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Alkylation of benzene with 1-dodecene in ionic liquids $[Rmim]^+Al_2Cl_6X^-$ (R = butyl, octyl and dodecyl; X = chlorine, bromine and iodine)

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Abstract

Alkylation of benzene with 1-dodecene had been investigated in 1-alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids comprising various alkyl groups (butyl-, octyl- and dodecyl-) and various halogens (chlorine, bromine and iodine) on the cations and anions, respectively. Among all these ionic liquids, $[bmim]^+Al_2Cl_6Br^-$ exhibited the best catalytic performance, which was ascribed to the proper strength of its Lewis acidity and its molecular polarizability demonstrated by FT-IR. The effects of varying anion molar compositions, ionic liquid dosage, reaction temperature, molar ratio of benzene to 1-dodecene and reactant moisture were explored using $[bmim]^+Al_2Cl_6Br^-$ as the catalyst; the results were systematically explained by the mechanism of the carbenium ions. The optimum conversion of 1-dodecene 91.8% with the selectivity to 2-dodecylbenzene 38.0% was obtained when the molar ratio of the ionic liquid $[bmim]^+Al_2Cl_6Br^-$ to 1-dodecene was as low as 0.005 under the mild reaction condition. The reuse of the ionic liquid was examined. The main cause of the deactivation was the loss of the highly Lewis acidic species $Al_2Cl_6Br^-$.

Keywords: Alkylation; Ionic liquids; Lewis acidity; Molecular polarizability; FT-IR; Acetonitrile; Carbenium ions

1. Introduction

Friedel-Crafts alkylation of benzene with long-chain alkenes is of great importance for the synthesis of linear alkylbenzenes (LABs), which are widely used raw materials in the production of detergents [1]. Among all the kinds of alkylbenzenes, 2-alkylbenzene is preferred because it yields detergents of better emulsibility and biodegradability for several applications [2].

However, the current manufacture of LABs uses highly corrosive and potentially lethal acids, such as aluminium trichloride ($AlCl_3$) and hydrofluoric acid (HF), both of which are not easily recovered without the release of environmentally unfriendly effluents. On account of the detrimental effects of these catalysts, great efforts directed toward the development of environmentally friendly catalysts have been made. Solid acid catalysts involving zeolites [3–6], clays [7], heteropoly acids [8] and fluorided silica–alumina [9] have been widely investigated. The disadvantage of the solid catalysts is that they are easily deactivated because of the accumulation of heavy products in the channels and reactive sites in the catalysts.

In recent years, room temperature ionic liquids have attracted much interest as relatively clean catalysts and alternative solvents that possess important attributes, such as negligible vapor pressure, excellent chemical and thermal stability, potential recoverability and ease of separation of products from reactants [10]. Many organic reactions, such as those involving alkylation, hydrogenation, epoxidation or Diels-Alder, have been performed in room temperature ionic liquids with excellent yields and selectivity [11]. Highly Lewis acidic chloroaluminate ionic

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liquids are well known to be both versatile solvents and effective catalysts, e.g., for Friedel-Crafts reactions. It is worth noting that they have interesting tunable physical and chemical properties that depend on the organic cations and inorganic anions employed [12]. As for 1-alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids, the Lewis acidity and molecular polarizability, which play dominating roles in alkylation reactions, can be varied by different alkyl groups and halogens [13]. Moreover, the ratio of aluminum chloride to organic bases greatly affects the Lewis acidity of ionic liquids through the anion equilibrium (chloride is an example) expressed in Eq. (1) [14]:

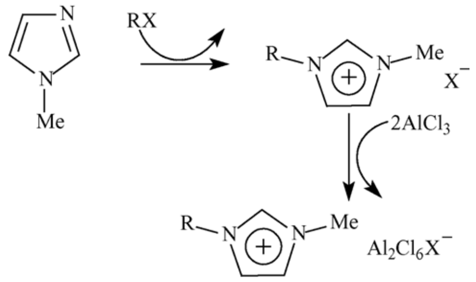
$$2\mathrm{AlCl}_4^- \rightleftharpoons \mathrm{Al}_2\mathrm{Cl}_7^- + \mathrm{Cl}^-, \quad K \approx 10^{-16.3} \qquad (1)$$

Smirniotis and co-workers [13] had studied the alkylation of isobutene with 2-butene using pure ionic liquids 1-alkyl-3-methylimidazolium halide-aluminum chloride as catalysts. They found that $[\mathrm{C_8mim}]\mathrm{Br}\text{-}\mathrm{AlCl_3}$ ($N = 0.58$, defined as the molar ratio of $\mathrm{AlCl_3}/(\mathrm{AlCl_3} + [\mathrm{Rmim}]\mathrm{X})$ displayed higher activity, which was attributed to its higher inherent Lewis acidity and to the greater solubility of the reactants. However, the alkylation of benzene with 1-dodecene had not been systematically studied in ionic liquids with the exception of a few studies in some pure ones, such as $[\mathrm{Et_3NH}]^+\mathrm{Al_2Cl_7}^-$ [15], $[\mathrm{bmim}]^+\mathrm{HSO_4}^-$ [16], $[\mathrm{emim}]^+\mathrm{Al_2Cl_7}^-$ modified by hydrogen chloride [17] and $[\mathrm{bmim}]^+\mathrm{Al_2Cl_7}^-$ [18], none of which represent the real catalytic properties of ionic liquids. In addition, the characterization of the Lewis acidity and molecular polarizability of the ionic liquids, which can help us further understand the behavior of ionic liquids in related catalytic reactions, had received little attention [19,20].

In this study, 1-alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids $[\mathrm{Rmim}]^+\mathrm{Al_2Cl_6X}^-$ (R = butyl, octyl and dodecyl; X = chlorine, bromine and iodine) were prepared and investigated for the alkylation of benzene with 1-dodecene. Acetonitrile was used as an IR spectroscopic probe to detect the Lewis acidity of the ionic liquids. Moreover, the molecular polarizability of ionic liquids was qualitatively measured through their solvent effects on the wavenumber of the benzene ring vibrations, as reflected in the IR spectra. The effects of varying reaction conditions on the synthesis of dodecylbenzene in the selected ionic liquids were extensively studied. Finally, a possible reason for the deactivation of the ionic liquid in the alkylation was discussed.

2. Experimental

All the experiments involving the preparation of ionic liquids, the FT-IR characterizations and the catalytic reactions were performed under an environment of highly purified nitrogen.



Scheme 1. Typical procedure of ionic liquids preparation.

2.1. Preparation of ionic liquids

N-Methylimidazole was obtained from the Aldrich Chemical Co. and was vacuum distilled from barium oxide (BaO) before use. Alkyl halides were of Chemical Grade from Shanghai Reagent Company (Shanghai, China) and were used as such. Anhydrous aluminum chloride was obtained from Beijing Chemical Regents Institute (Beijing, China) and was used without further purification.

The precursors and the chloroaluminate ionic liquids were synthesized according to the literature [21–23]. The typical procedure is illustrated in Scheme 1 and the ionic liquids employed in this study are listed in Table 1.

2.2. FT-IR characterization of ionic liquids

IR spectra were obtained on a Nicolet Magna-IR 750 spectrometer equipped with a MCT (B) liquid nitrogen cooled detector, by collecting 100 scans at a resolution of 1 cm^{-1} to investigate the Lewis acidity and the molecular polarizability of the ionic liquids. All spectra were manipulated by Nicolet OMNIC 5.2 Software. Analytic purity acetonitrile, obtained from Aldrich Chemical Co., was refluxed over $\mathrm{P_2O_5}$ and then distilled under the protection of highly purified nitrogen. Chloroform and benzene were chemical purity gradematerials obtained from Beijing Chemical Reagent Institute (Beijing, China), and were highly purified through standard methods before use [24].

IR samples for the Lewis acidity characterization were prepared by mixing acetonitrile and ionic liquids in the

Table 1
Ionic liquids employed in this study

Ionic liquid	Alkyl	Halogen	Anion molar composition N	ρ (g/mL)[a]
$[\mathrm{bmim}]^+\mathrm{Al_2Cl_7}^-$	Butyl	Chlorine	0.67	1.50
$[\mathrm{bmim}]\mathrm{Br}\text{-}\mathrm{AlCl_3}$	Butyl	Bromine	0.71	1.62
$[\mathrm{bmim}]^+\mathrm{Al_2Cl_6Br}^-$	Butyl	Bromine	0.67	1.58
$[\mathrm{bmim}]\mathrm{Br}\text{-}\mathrm{AlCl_3}$	Butyl	Bromine	0.60	1.49
$[\mathrm{bmim}]\mathrm{Br}\text{-}\mathrm{AlCl_3}$	Butyl	Bromine	0.55	1.32
$[\mathrm{bmim}]\mathrm{Br}\text{-}\mathrm{AlCl_3}$	Butyl	Bromine	0.50	1.23
$[\mathrm{bmim}]^+\mathrm{Al_2Cl_6I}^-$	Butyl	Iodine	0.67	1.62
$[\mathrm{omim}]^+\mathrm{Al_2Cl_6Br}^-$	Octyl	Bromine	0.67	1.41
$[\mathrm{dmim}]^+\mathrm{Al_2Cl_6Br}^-$	Dodecyl	Bromine	0.67	1.36

[a] The density of the ionic liquids was measured using a pycnometer.