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Identification of acidic species in chloroaluminate ionic liquid catalysts

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ABSTRACT

Chloroaluminate ionic liquids (ILs), especially composite ionic liquids (CILs) which are ILs modified with copper(I) chloride, are highly active and selective catalysts for the alkylation of 2-butene with isobutane. The Lewis and Brønsted acidic species of these ILs were investigated by NMR spectroscopy. Pyridine is found to be a suitable indicator. Lewis acidity arises mainly from $Al_2Cl_7^-$ having a chemical shift at 102 ppm in the ^{27}Al NMR spectrum, while Brønsted acidity arises from $Al_2Cl_6OH^-$ (chemical shift at 97 ppm). The peak at 94 ppm in the ^{27}Al NMR spectrum is related to $Al_2Cl_5O^-$. These new insights have improved our understanding of the structure of the active species in chloroaluminate ionic liquid alkylation catalysts.

1. Introduction

Since the ninth decade of last century, room temperature ionic liquids (ILs) especially chloroaluminate ILs have been discovered as alternative alkylation catalysts [1–4]. Their adjustable acidity and negligible vapor pressure made them attractive alternatives for the current liquid acid catalysts, hydrofluoric acid, and sulfuric acid, to produce alkylate for gasoline from isobutane and butene [5–8].

The acidity study of chloroaluminate ILs has been reviewed by Welton and Wasserscheid [9,10]. Yoo et al. [11] studied [omim]Br–$AlCl_3$ by FT-IR and ^{27}Al NMR spectroscopy to explain the good activity by the strongly Lewis acidic anion $Al_2Cl_6Br^-$. Kou [12] used pyridine as probe in IR spectroscopy to determine the acidity of [bmim]Cl–$AlCl_3$ and concluded that chloroaluminate ILs have both Lewis and Brønsted acidity. Other works described that Brønsted acidity in chloroaluminate ILs may come from traces of water or HCl, which could also improve the catalyst activity [13–15]. $HAlCl_4$ was proposed as a most likely Brønsted acidity specie in chloroaluminate ILs [16]; although the potential existence and stability of $HAlCl_4$ has been questioned by other researchers [17,18]. Hence, there is ongoing interest in the role of Brønsted acidity in chloroaluminate ILs.

Our research group has developed a composite ionic liquid (CIL) [19], which is a kind of chloroaluminate IL modified with CuCl and showing excellent activity and selectivity of isobutane alkylation. The research octane number of our alkylate is above 98, which is better than that of the commercial catalysts. We later found that the acidity can be increased or even restored by addition of HCl or water [20]. The rejuvenation of deactivated CIL catalyst with HCl can effectively recover the activity (Tables S1 and S2). The more HCl dissolved in deactivated CIL, the longer lifetime in the alkylation reaction (Table S1). Similar findings have been reported by Chevron [21] and Jess et al. [15,16,22]. The hydrolysis of chloroaluminate IL was found to be a minor but significant factor for alkylation activity, because Brønsted acidic proton could provide initial supply of carbonium ion to initiate alkylation as follows (Fig. 1).

Here, the effects of the acidity of chloroaluminate IL, especially CIL, on the catalytic performance prompted us to study these phenomena on a molecular level mainly using NMR. This paper describes our initial study on identification of the acidic species.

2. Experimental

2.1. Materials

Synthesis grade: Triethylamine hydrochloride (99.99%) was purchased from Merck KGaA. Aluminum chloride (99.99%) and

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copper(I) chloride (⩾99.00%) were purchased from Sigma-Aldrich. All these chemicals were stored in a glove box.

Technical grade: Triethylamine hydrochloride (98%), aluminum chloride (anhydrous reagent grade), and copper(I) chloride (90+%) were purchased from Alfa Aesar.

Water content in triethylamine hydrochloride was determined by Karl Fischer method (Table 1).

Pyridine (⩾99.50%) and dichloromethane-d$_2$ (99.8%) were purchased from Merck KGaA, dried over molecular sieves 4 Å, and stored in a glove box.

2.2. Preparation of ILs

2.2.1. Basis ionic liquids ($Et_3NHCl–AlCl_3$, BILs)

BILs with different $AlCl_3$ molar fractions were prepared according to the typical procedure [23] under the protection of dry nitrogen using Schlenk techniques. A typical example is given for a BIL with $AlCl_3$ molar fraction of 0.64 ($X_{AlCl3} = 0.64$). Synthesis grade Et_3NHCl (13.77 g, 0.10 mol) was placed in a flask. $AlCl_3$ (99.99% grade, 24.00 g, 0.18 mol) was slowly added to the flask in 30 min while keeping the reaction temperature below 80 °C. The mixture was then heated to 80 °C and maintained at that temperature until all solids "dissolved." The BILs were generally formed within 3–4 h.

2.2.2. Addition of water to BILs

BIL (*ca.* 10.00 g, precisely weighed) was placed in a Schlenk vessel, and specific molar equivalent of water was added via syringe. The molar equivalent was defined as mol H_2O per mol of N in the ionic liquid.

2.2.3. Wet composite ionic liquid ($Et_3NHCl–AlCl_3$-CuCl, wet CIL)

CIL was synthesized according to patent application US20040133056A1 [19]: Anhydrous aluminum chloride was slowly added to a round-bottomed flask containing technical grade Et_3NHCl under atmospheric conditions at 80 °C. After the formation of chloroaluminate IL (see the procedure for the BILs), cuprous chloride was introduced. The reaction mixture was stirred at 100 °C for 2 h, until the complete homogenization of the resulting ionic liquid.

2.2.4. Dry composite ionic liquid ($Et_3NHCl–AlCl_3$–CuCl, dry CIL)

The procedure was repeated as for wet CIL using synthesis grade feedstock and under the protection of nitrogen atmosphere.

2.2.5. Evacuated wet CIL (ECIL)

Wet CIL was evacuated with a vacuum pump ($P < 0.1$ mbar) at 50 °C for 12 h with stirring. Lots of bubbles were generated at the surface of CIL indicating the loss of gas (HCl).

2.2.6. Addition of HCl to ECIL (ECIL + HCl)

Hydrogen chloride was introduced into ECIL (*ca.* 10 g) *via* a tube filled with anhydrous calcium chloride.

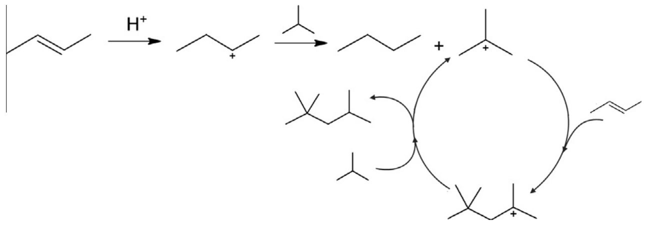


Fig. 1. Protonation of butene, formation of *tert*-butyl cation, and alkylation of 2-butene.

Table 1
Water content in Et_3NHCl.

Et_3NHCl	Water in Et_3NHCl (mg/kg)	Water in Et_3NHCl (mmol/mol)
Synthesis grade	5.9	0.045
Technical grade	440.2	3.4

2.3. NMR analysis

All the samples were prepared in a glove box. An ionic liquid sample (*ca.* 35 mg) was placed into an NMR tube (5 mm, borosilicate glass). Deuterated dichloromethane was added (*ca.* 1 mL). The tube was closed with a standard cap and removed from the glove box immediately prior to the measurement.

^{1}H and ^{27}Al NMR spectra were recorded at 25 °C on an Agilent NMR spectrometer at 400 and 104 MHz, respectively.

Typical ^{1}H NMR spectral data are as follows (400 MHz, CD_2Cl_2, residual $CDHCl_2$ referenced at 5.32 ppm):

BIL with $AlCl_3$ molar fraction of 0.64: δ (ppm) 1.43 (t, $J = 7.6$ Hz, CH_3, 9H), 3.32 (qd, $J = 7.4$ Hz, $J = 5.2$ Hz, CH_2, 6H), and 5.68 (t, $J = 52.8$ Hz, NH, 1H).

BIL + 10 mol% H_2O: δ (ppm) 1.42 (t, $J = 7.4$ Hz, CH_3, 9H), 3.31 (qd, $J = 7.4$ Hz, $J = 5.2$ Hz, CH_2, 6H), 4.85 (s), and 5.69 (t, $J = 53.3$ Hz, NH, 1H).

E (BIL + H_2O): δ (ppm) 1.41 (t, $J = 7.4$ Hz, CH_3, 9H), 3.31 (qd, $J = 7.4$ Hz, $J = 5.2$ Hz, CH_2, 6H), 4.85 (s), and 5.71 (t, $J = 52.0$ Hz, NH, 1H).

Dry CIL: δ (ppm) 1.42 (t, $J = 7.4$ Hz, CH_3, 9H), 3.31 (qd, $J = 7.4$ Hz, $J = 5.2$ Hz, CH_2, 6H), and 5.97 (t, $J = 52.0$ Hz, NH, 1H).

Wet CIL: δ (ppm) 1.42 (t, $J = 7.4$ Hz, CH_3, 9H), 3.30 (qd, $J = 7.4$ Hz, $J = 5.2$ Hz, CH_2, 6H), 4.81 (s), and 5.96 (t, $J = 51.6$ Hz, NH, 1H). The precise integral ratio was CH_3: CH_2: NH: AlOH = 54.11: 36.72: 5.94: 0.17.

ECIL: δ (ppm) 1.42 (t, $J = 7.4$ Hz, CH_3, 9H), 3.30 (qd, $J = 7.4$ Hz, $J = 5.2$ Hz, CH_2, 6H), and 6.03 (t, $J = 51.6$ Hz, NH, 1H).

ECIL + HCl: δ (ppm) 1.42 (t, $J = 7.4$ Hz, CH_3, 9H), 3.31 (qd, $J = 7.3$ Hz, $J = 5.2$ Hz, CH_2, 6H), 4.81 (s), and 5.99 (t, $J = 51.6$ Hz, NH, 1H).

Pyridine: δ (ppm) 7.25 (t, $J = 1.6$ Hz, *meta*, 2H), 7.66 (t, $J = 8.0$ Hz, *para*, H), and 8.58 (d, $J = 4.0$ Hz, *ortho*, 2H).

ECIL + pyridine (extra signals): Lewis acid complex: $–CH_a–$ ($\delta = 8.91$ ppm), $–CH_b–$ ($\delta = 8.34$ ppm), and $–CH_c–$ ($\delta = 7.87$ ppm), ratio of H_a:H_b:H_c = 0.77:0.39:0.79 (Fig. 11).

Wet CIL + pyridine (extra signals): Pyridinium: $–CH_\alpha–$ ($\delta = 8.85$ ppm), $–CH_\beta–$ ($\delta = 8.15$ ppm), $–CH_\gamma–$ ($\delta = 8.71$ ppm), and $–NH_\delta$ ($\delta = 12.79$ ppm, t, $J = 68.0$ Hz), the ratio of H_α:H_β:H_γ:H_δ was almost at 2:2:1:1 (Fig. 11).

Some typical ^{1}H NMR spectra of BIL and CIL before and after different treatments are shown in Fig. S1. Other NMR spectral data (all in CD_2Cl_2 unless indicated otherwise) are given in the results and discussion part.

2.4. IR analysis

Infrared spectra were recorded in KBr disks by means of a Nicolet FTIR spectrophotometer. In the glove box, IL samples (0.5 mL) were put in between the KBr disks and removed from the glove box immediately prior to measurement. FT-IR spectra were recorded on a Nicolet 380/FT-IR Nexus infrared spectrometer in the typical KBr range of the 4000–400 cm^{-1} at room temperature, with a resolution of 4 cm^{-1} in 32 parallel scans.

2.5. Alkylation test with dry, wet CIL and ECIL and product analysis

In a typical experiment, 50 mL of ionic liquid catalyst was placed in a 250 mL semi-continuous glass autoclave (Fig. 2). An isobutane/2-butene (a mixture of *cis*- and *trans*-isomers) mixture (molar ratio isobutane/butenes of 20) was introduced into the reactor at 5 mL/min flow rate. Stirring was applied at 500 rpm, generating a well-mixed zone in the bottom and a non-mixed hydrocarbon phase in the top of the reactor. The reaction temperature was controlled by a thermostatic oil bath at 23 °C.

After the autoclave was filled, samples were taken from the hydrocarbon leaving the top of the reactor when 500 mL and 1000 mL of C4 feed was fed into the system. Samples were analyzed with a gas chromatograph (Hewlett–Packard, 6890) equipped with a HP-1 methyl silox Agilent column ($50\ \mathrm{m} * 320\ \mu\mathrm{m} * 0.25\ \mu\mathrm{m}$).

The olefin conversion data are given in Fig. 3. Detailed results are given in the supporting material in Tables S1 and S2.

3. Results and discussion

3.1. Alkylation test results

Alkylation tests were done by wet CIL (prepared from technical grade starting materials and without nitrogen protection) and evacuated wet CIL (ECIL) and dry CIL (prepared from starting materials at synthesis grade and under nitrogen protection). The results showed that wet CIL kept its activity after 1000 mL of C4 feed, while ECIL and dry CIL started losing activity already after 500 mL of feed (Fig. 3). Apparently, the presence of trace amounts of water has a dramatic influence on the catalyst activity. According to the literature, [24,25], water has most likely reacted with chloroaluminate ILs to form HCl, which is assumed to be the active Brønsted acid. Evacuation leads to removal of HCl and apparently also to loss of catalyst activity. By these tests, we were even more triggered to study the structure and effect of acidity of our CIL alkylation catalyst.

3.2. ^{27}Al NMR analysis of BIL

To simplify the structural study, we started with BIL. This system is also known to be catalytically active, but with lower selectivity [23] for alkylation of isobutane and 2-butene.

Previous studies [12,26] concluded that, when the molar fraction of $AlCl_3$ in BIL is equal or below 0.5, the major chloroaluminate anion is $AlCl_4^-$. Additional Lewis acidic ionic species, $Al_2Cl_7^-$ (mainly) and $Al_3Cl_{10}^-$, had been proposed for BILs with $AlCl_3$ molar fractions of above 0.5 [27] Eqs. (1)–(3). These Lewis anions are interrelated according to equilibria shown in Eqs. (4) and (5).

$$Cl^- + AlCl_3 \rightleftharpoons AlCl_4^- \quad (1)$$

$$AlCl_4^- + AlCl_3 \rightleftharpoons Al_2Cl_7^- \quad (2)$$

$$Al_2Cl_7^- + AlCl_3 \rightleftharpoons Al_3Cl_{10}^- \quad (3)$$

$$Al^*Cl_4^- + Al_2Cl_7^- \rightleftharpoons Al^*AlCl_7^- + AlCl_4^- \quad (4)$$

$$2Al_2Cl_7^- \rightleftharpoons AlCl_4^- + Al_3Cl_{10}^- \quad (5)$$

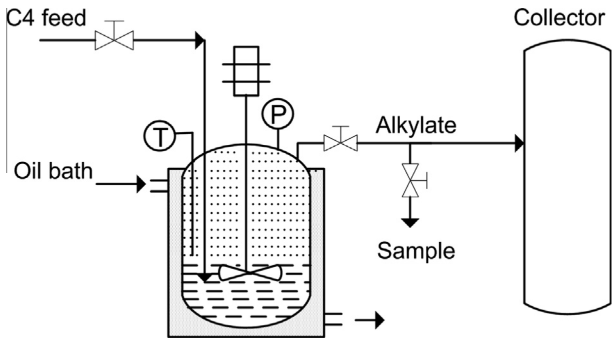


Fig. 2. Apparatus for isobutane alkylation.

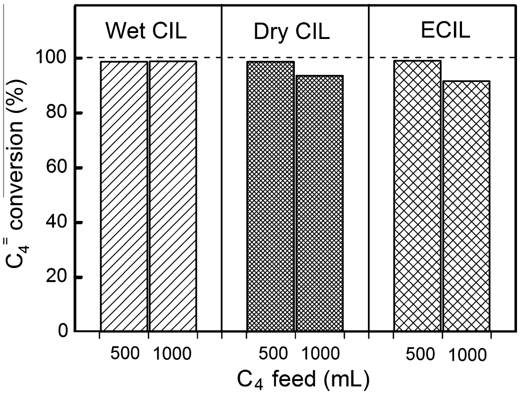


Fig. 3. Butene conversion after 500 and 1000 mL of isobutane/butene feed at 20 M ratio over 50 mL of catalyst at 23 °C.

^{27}Al NMR spectra of various BILs with different $AlCl_3$ molar fractions were recorded and only one peak at about 102 ppm was observed: a sharp peak in case of $AlCl_3$ molar fraction of 0.5 and a broad signal of which the peak width increased with increasing $AlCl_3$ molar fraction (Fig. 4A). The changes in chemical shift as well as the peak broadening show an almost linear trend with the $AlCl_3$ molar fraction (Fig. 4B). The broadening was explained by the rate of the interchange reactions between those anions taking place at the NMR time scale, resulting in the more broadening with more $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ present. These observations and conclusions are consistent with the findings of Takahashi et al. [28] who studied the NMR behavior of 1-ethyl-3-methylimidazolium chloroaluminate and measured the lifetime of the chloroaluminate anions to be fast on the ^{27}Al NMR timescale.

The chemical shift did only change a little to upfield with changing the $AlCl_3$ molar fraction as shown in Fig. 4. It is therefore concluded that the chemical shifts of $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, *etc.* were close to that of $AlCl_4^-$. The signal at 102 ppm (width and intensity) is thus indicative for Lewis acidic species in ILs with $AlCl_3$ molar fraction of above 0.5.

3.3. ^{27}Al NMR spectroscopy of neat CIL and diluted CIL

The study was intended to investigate the structure of CIL, which in reality is applied in pure form as alkylation catalyst. However, NMR analysis is normally being done in deutero solvent, *e.g.* CD_2Cl_2. Therefore, ^{27}Al NMR analysis of CIL solution was compared with the ^{27}Al NMR analysis of neat CIL.

Neat CIL was analyzed using dimethylsulfoxide-d_6 (DMSO) as external lock agent, using an insert filled with CIL. At room temperature, a very broad signal at *ca.* 102 ppm was obtained and it sharpened with increasing temperature (Fig. 5). The broad signals of neat CIL clearly showed that it will be difficult to get structural information from those ^{27}Al NMR spectra. When this sample was heated to 75 °C, the peaks sharpened and became close to that of the CIL sample diluted in CD_2Cl_2 which was measured at room temperature (Fig. 5). Thus, the exchange between the anion species in solution is faster than that in neat CIL, while the structures of CIL, the species as observed in CD_2Cl_2 solution, are similar to those in neat CIL.

The ^{27}Al NMR spectrum of CIL in CD_2Cl_2 showed three peaks at 102, 97, and 94 ppm, respectively (Fig. 5 bottom). The broad signal at 102 ppm is similar to that in the ^{27}Al NMR spectrum of BIL and can be assigned to the mixture of $AlCl_4^-$, $Al_2Cl_7^-$, *e.g.* $Al_xCl_{3x+1}^-$ anions. Thus, the intensity and broadening of the peak at 102 ppm indicated a high content of Lewis acidic species in CIL.

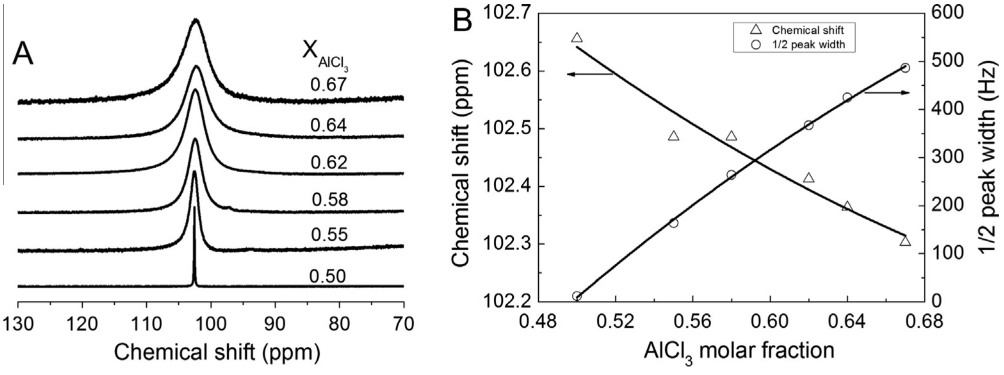


Fig. 4. Change of ^{27}Al NMR spectra of BILs with various $AlCl_3$ molar fractions at room temperature.

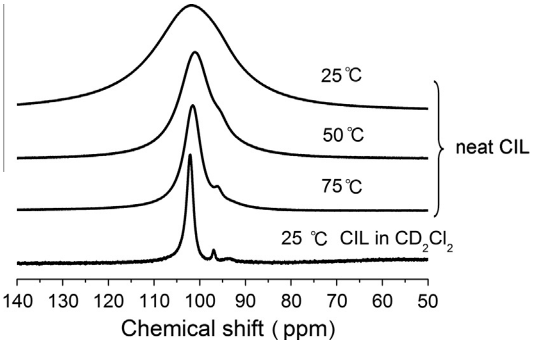


Fig. 5. ^{27}Al NMR spectra of neat CIL (DMSO-d_6 as external lock agent) at various temperatures and of CIL in CD_2Cl_2 solution at 25 °C.

3.4. Brønsted acidic species

Brønsted acidic species in chloroaluminate ILs were investigated by addition of water and HCl to BIL and CIL. Water (10 mol%) added to BIL ($X_{AlCl3} = 0.64$) yielded a new peak at 97 ppm (Fig. 6B), while the peak at 102 ppm sharpened. Obviously, the 97 ppm peak is related to the product formed by the addition of water. The same signal was found in wet CIL that was prepared with wet feedstock (Fig. 6E). Takahashi et al. [28] also concluded earlier that this 97 ppm signal was attributed to a contaminant derived from reaction of chloroaluminate with water. The reaction to be expected to occur is given in Eq. (6).

$$Al_2Cl_7^- + H_2O \rightarrow Al_2Cl_6OH^- + HCl\uparrow \tag{6}$$

$$Al_2Cl_6OH^- \rightleftharpoons Al_2Cl_5O^- + HCl\uparrow \tag{7}$$

Hence, it explains that the addition of water into chloroaluminate ILs can generate Brønsted acid HCl.

Berenblyum et al. [14] found that the HCl solubility in chloroaluminate ILs depends on the system pressure and the $AlCl_3$ molar fraction. Therefore, CIL was evacuated in order to remove any dissolved HCl in wet CIL. Fig. 6F shows the ^{27}Al NMR spectrum of wet CIL after evacuation (ECIL). The peak at 97 ppm almost disappeared, while the intensity of peak at 94 ppm increased. Such behavior was also observed at evacuating BIL after 10 mol% of water had been added (*cf.* spectra B and C in Fig. 6). It seemed that the aluminate anion with signal at 97 ppm was converted into a species resonating at 94 ppm. Most likely, the evacuation not only removed dissolved HCl, which would not lead to such a change in the ^{27}Al NMR spectrum, but also induced a chemical conversion as shown in Eq. (7) [24,26].

In order to support this assumption, anhydrous HCl was introduced into ECIL under nitrogen protection. The addition of HCl to ECIL resulted in an increase of the 97 ppm peak and a slight decrease of the 94 ppm peak (Table S3). As expected, the ^{27}Al NMR spectrum of ECIL with the addition of HCl was almost returned to the one of CIL before evacuation. This phenomenon verified the hypothesis that the 97 ppm peak is related to chlorohydroxy aluminate species and the 94 ppm peak is related to chlorooxy aluminates. In addition, the chloro(hydr)oxy aluminates species $Al_2Cl_6OH^-$ and $Al_2Cl_5O^-$ have been identified by electrospray ionization mass spectrometry [3,29].

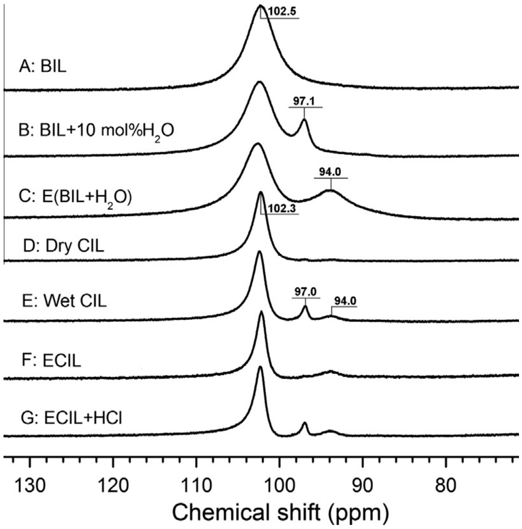
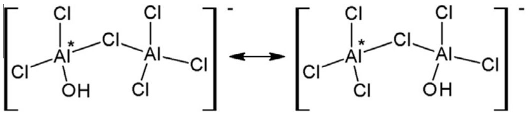


Fig. 6. ^{27}Al NMR spectra of BIL and CIL before and after different treatments.

The ^{1}H NMR spectra of BIL + 10 mol% H_2O, wet CIL and ECIL + HCl showed a small peak at *ca.* 4.8 ppm (Section 2.3) that was not observed in the ^{1}H NMR spectra of BIL, dry CIL, and the evacuated ILs. This extra peak is most likely related to the Brønsted acidic proton. This observation is consistent with the study of Berenblyum et al. [14]. The integral of the signal at 4.8 ppm in the ^{1}H NMR spectrum of wet CIL was about 3 mol%, while the integral of the 97 ppm peak in ^{27}Al NMR spectrum was *ca.* 7 mol%. Therefore, the peaks at 97 ppm in the ^{27}Al NMR spectra and at *ca.* 4.8 ppm in the ^{1}H NMR spectra both can be assigned to $Al_2Cl_6OH^-$, which plays a Brønsted acidic role in CIL *via* the equilibrium in Eq. (7).

Although $Al_2Cl_6OH^-$ might have two different Al centers, we assume that in the ^{27}Al NMR spectrum only one signal (at 97 ppm) was observed due to a fast internal exchange (Eq. (8)).



(8)

The formation of the 97 ppm peak in the ^{27}Al NMR spectrum was followed for BILs with different $AlCl_3$ molar fractions as a function of amount of water added. Several phenomena were observed. The peak at 102 ppm sharpened with the addition of water, which was explained by the consumption of $Al_2Cl_7^-$ to form $Al_2Cl_6OH^-$ (Fig. 7). The sharpening stopped and solids were formed when all $Al_2Cl_7^-$ was consumed (Fig. 8). For $X_{AlCl3} = 0.64$, this happened at a H_2O/IL molar ratio of about 0.8; for $X_{AlCl3} = 0.58$, this happened at a H_2O/IL molar ratio of about 0.4. This can be explained by the following stoichiometries:

$$X_{AlCl3} = 0.64 \rightarrow Al/N = 1.8 \rightarrow (Al_2Cl_7^-)_{0.8}(AlCl_4^-)_{0.2}NHEt_3^+$$

$$X_{AlCl3} = 0.58 \rightarrow Al/N = 1.4 \rightarrow (Al_2Cl_7^-)_{0.4}(AlCl_4^-)_{0.6}NHEt_3^+$$

During the water addition, another small signal at 89 ppm appeared. It is thus far unknown to which species this signal belongs. It might be a dihydroxy chloroaluminate, which is only slightly soluble.

The experimental integral ratio of the 102 and 97 ppm peaks was compared with the calculated value assuming the stoichiometry of Eq. (6). The experimental data showed a good fit with the calculated data (Fig. 8), being another confirmation of the formation of $Al_2Cl_6OH^-$ from $Al_2Cl_7^-$.

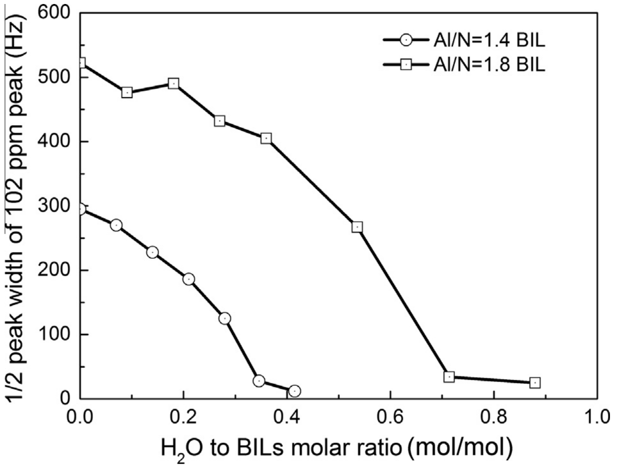


Fig. 7. Change of 1/2 peak width of 102 ppm signal in ^{27}Al NMR at the addition of water to BILs with $X_{AlCl3} = 0.64$ (Al/N = 1.8) and $X_{AlCl3} = 0.58$ (Al/N = 1.4).

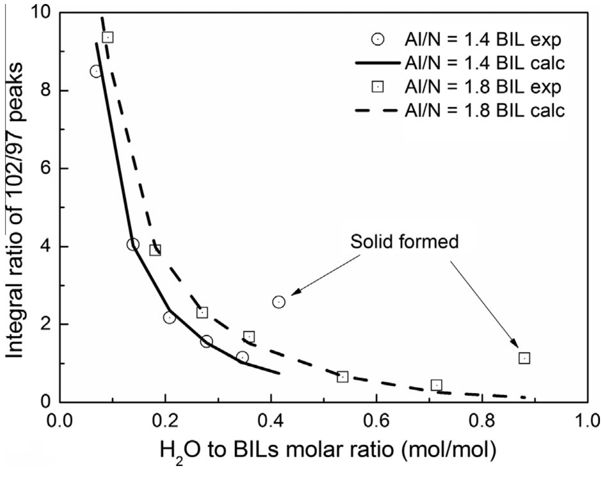


Fig. 8. Integral ratio of 102/97 peaks in ^{27}Al NMR with the addition of water to BILs for $X_{AlCl3} = 0.64$ (Al/N = 1.8) and $X_{AlCl3} = 0.58$ (Al/N = 1.4).

In comparison with BIL, the signals of wet CIL showed much sharper signals in the ^{27}Al NMR spectrum indicating that cuprous chloride might have a positive effect on stabilizing chlorooxy aluminate species. In our previous work [3], a new composite anion $AlCuCl_5^-$ was proposed based on ESI-MS and ^{27}Al NMR spectroscopy, and the chemical shift at 97 ppm was assigned to this anion. However, at present, there is no evidence of $AlCuCl_5^-$ resonating at 97 ppm, and this peak is now proved further to be from $Al_2Cl_6OH^-$. Bui [16] speculated the formation of super acids by interaction of CuCl with the Et_3NH^+ cation, forming Et_3NCu^+ and HCl. The ^{1}H NMR analysis of wet CIL, showing the CH_3, CH_2, and NH signals in the expected 9:6:1 ratio (see experimental part), does not support the proposal of CuCl reacting with Et_3NH^+. The role of copper still remains unclear.

3.5. The determination of acidic species by pyridine

Pyridine is a well-known indicator to determine the acidity of ionic liquid by IR spectroscopy [12,16]. Pyridine added to CIL resulted in absorption bands at 1538 and 1454 cm^{-1} (Fig. 9), which can be assigned to pyridine molecules interacting with Brønsted and Lewis acid sites, respectively.

NMR spectroscopy was used to evaluate the structures of Lewis and Brønsted acidic species in the wet CIL interacting with pyridine. Pyridine was added in 0.1 and 0.3 M equivalent to wet CIL. The ^{27}Al NMR spectra are shown in Fig. 10B, and C, respectively. Compared with the ^{27}Al NMR spectrum of wet CIL in Fig. 6E, a new peak at 105 ppm appeared, which was also found in the ^{27}Al NMR spectrum of ECIL with pyridine addition. When the Py/CIL ratio was 0.3, the 97 ppm peak almost disappeared while the 102 ppm signal sharpened. These changes indicated that pyridine had reacted with the aluminate anions resonating at 97 and 102 ppm forming a new aluminate complex with a signal at 105 ppm. The latter is considered to be the Lewis acidic aluminate species coordinating to pyridine. When the Py/CIL ratio was 0.35, the 97 ppm signal, belonging to the Brønsted acid aluminate, was completely disappeared.

The pyridine regions of the ^{1}H NMR spectra of ECIL and wet CIL after adding pyridine are shown in Fig. 11. The signals in the Et_3NHCl region did not change with the addition of pyridine (Section 2.3). With the addition of pyridine to ECIL, new signals appeared in the 7.5–9.0 ppm region (a, b, and c in Fig. 11A), which were different from pure pyridine (Section 2.3). With the addition of pyridine to wet CIL, a second set of new pyridine signals

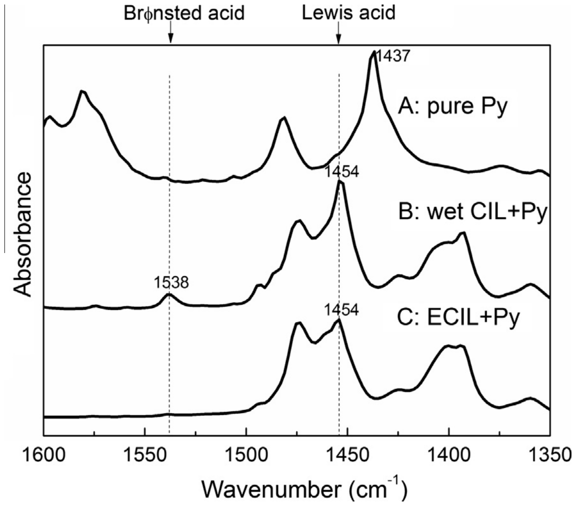


Fig. 9. FT-IR spectra of pure Py, wet CIL, and ECIL interacting with 10 mol% of Py.

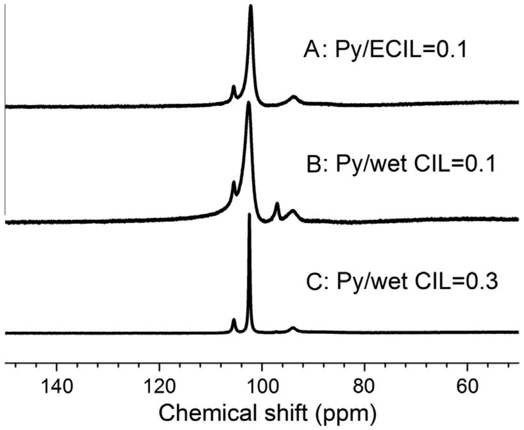


Fig. 10. ^{27}Al NMR spectra of ECIL and wet CIL after addition of Py.

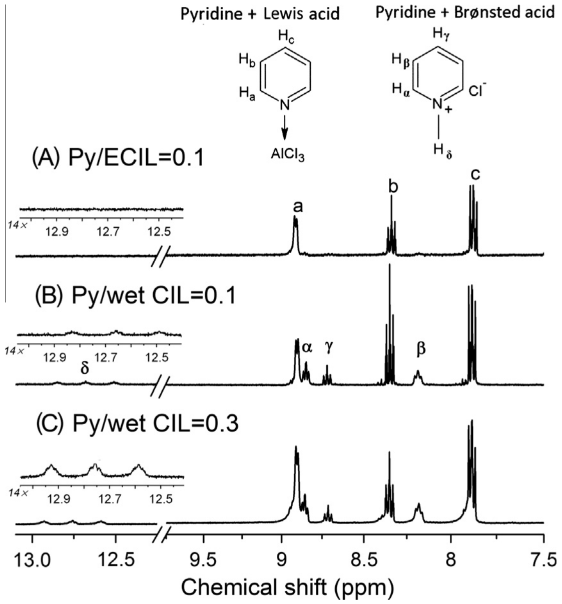


Fig. 11. ^{1}H NMR spectra of ECIL and wet CIL after addition of Py (only pyridine and pyridinium signals are shown).

appeared in the ^{1}H NMR spectrum (α, β, and γ in Fig. 11B). The co-appearance of the latter signals with a new triplet δ at 12.8 ppm with a ^{14}N–H coupling constant of 68.0 Hz is a clear identification of a hydrogen pyridium salt PyH^{+} derived from the reaction with Brønsted acid. The other set of pyridine signals (a, b, and c) is identified as pyridine-AlCl$_3$ formed from the reaction with Lewis acid (Eq. (9)). Thus, pyridine is a good indicator of the different acidic species in chloroaluminate ILs.

$$Al_2Cl_7^- + Py \rightarrow AlCl_4^- + Py - AlCl_3 \quad (9)$$

The 105 ppm signal in the ^{27}Al NMR spectrum was related to the pyridine-Lewis acid complex observed in ^{1}H NMR spectrum, while the disappearance of the 97 ppm signal in the ^{27}Al NMR spectrum was related to the formation of pyridinium cation from pyridine and Brønsted acid. Thus, $Al_2Cl_7^-$ is the main Lewis acid in our catalytic system, and $Al_2Cl_6OH^-$ is the main Brønsted acid that is in equilibrium with HCl. The overall pathway of identification of Lewis and Brønsted acidic species in chloroaluminate ILs is shown in Fig. 12.

Finally, pyridine was used to determine the amount of Brønsted acid present in wet CIL. Wet CIL was titrated with pyridine until the 97 signal in the ^{27}Al NMR spectrum was disappeared, and then, in the ^{1}H NMR spectrum, the amount of the PyH^{+} triplet signal at 12.8 ppm relative to the amount of the N–H of Et$_3$NH^{+} was determined. Thus, the amount of $Al_2Cl_6OH^-$ in wet CIL was determined to be 5.3 mol%, which was much higher than the water content in the triethylamine hydrochloride. Besides that, $Al_2Cl_5O^-$ was also present, which was also originating from the reaction of the aluminate with water. Apparently, lots of extra water was introduced during the wet CIL synthesis by not working under inert conditions.

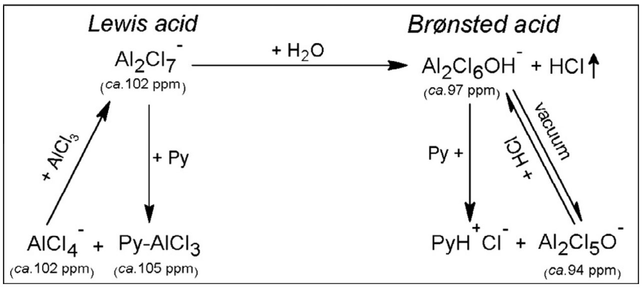


Fig. 12. Formation pathways and identification of acidic species of chloroaluminate ILs with ^{27}Al NMR.

4. Conclusions

Lewis and Brønsted acidic species were found in chloroaluminate ILs by ^{1}H NMR, ^{27}Al NMR, and IR analysis. Lewis acidic species were mainly provided by $Al_2Cl_7^-$ represented by a broad signal at 102 ppm in the ^{27}Al NMR spectrum. Lewis acidic species were furthermore demonstrated by using pyridine as indicator giving a pyridine-Lewis acid complex that was identified by ^{1}H NMR, ^{27}Al NMR, and IR spectroscopy. The Brønsted acidic species were related to chlorohydroxy aluminate $Al_2Cl_6OH^-$ resonating at the 97 ppm in the ^{27}Al NMR spectrum. This anion could lose HCl, *e.g.* by evacuation, to form non-reactive chlorooxy aluminate $Al_2Cl_5O^-$ (at 94 ppm). The reappearance Brønsted acidity, *e.g.* of the 97 peak, was demonstrated by rejuvenation of evacuated CIL with HCl.

Brønsted acidity was furthermore demonstrated by using pyridine as indicator with ^{1}H NMR, ^{27}Al NMR, and IR spectroscopy, showing the disappearance of the Brønsted acid $Al_2Cl_6OH^-$ and the formation of a pyridium hydrogen salt.

^{27}Al and ^{1}H NMR spectroscopy has been proven to be a strong and efficient tool to characterize the acidity of chloroaluminate ILs. This study has provided a new insight into Brønsted acidity formed in chloroaluminate ILs. However, the effects of CuCl, HCl, and H$_2$O are still not fully understood, especially that of CuCl on selectivity, and are being investigated further.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.09.004.

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