non-porous and microporous silicas give catalysts that show relatively poor selectivity. The best selectivity is achieved using silica gel with an average pore diameter of *ca.* 70 Å which is consistent with studies on the effect of pore diameters on the activity of supported zinc chloride.[17] Acid treated montmorillonite (K10) has also been shown to be at least partly mesoporous.[18] It is interesting to note that non-porous silica gives better selectivity as a support at lower loadings of aluminium chloride and this suggests that the relatively poor selectivity of this material and the microporous silica gel is caused by the presence of excess, 'free' $AlCl_3$. The best selectivity obtained using a supported catalyst under the standard conditions is considerably greater than can be achieved using $AlCl_3$ itself. This may imply a degree of product shape selectivity but the rapid diffusion of alkylated product molecules from the highly polar pores is likely to play an important role as has been suggested for other Friedel–Crafts supported reagent catalysts.[19] The selectivity towards the monoalkylated product can be further improved at higher dilutions of the alkene (Table 2). At a benzene: oct-1-ene mole ratio of 20:1, a remarkable 92% selectivity can be achieved.

The loading of aluminium chloride on the support is an important factor as has already been indicated. To further study this variable we carried out a series of experiments on a K10-based catalyst with different loadings of reagent (Table 3). This clearly shows an optimum loading at *ca.* 0.75 mmol aluminium chloride g^{-1} support. This is lower than that observed for K10–

$ZnCl_2$[20] but these supported reagents are not strictly comparable as $AlCl_3$ is expected to react with the surface[6] whereas $ZnCl_2$ is believed to stay as intact molecules residing within the pores of the support.[8] The optimum loading for the mesoporous silica gels was found to be *ca.* 1.5 mmol g^{-1} presumably due to their higher surface area.

If the $AlCl_3$ reacts with the surface hydroxy groups on materials such as silica gels to give active centres such as $-O-AlCl_2$[6] then it should be possible to obtain active heterogeneous catalysts by treatment of supports with $MeAlCl_2$ (which should preferentially react with surface hydroxyls *via* elimination of methane) similar to those obtained by treatment with $AlCl_3$. Using the model benzene–oct-1-ene reaction, we have found that whereas unsupported $MeAlCl_2$ itself is rather inactive and gives poor product selectivity (compared to $AlCl_3$), mesoporous silica treated with $MeAlCl_2$ has an activity and selectivity comparable to that achieved using the analogous $AlCl_3$ based material (Table 4). Interestingly, the behaviour of the corresponding material prepared from treatment of K10 with $MeAlCl_2$ is similar to the unsupported reagent and this may suggest that the evolution of HCl in the K10–$AlCl_3$ preparation is important perhaps by helping to convert the microporous clay structure into a more mesoporous silica structure.[18] Catalysts prepared by treatment of either mesoporous silica gel or K10 with Me_2AlCl are quite inactive, consistent with the formation of relatively weakly Lewis acidic $-O-Al(Me)Cl$ sites.

Table 1 Activity of supported aluminium chloride and other solid acids in the reaction of benzene and oct-1-ene

Catalyst[a]	Reaction conditions[b] t/h (T/°C)	Octylbenzene GC %	Dioctylbenzene	Other products[c]
SiO_2 (70 Å)[d]–$AlCl_3$	1.25 (20)	78.3[e]	21.2	—
SiO_2 (non-porous)–$AlCl_3$	3.25 (20)	62.0	26.5	11.3
SiO_2 (20 Å)–$AlCl_3$	3 (20)	64.0	26.3	9.7
SiO_2 (40 Å)–$AlCl_3$	3 (20)	75.2	24.2	—
SiO_2 (100 Å)–$AlCl_3$	1.5 (20)	75.0	24.9	Trace
SiO_2 (205 Å)–$AlCl_3$	2 (20)	68.6	29.6	1.8
$AlCl_3$ (no support)	2 (20)	61.6	20.7	17.3
K10–$AlCl_3$	2 (20)	62.1[e]	22.3	15.5
K10–$AlCl_3$[f]	1.5 (20)	57.8	18.6	23.3
K10–$AlCl_3$[g]	2 (20)	—	—	—
K10–$AlCl_3$[g]	16 (reflux)	78.5	21.5	—
K10–$AlCl_3$[h]	2 (20)	76.3	23.7	—
Alumina (neutral)–$AlCl_3$[h]	24 (20)	35.7	10.1	20.8
Alumina (acidic)–$AlCl_3$[h]	1.3 (20)	71.0	19.3	8.9
K10	24 (20)	32.8	4.0	
Clayzic	4 (reflux)	39.9	17.6	24.9
SiO_2	20 (20)	—	—	—

[a] The loading of $AlCl_3$ is 1.5 mmol g^{-1} support and the catalysts were prepared in benzene (see text) unless stated otherwise (10 g catalyst/mol PhH). [b] Oct-1-ene (0.5 mole) normally added over a period of 1–2 h to benzene (1.0 mol). [c] Polyalkylates and octene oligomers (significant quantities of the latter were only detected in the reaction with clayzic). [d] Average pore diameters. [e] Typical isolated yields of crude alkylated products were >90%. We were able to maintain the same level of activity and selectivity (±5%) for up to 8 runs using SiO_2–$AlCl_3$: after completion of each reaction, the liquid was decanted off and fresh benzene added followed by addition of oct-1-ene in the normal way. The reusability of the best K10 based catalyst was less impressive with a maximum of 5 runs before a marked reduction in activity (and selectivity) was observed. [f] Catalyst preparation time of 15 h. [g] Prepared in *iso*-octane; *iso*-octane filtered off under N_2 and catalyst washed with hot benzene. [h] 0.75 mmol g^{-1} loading.

Table 2 Effect of dilution on the reaction of benzene and oct-1-ene with K10–$AlCl_3$ (0.75 mmol g^{-1}) at room temperature

Mole ratio benzene : oct-1-ene	t/min	Octylbenzene GC %	Dioctylbenzene	Trioctylbenzene
20 : 1	7	91.7	7.6	0.72
10 : 1	20	89.4	9.3	1.3
10 : 1	120	89.3	9.1	1.6
5 : 1	150	86.3	13.7	Trace
2.5 : 1	180	74.2	24.3	Trace
2 : 1	210	73.6	24.7	1.7
2 : 1	1440	71.4	27.3	1.3

Table 3 Effect of loading on the activity of K10–$AlCl_3$ in the reaction of benzene and oct-1-ene at room temperature

Aluminium chloride loading (mmol g^{-1} support)	t/h	Octylbenzene GC %	Dioctylbenzene	Trioctylbenzene
1.5	2	62.1	22.3	15.5
1.2	1.5	65.8	19.9	14.3
0.75	2	76.3	23.7	—
0.375	2	73.5	26.5	trace
0.25	22	76.3	23.5	—[a]
0.19	24	71.1	22.4	1.0[b]

[a] Along with 0.35% starting material (slow reaction). [b] Along with 5.5% starting material.

Immobilised aluminium chloride also shows comparable activity to $AlCl_3$ itself in other alkene–benzene reactions and the selectivity of the supported reagent is generally superior with an increase in selectivity towards the monoalkylated product in all cases (Table 5). It is also worth commenting on the selectivity towards the most desirable 2-isomer of the dodecene–benzene reaction (which possesses the best emulsibility characteristics for applications in detergency)[21] which while not apparantly that high (47%) is considerably better than can be achieved using $AlCl_3$ (32%), HF(13–20%), acid resins, acid-treated clays and even most zeolites with only less active zeolites (which give incomplete conversion of the dodecene even after 10 h at >100 °C using high alkene dilutions) giving better selectivity.[21,22]

Broadening the range of aromatic substrates produced results that demonstrated some of the limitations of the supported aluminium chloride catalysts (Table 6). While alkyl benzenes worked well again giving rapid reactions with oct-1-ene at room temperature and affording better selectivity towards monoalkylated products than $AlCl_3$ itself, the reactivity of the monohalobenzenes was significantly lower than benzene itself. The observed order of reactivities is actually the same as that observed with $AlCl_3$ itself, *i.e.* PhH > PhF > PhCl > PhBr and this has been explained on the basis of electronic factors.[23] Interestingly, in the clayzic catalysed benzylation of halobenzenes, the observed order of reactivities is different (PhBr > PhCl > PhH = PhF for unactivated clayzic and PhH > PhBr > PhCl > PhF for thermally activated clayzic) and this has been explained by allowing for the relative diffusion rates of the halobenzenes into the catalyst pores (which will be controlled by molecular polarities/polarisibilities).[19] While we still expect diffusion rates to be important for these porous aluminium chloride catalysts (see above) the greater similarity with the relative rates using $AlCl_3$ is consistent with a catalyst of activity comparable to the homogeneous analogue.

Apart from alkenes, chloroalkanes are widely used and commercially important alkylating agents. We have studied the reaction of several chloroalkanes in the presence of the supported aluminium chloride catalysts (Table 7). Clayzic is one of the most reactive solid catalysts known for this type of reaction but is only effective with the more reactive chloroalkanes and even then only with heat (with the notable exception of benzyl chlorides).[24] Drago *et al.*[7] described a form of immobilised aluminium chloride that is capable of catalysing

Table 4 Activity of supported methylaluminium chloride compounds in the reaction of benzene and oct-1-ene

Catalyst	Reaction conditions *t*/h (*T*/°C)	Octylbenzene	Dioctylbenzene	Trioctylbenzene	Tetraoctylbenzene
		GC %			
SiO_2 (150 Å)–$MeAlCl_2$	2 (20)	73.3	25.3	0.6	0.24
K10–$MeAlCl_2$	2 (20)	40.7	14.1	20.4	23.4
$MeAlCl_2$	2 (20)	27.2	15.6	19.8	12.3
$MeAlCl_2$	22 (20)	39.7	20.6	22.5	16.8
SiO_2 (150 Å)–Me_2AlCl	96 (reflux)	64.4	29.3	<0.2	<0.2
K10–Me_2AlCl	18 (reflux)	3.6	1.3	1.6	0.3

Table 5 Activity of K10–$AlCl_3$ catalyst[a] in the reaction of benzene and alkenes at room temperature

Alkene[b]	Monoalkylbenzene	Dialkylbenzene	Trialkylbenzene
	GC %		
Hex-1-ene	69.2	28.1	2.5[c]
Oct-1-ene	75.3[d]	23.8	—
Dodec-1-ene	77.3[e]	21.3	—
Hexadec-1-ene	71.0[f]	14.5[f]	—

[a] 0.75 mmol g^{-1} K10; catalyst prepared as described in ref. 11. [b] Alkene (0.5 mol) added to benzene (1.0 mol) plus catalyst (10 g) over a 1–2 h period; the reactions were complete after a further 0.5 h. [c] Trace of starting material remaining. [d] 2-Phenyloctane represents 50% of the monoalkylated products. [e] 2-Phenyldodecene represents 47% of the monoalkylated products. [f] Isolated yields of products.

Table 6 Reaction of aromatics with oct-1-ene in the presence of K10–$AlCl_3$[a]

Aromatic substrate	Reaction conditions *t*/h (*T*/°C)	Octylaromatic	Dioctylaromatic	Other products[b]	Unreacted octene[c]
		GC %			
PhH	2.5 (20)	75.3	23.8	—	—
PhMe	1.5 (20)	80.9	19.1	—	—
PhEt	3.5 (20)	74.3	22.8	2.4	0.2
PhF	4 (20)	29.6	2.0	8.9	59.5
PhF	22 (reflux)	52.3	7.5	25.4	14.8
PhCl	4.5 (20)	14.2	—	12.3	73.5
PhCl	22 (105)	15.5	—	58.4	26.1
PhBr[d]	4 (20)	8.5	—	20.2	70.9
PhBr[d]	22 (105)	14.7	—	65.9	19.5

[a] 0.75 mmol $AlCl_3$ g^{-1} K10; catalyst prepared as described in ref. 11 but using the appropriate PhX (see footnote *d*). Reactions carried out using 1 mol aromatic to 0.5 mol oct-1-ene and 10 g of catalyst. [b] Polyalkylates and octene oligomers. [c] Isomers other than oct-1-ene were observed in the reactions carried out at elevated temperatures. [d] Products derived from benzene (*e.g.* octylbenzene) are observed in reactions using a catalyst prepared in bromobenzene due to debromination at the high (reflux) temperature employed. By preparing the catalyst in benzene followed by complete removal of the benzene before use, these products are not observed.

Table 7 Reactions of benzene and chloroalkanes in the presence of K10–$AlCl_3$^{a}

Chloroalkane	Reaction conditions t/h (T/°C)	Products (%)	Unreacted chloroalkane (GC %)
1-Chlorooctane	2.75 (20)	Monooctylbenzenes (53.3)^b Dioctylbenzenes (10.6)^b	36.1
tert-Butylchloride	5 (20)	Monobutylbenzenes (81.4)^b Dibutylbenzenes (13.8)^b	4.8
1,2-Dichloroethane^c	3.5 (reflux)	Bibenzyl (62.1)^b Other products (37.9)^{b,d}	—
Dichloromethane^e	2.5 (reflux)	Diphenylmethane (62.0)^f Alkylated diphenylmethanes (11.5)^f	—
Trichloromethane^g	4.7 (reflux)	Triphenylmethane (24.7)^f Diphenylmethane (2.1)^f	—
Tetrachloromethane^h	18 (reflux)	Triphenylmethane (0.6)^f Triphenylmethanol (0.2)^f Tetraphenylmethane (0.06)^f	—

^{a} 0.75 mmol $AlCl_3$ g^{-1} K10 unless stated otherwise; catalyst prepared as described in ref. 11. Reactions carried out using 1 mol of benzene to 0.5 mol of chloroalkane, and 10 g of catalyst, unless stated otherwise. ^{b} GC yields (corrected for response factors where appropriate). ^{c} Acidic silica (70 Å) support; 1.5 mmol $AlCl_3$ g^{-1} loading. ^{d} Mostly alkylated bibenzyls. ^{e} Acidic silica (70 Å) support; 0.75 mmol $AlCl_3$ g^{-1} loading. Mole ratio benzene : dichloromethane = 3 : 1. ^{f} Based on isolated crude product mixture. ^{g} Acid treated montmorillonite support; 0.75 mmol $AlCl_3$ g^{-1} loading. Mole ratio benzene : trichloromethane = 5 : 1. ^{h} Silica (70 Å) based support; 1.5 mmol $AlCl_3$ g^{-1} loading. Mole ratio benzene : tetrachloromethane = 4 : 1.

some of these reactions in refluxing CCl_4 but only the highly reactive tertiary chloroalkanes give moderate yields (primary chloroalkanes are unreactive). The activity of the supported catalysts described here are clearly superior to these materials and indeed to any solid acid catalysts that we are aware of.[2] *tert*-Butyl chloride reacts quickly with benzene at room temperature. 1-Chlorooctane reacts slowly with benzene at room temperature, while the less reactive 1,2-dichloroethane and dichloromethane only react with benzene at a reasonable rate on heating. Selectivity towards monoalkylation is again significantly better with the solid catalysts than with $AlCl_3$. In the dichloromethane–benzene reaction for example, an impressive >80% selectivity towards diphenylmethane (an important pharmaceutical intermediate) can be obtained, rivalling any alternative process (which normally use benzyl chloride and benzene).[3] Not surprisingly, trichloromethane and tetrachloromethane only react very slowly with benzene in the presence of supported aluminium chloride, although any reaction with these highly unreactive substrates is remarkable and the selectivity towards triphenylmethane in the trichloromethane–benzene reaction (92%) is impressive. It should be noted that ordinary reagent grade trichloromethane gave only 1–2% conversion on reaction (27% isolated yield with spectroscopic grade $CHCl_3$) and this is believed to be due to the presence of ethanol stabiliser that is likely to poison the catalyst by acting as a base. This is confirmed by the failure to achieve any reaction between ethanol or even octan-1-ol and benzene under the supported reagent conditions.

In conclusion, we have shown that it is possible to prepare forms of immobilised aluminium chloride that are highly active in the alkylation of aromatic molecules using alkenes and chloroalkanes. The activity of the best catalysts is greater than other heterogeneous catalysts and is comparable to $AlCl_3$ while the selectivity towards the formation of monoalkylates is considerably better than under homogeneous conditions, and the supported reagent catalysts are reusable and easily recovered from the reactions by filtration. The results reported here are of direct significance to the manufacture of a number of important industrial products including linear alkylbenzenes used in detergents and are highly promising with regard to the availability of a general purpose solid, reusable Friedel–Crafts alkylation catalyst.[21]

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