

Production of alkylated gasoline using ionic liquids and immobilized ionic liquids

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Abstract

Ionic liquids (ILs) and immobilized ionic liquids were used as acid catalysts for the liquid phase alkylation of raffinate II and isobutane. The influences of reactant concentration (molar ratio of $iC_4/C_4^{=}$), time, temperature and acid strength of the ionic liquids were studied. Using a step-up design under batch conditions with a very dilute mixture of isobutane and alkene, the conversion for a variety of ionic liquids was found to follow a pattern based on acid strength of the catalyst. Imidazolium based ILs were found to be superior to phosphonium based ILs. Novel Lewis-Acid Catalysts II (NLAC II, immobilization by grafting on siliceous MCM 41 or on silica FK 700) are better than other solid acid catalysts tested, such as SAC 13, zeolite H-Beta (Si/Al = 14) and NLAC I (impregnation of ILs on silica FK 700). Possible leaching of the ionic liquid from the catalyst surface was followed by ICP measurements of the catalyst after reaction and of the reaction mixture.

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1. Introduction

Currently, there is a general trend to develop a clean and eco-efficient catalytic processes which minimize the generation of unwanted and harmful waste. In this context heterogeneous acidic catalysts, either prepared from or based on the example of Lewis-acid ionic liquids offer new possibilities and challenges. The use of ionic liquids (ILs) as alternative catalytic systems is based on their tunable properties [1–3]. Depending on the organic cation and inorganic anion the ILs can have very different physical and chemical properties. Ionic liquids show Lewis acidity when a Lewis acid (e.g., $AlCl_3$), which forms the counter-anion, is used in excess. The organic cation determines solubility, density and viscosity of the liquids. By using the Lewis-acidic ionic liquids immobilized on solid supports, we introduced a new kind of catalysts called “Novel Lewis-Acid Catalyst” (NLACs) whose experimental results obtained by our group during the past years are well documented in the literatures [4–10]. Very similar

approach was also reported on various supported ionic liquids compositions [11].

One of the most important reactions in the petroleum industry is the butene alkylation of isobutane for the production of iso-octane/alkylated gasoline. At present this process is industrially carried out using sulfuric or hydrofluoric acid [12–14]. A variety of solid catalytic materials, starting from zeolites to Bronsted and Lewis acids on various supports, heteropolyacids and organic resins, both supported and unsupported, have been examined as alternatives [15–22]. However, so far no process utilizing a solid acid is operative on industrial scale, although some companies offer their developed processes for licensing [14,15].

Very recently, studies on ionic liquid-catalyzed alkylation of isobutane with 2-butene have been reported [23–26]. However, these materials are limited to either the use of supports impregnated with pre-formed ionic liquids as catalysts [25,26] or just plain imidazolium based chloroaluminates species [23,24]. A few examples of alkylation of aromatics with alkene such as Friedel–Crafts reaction using immobilized ionic liquids can be found in literature, too [27]. However, to the best of our knowledge there is no study about isobutane alkylation using immobilized ionic liquids of the NLACs type as catalysts. The immobilization of ILs results in acid catalysts containing ionic

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complexes in which either anion or cation is bonded covalently to a solid support [11,27].

Now for the first time we are reporting activity tests of ILs and NLACs as catalysts using a reaction mixture of pure isobutane and an industrially obtained raffinate II. This raffinate II is the remaining C4-cut of the steam cracker effluent after removal of butadienes/isobutene and propane/propene and has been used as a source of alkenes. Recently, the use of raffinate II as an alkene source for isobutane alkylation has been explored [22]. The industrial raffinate II used in our experiments was of following composition (wt.%): propane 0.9, isobutane/isobutylene 31.2, 1-butene 10.6, *n*-butane 14.7, 2-butene (*trans*) 26.9, 2-butene (*cis*) 15.3 and isopentane 0.5. Based on this the molar ratio of isobutane to total butene present in raffinate II is 0.57.

2. Experimental

2.1. Catalyst preparation and analytical methods

All experiments were carried out under inert atmosphere, in order to ensure that the reaction could be carried out free of any water. The silica support materials were calcined at 823 K for 3 h, and then stored under argon. The 1-methyl-3-butyl imidazolium chloride ([bmim]Cl), 1-methyl-imidazole and trihexyl (tetradecyl) phosphonium chloride used for the preparation of the ionic liquids were kindly provided by Elementis Specialists, Durham, UK. The silica support, FK 700, was kindly provided by Degussa AG. The all silica MCM-41 was prepared in our laboratory following the literature procedure [28].

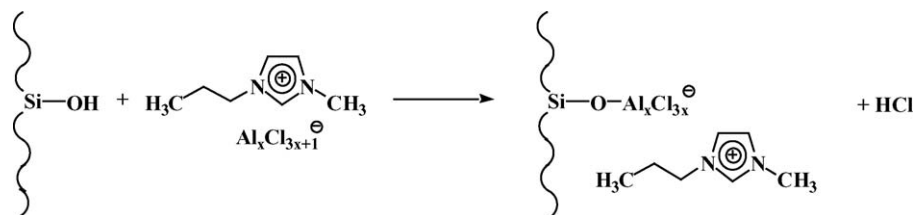
The pure AlCl_3 based ionic liquids were prepared by slow addition of the desired amount of aluminum (III) chloride to the ([bmim]Cl). The reaction mixture was stirred at 0 °C over night, in order to allow a complete homogenization of the resulting ionic liquid. The ionic liquids, once prepared, could be stored for weeks in an inert atmosphere before the impregnation, if required.

The ionic liquid based on trihexyl (tetradecyl) phosphonium chloride and aluminum (III) chloride ($\text{C}_{32}\text{H}_{68}\text{P}^+\text{AlCl}_4^-$) was also prepared at 60 °C. In this case, the temperature was raised to obtain a homogeneous mixture. A variety of ionic liquids based on bmim/phosphonium and aluminum chloride with different *N* ($\text{AlCl}_3/(\text{AlCl}_3 + \text{bmim}$ or phosphonium)) were

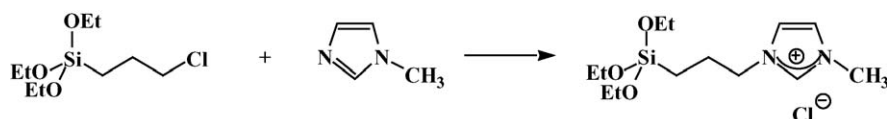
prepared. The catalytically most active materials are the acidic ionic liquids with *N* = 0.55–0.67.

The immobilization technique was followed as developed in our laboratory [4–9]. NLAC I was prepared by using incipient wetness impregnation techniques using silica (FK 700) and [bmim]Cl followed by Soxhlet extraction. In this approach the IL is immobilized via the covalent bonds between the IL's anion and silanol groups on the surface (Scheme 1). NLAC II (using siliceous MCM-41 as support), on the other hand, is prepared by grafting a new organic molecule, 1-(3-triethoxysilyl)-propyl-3-methylimidazolium chloride (Si[pmim]Cl) on to the surface of the support. Si[pmim]Cl was synthesized using 1-methylimidazole (1 mmol) and 3-(chloropropyl)-triethoxysilane (1 mmol, Aldrich) after refluxing at 363 K for 2 h followed by extraction with diethyl ether (Scheme 2). After the grafting step, the imidazolium ring will be separated from the surface of the support by a propyl chain, allowing a certain flexibility of the organic groups. The grafting step itself was performed under anhydrous conditions in toluene. For example, in a distillation apparatus 10 g of support material (Si-MCM-41) was dispersed in dried toluene. After the addition of 6 g of Si[pmim]Cl the mixture was stirred at 363 K for 16 h. In the following step, solvent and ethanol created in the grafting step were distilled off. The remaining solid was dried under vacuum and the excess of 1-(3-triethoxysilyl)-propyl-3-methylimidazolium removed by extraction with boiling dichloromethane. The dried support was then added to a solution of 7 g aluminum (III) chloride in toluene and left stirring for 3 h at room temperature. After filtration, the excess of aluminum (III) chloride was removed by extraction with boiling CH_2Cl_2 in a Soxhlet apparatus and the material obtained was dried under vacuum and stored in argon (Scheme 3).

The concentration of Al and Si in the samples was determined by ICP–AES, using a Spectro-Flame D machine from Spectro. CHN analysis was performed on an Elementar Vario EL. The solid catalysts were also characterized for BET surface area and pore volume (Micromeritics ASAP 2010). Prior to the measurement the samples were degassed at 120 °C under high vacuum for 2 h. The immobilized ionic liquids thus obtained were of good quality and reproducible (Table 1). Based on the elemental analyses, the amount of ionic liquid



Scheme 1. Preparation of NLAC I.



Scheme 2. Preparation of 1-(3-triethoxysilyl)-propyl-3-methylimidazolium chloride (Si[pmim]Cl).

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