



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 $\text{Al}_2\text{Cl}_6\text{OH}^-$ (chemical shift at 97 ppm). The peak at 94 ppm in the ^{27}Al NMR spectrum is related to $\text{Al}_2\text{Cl}_5\text{O}^-$. These new insights have improved our understanding of the structure of the active species in chloroaluminate ionic liquid alkylation catalysts.

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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 $\text{Al}_2\text{Cl}_6\text{Br}^-$. 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]. HAICl_4 was proposed as a most likely Brønsted acidity specie in chloroaluminate ILs [16]; although the potential existence and stability of HAICl_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 ($\geq 99.00\%$) 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 ($\geq 99.50\%$) 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 ($X_{AlCl_3} = 0.64$). 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.

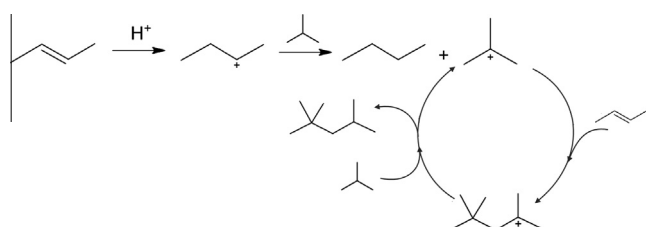


Fig. 1. Protonation of butene, formation of *tert*-butyl cation, and alkylation of 2-butene.

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.

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

Typical 1H 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 1H 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

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