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Preparation of high energy fuel JP-10 by acidity-adjustable chloroaluminate ionic liquid catalyst

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ABSTRACT

The isomerization of *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) to its *exo*-isomer (JP-10) has been investigated by using chloroaluminate ionic liquids (ILs) as catalysts. The catalyst activity and selectivity could be optimized by varying the mole fraction of $AlCl_3$ in the IL. Undesirable by-products derived from side-reactions such as skeletal rearrangement, alkylation, cracking, and dimerization could be minimized by appropriate catalyst design and adjustment of the reaction conditions. The catalyst system was further optimized by selecting 1-butyl-3-methylimidazolium chloride as the basic IL and adding 0.60–0.65 mole fraction of $AlCl_3$ as the promoter. Using the optimized catalyst system, the isomerization of *endo*-THDCPD to exo-THDCPD proceeded at a fast rate at 50 °C with 98.9% conversion and 100% selectivity. The catalyst longevity has been demonstrated by recycling the IL several times without a noticeable reduction in catalytic activity.

1. Introduction

Ionic liquids (ILs), defined as salts with melting point below 100 °C, are attractive for both industrial and academic research because of their unique chemical and physical properties. ILs have been used as catalysts, solvents, extractants, adsorbents, electrolytes, acid scavengers, and performance additives [1] by virtue of their unique properties, namely low vapor pressure, good solvation of a wide range of organic/inorganic chemicals, adjustable hydrophilic/lipophilic solvating properties, high charge density [1]. ILs are commonly used as environmentally benign catalysts and solvents in the syntheses of both organic and inorganic compounds, and biomaterials. Improved reaction processes characterized by high activity, high selectivity, and low vapor pressure can be developed.

Since their early development in the 1960s, chloroaluminate ILs have been broadly accepted as replacements for conventional Lewis acid catalysts for many different applications [1–4]. Although $AlCl_3$ is widely used in industry, it suffers from several drawbacks. For instance, it is not recyclable after the reaction. It must be hydrolyzed in a stoichiometric manner by adding aqueous sodium hydroxide before one can proceed with product separation. The hydrolyzed by-products stream is corrosive and not only causes environmental disposal problems, but also complicates the selection of processing equipment. It is therefore advantageous to develop improved and readily recyclable IL analogues such as chloroaluminate ILs for substituting the conventional $AlCl_3$.

In general, reacting $AlCl_3$ with a quaternary ammonium chloride salt may lead to the formation of quaternary ammonium chloroaluminate ILs. Depending on the mole fraction of $AlCl_3$, the equilibrium mixture may consist of multinuclear chloroaluminate anions. When the mole fraction of $AlCl_3$ is higher than 0.5, $[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$, and $AlCl_3$ are present in the equilibrium mixture [4]. The activity of the acidic IL catalyst may be adjusted by varying the mole fraction of $AlCl_3$, has been demonstrated in the alkylation of isobutane with 2-butene [5]. The conversion of isobutane and the product distribution have been shown to depend on the mole fraction of $AlCl_3$ in the IL catalyst [5]. This new degree of freedom in adjusting the level of $AlCl_3$ and consequently the Lewis acidity of the IL catalyst offered a possible means of optimizing the reaction rate, the product, and the yield.

Abbreviations: ADM, Adamantane; BMIB, 1-butyl-3-methylimidazolium bromide; BMIC, 1-butyl-3-methylimidazolium chloride; BMPC, 1-butyl-4-methyl pyridinium chloride; DCPD, dicyclopentadiene; HMIC, 1-hexyl-3-methylimidazolium chloride; HDMIC, 1-hexadecyl-3-methylimidazolium chloride; IL, ionic liquid; JP-10, Jet Propellant-10; OMIC, 1-octyl-3-methylimidazolium chloride; PHB, pyridine hydrobromide; PHC, pyridine hydrochloride; TEAC, triethylamine hydrochloride; THDCPD, tetrahydrodicyclopentadiene.

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exo-THDCPD is a valuable industrial product useful for high energy density fuels, especially for short-range missiles and aircraft, as well as for other industrial applications, for example as a solvent for paints and as a diluent for surfactants, waxes and washing agents for semiconductors, lubricating oils [6]. *exo*-THDCPD is derived from the corresponding *endo*-isomer, which in turn is derived from the hydrogenation of dicyclopentadiene isolated from a C5 stream cracker. For fuel applications such as Jet Propellant-10 (JP-10), *exo*-THDCPD of purity higher than 98.5% is required. Hence, the isomerization of *endo*-THDCPD with a high selectivity is advantageous because of the low contamination with the high freezing-point *endo*-isomer and adamantane (ADM) by-product.

Conventionally, a sulfuric acid catalyzed process has been used for the conversion of the *endo*-isomer of THDCPD to the *exo*-isomer [7]. However, this sulfuric acid catalyzed process lacks selectivity. In addition to *exo*-THDCPD, by-products such as decalin and ADM are also produced. Since the 1960s, $AlCl_3$ has been the preferred catalyst for this isomerization [8–11]. But the low selectivity in favor of the *exo*-isomer and the formation of undesirable by-products remained unsatisfactory. In several patent disclosures, the production of *exo*-THDCPD by using $AlCl_3$ in conjunction with various solvents and co-catalysts has been described [12–14]. Although these approaches offered better selectivity and yield, product separation and waste disposal remained problematic. Recent developments concerning the use of zeolites [6,15] or heteropolyacids [16,17] in place of $AlCl_3$ have resolved some of the processing problems. However, the use of HY zeolites and heteropolyacids as catalysts requires high processing temperatures of 195 °C and 185 °C, respectively. Such high temperatures can lead to the formation of by-products such as ADM, heavier by-products, and coke. The formation of ADM complicates *exo*-THDCPD purification. The formation of coke diminishes the catalyst life. These outcomes have prompted our quest for the development of a recyclable and selective catalyst.

Herein we report the development of an improved catalyst for the commercial production of *exo*-THDCPD (JP-10). The approach involves the modification of ILs to generate an active and selective catalyst composition. Various types of ILs and variation of the process conditions such as reaction temperature and catalyst/feed ratio have been investigated with regard to optimization of the conversion and selectivity in the isomerization of *endo*-THDCPD to *exo*-THDCPD.

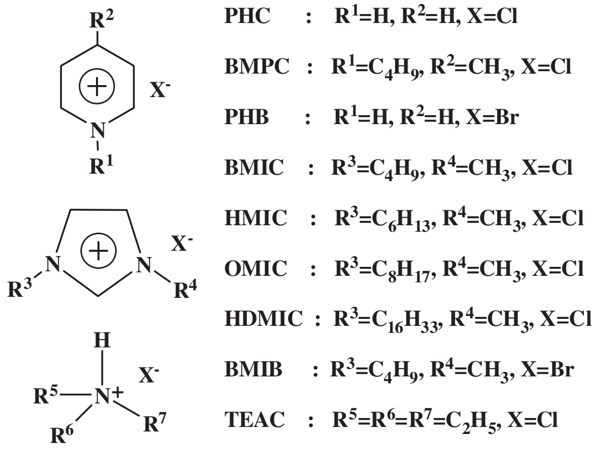
2. Experimental

2.1. Materials

Various quaternary ammonium halides (Fig. 1), including pyridine hydrochloride (PHC), 1-butyl-4-methyl pyridinium chloride (BMPC), pyridine hydrobromide (PHB), 1-butyl-3-methylimidazolium chloride (BMIC), 1-hexyl-3-methylimidazolium chloride (HMIC), 1-octyl-3-methylimidazolium chloride (OMIC), 1-butyl-3-methylimidazolium bromide (BMIB), and triethylamine hydrochloride (TEAC), were purchased from Fluka Chemicals. 1-Hexadecyl-3-methylimidazolium chloride (HDMIC) and $AlCl_3$ were purchased from Merck Chemicals. *endo*-Tetrahydrodicyclopentadiene (*endo*-THDCPD) was purchased from Tokyo Kasei Kogyo. Molecular sieves (3A) were purchased from Peak Scientific and were dried at 120 °C and 0.5 Torr for 3 h before use. The feedstock, *endo*-THDCPD solution, was prepared by dissolving solid *endo*-THDCPD in heptane at a 1:1 weight ratio and drying over molecular sieves at room temperature overnight.

2.2. Preparation of acidic chloroaluminate ILs

Acidic chloroaluminate ILs were prepared and handled under a nitrogen atmosphere. In a dry, nitrogen-filled glove box, the quaternary ammonium halide was placed in a two-necked, round-bottomed flask fitted with a magnetic stirring bar. A measured amount of $AlCl_3$ was slowly added at room temperature with stirring. When all of the $AlCl_3$ had been added, the reaction mixture was stirred for an additional 5 min to complete the formation of the acidic chloroaluminate IL catalyst.



PHC : R^1=H, R^2=H, X=Cl
BMPC : $R^1=C_4H_9$, $R^2=CH_3$, X=Cl
PHB : R^1=H, R^2=H, X=Br
BMIC : $R^3=C_4H_9$, $R^4=CH_3$, X=Cl
HMIC : $R^3=C_6H_{13}$, $R^4=CH_3$, X=Cl
OMIC : $R^3=C_8H_{17}$, $R^4=CH_3$, X=Cl
HDMIC : $R^3=C_{16}H_{33}$, $R^4=CH_3$, X=Cl
BMIB : $R^3=C_4H_9$, $R^4=CH_3$, X=Br
TEAC : $R^5=R^6=R^7=C_2H_5$, X=Cl

Fig. 1. Structures of the quaternary ammonium halides investigated in this study.

2.3. Isomerization of endo-THDCPD by chloroaluminate ILs

Isomerization using the chloroaluminate IL catalysts was conducted as follows. The prepared catalyst in the reaction flask was first removed from the glove box. The reactor was fitted with a condenser, a syringe septum, and an inlet for nitrogen flow to maintain an inert atmosphere. A measured amount of *endo*-THDCPD in heptane (1:1 weight ratio) was added by means of a syringe. For sampling, stirring of the reaction mixture was stopped for 2 min to allow phase separation of the organic layer and the IL catalyst. Samples of 0.5 mL were withdrawn from the upper organic phase using a syringe at designated intervals and analyzed by gas chromatography.

The recyclability of the chloroaluminate IL catalyst was assessed by withdrawing the upper organic phase from one run by means of a syringe and then recharging with fresh feed. The progress of the reaction with the reused IL was followed by sampling and analytical procedures similar to those used for the original reaction.

2.4. Analytical methods

Reaction mixtures were qualitatively analyzed on a HP6890/5973 inert GC/MS equipped with a Frontier Ultra ALLOY-5 column (30 m × 0.25 mm, 0.25 μm). Reaction products were quantitatively determined on a HP6890 GC equipped with an automatic injector (HP7683), a capillary column (Chrompack CP-Sil 5CB, 30 m × 0.32 mm, 5 μm), and a flame ionization detector. No pre-treatment was necessary for the homogeneous samples. The ratio of GC response factors (peak area divided by the substance weight) for *endo*-THDCPD/*exo*-THDCPD/ADM was 1.00:1.00:1.06. It was assumed that the GC response factors for the other minor by-products were the same as that for *endo*-THDCPD. Since the minor components were only present at very low levels in all cases, this assumption has no material effect on the analytical result. The conversion and selectivity were calculated from the results of the GC analyses. FT-IR spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier-transform infrared spectrophotometer. Conditions for