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Highly efficient trimerization of isobutene over silica supported chloroaluminate ionic liquid using C4 feed

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ABSTRACT

A series of silica, glass and molecular sieves supported chloroaluminate ionic liquids (ILs) were prepared and their catalytic performance on the trimerization of isobutene based on C4 mixture was investigated. Interestingly, it was found that the carrier played a key role in the reaction route. Among these supported catalysts, silica supported chloroaluminate ionic liquid was highly efficient for the trimerization of isobutene. X-ray photoelectron spectroscopy (XPS) and differential scanning calorimetry (DSC) characterizations suggested that the synergy between $Al_2Cl_7^-$ anion and silica induced the catalytic activity for isobutene oligomerization due to the strong interaction between ILs and silanol group. The reaction conditions including loading amount, temperature, reactant concentration, and space velocity for the isobutene oligomerization were optimized. Ultimately, complete conversion of isobutene and 91.4% selectivity of trimers were obtained over the IL/silica (30 wt.%) catalyst at mild conditions. Moreover, catalyst stability and deactivation were preliminarily studied.

1. Introduction

C4 fractions (mainly C4-olefins and C4-isoparaffins) as by-products formed from the fluid catalytic cracking (FCC) process, are important raw materials in the petrochemical industry, because they could be further utilized to produce useful nonaromatic higher hydrocarbons via isobutane/butene alkylation [1,2] and olefins oligomerization processes [3–5]. In recent years, growing attention has been paid to oligomerization, especially on isobutene trimerization, because it is a very promising process for the production of isobutene trimers and for the separation of isobutene from C4 mixtures [6]. Trimers of isobutene namely triisobutenes are considered as ideal starting materials for the synthesis of neo-acid compounds after carboxylation with carbon dioxide [7,8]. Moreover, the trimers are also used to produce epoxy resin solidifying agents, dodecylbenzene, antirusts, lubricants, and gas oil additives [9,10]. Since 2004, due to legal restrictions on the use of oxygenated gasoline additives such as methyl-tert-butyl ether (MTBE), a surplus of isobutene has been expected, as it is the main raw material for MTBE synthesis [11,12]. In this context, isobutene oligomerization attracted considerable interest in the petrochemical industry. At present, the isobutene oligomerization is mainly conducted over solid acid catalysts, such as cation exchange resins [13], zeolite [14] and sulfated titania [9], but the main challenge for this reaction still is the development of catalysts with high conversion and high selectivity [15].

In the past decade, it was widely accepted that ionic liquids (ILs) as alternative solvents for various organic syntheses and catalytic reactions showed strongly positive effects due to their particular physicochemical properties [16–18]. In previous reports, acidic ILs have been used to catalyze the oligomerization of butenes, and were proven very efficient for this process [15,19,20]. Chloroaluminate ILs as acidic catalysts were widely investigated as high-efficiency catalysts in catalytic reactions because of the strong Lewis acidity of the anions and their interesting tunable acidity [21], which could also catalyze olefins oligomerization without the addition of transition metal complexes or salts [22]. Recently, the concept of immobilization of catalytic ILs on porous supports has been established because it provides a very attractive way to bridge the gap between homogeneous and heterogeneous catalysis [23]. The supported ionic liquid catalyst (SILC) systems have been successfully applied in different catalytic processes, such as hydrogenations [24], alkylations [25], and carbonylations [26]. The SILCs systems could effectively accelerate reaction rate, and enhance reactivity and the selectivity [27]. Additionally, due to the extremely low vapor pressure of ILs, SILCs can be used in continuous gas-phase reactions using the classical fixed-bed reactor technology, which could avoid the problems on solvent handling, solvent/product separation, and solvent purification [28].

Although a few examples of alkylation reaction using immobilized ILs as catalysts have been studied in previous literature, such as alkylation of aromatics and isobutene [25,29], to the best

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of our knowledge, no studies on isobutene trimerization over silica supported chloroaluminate ILs have been reported. In this work, we investigated the performance of those catalysts for isobutene trimerization using industrially obtained C4 fraction as feed. Isobutene oligomerization could be successfully carried out over this simple, convenient catalytic system. Thus, it is an efficient strategy not only for the industrial application of isobutene, but also for the separation of isobutene from the C4 mixture. Meanwhile, the process of isobutene trimerization was operated in a typical continuous gas-phase operation using the classical fixed-bed reactor technology at mild conditions, which is helpful in product separation after the reactions. It is interesting that the isobutene oligomerization was carried out on those catalytic systems, whose supports contain silanol group (Si–OH) on the surface, even though abundant isobutane was present in the raw material. However, when the chloroaluminate ILs were supported on other supports such as glass and activated carbon, the reaction pathway switched to isobutane/butene alkylation. Furthermore, the conditions for the catalytic synthesis of isobutene trimers (such as the reaction time, temperature, concentration, and space velocity) were optimized and the stability of the SILCs was also investigated in this work.

2. Experimental

All manipulations of the acidic catalyst systems and handling of the reactants prior to reaction were carried out under strictly inert conditions in a glove box ($H_2O < 0.5$ ppm, $O_2 < 1$ ppm).

2.1. Chemicals and catalyst preparations

All chemicals used in the experiments were analytical grade without further purification. Dichloromethane and other reactants were dehydrated by 4 Å molecular sieves (MS) before use. The C4 feed received from the China National Petroleum Corporation (Lanzhou) was used as the butene source. The composition of C4 feed was confirmed by an HP 6890/5973 gas chromatography mass spectrometer (GC–MS): propane (0.5 wt.%), n-butane (8.0 wt.%), isobutane (45.9 wt.%), isobutene (27.5 wt.%), 1-butene (7.3 wt.%) and 2-butene (*trans* and *cis*, 10.8 wt.%). Isobutane (Kodi, 99%) was used as dilute gas.

The acidic chloroaluminate ILs were prepared by mixing a defined molar ratio of $AlCl_3$ and 1-butyl-3-methylimidazolium chloride (BMImCl) at 70 °C until complete dissolution of $AlCl_3$ and a clear liquid was observed. Silica (80–100 mesh, surface area = 600 m^2/g, pore volume = 0.74 cm^3/g, average pore diameter = 4.93 nm) were calcined at 500 °C for 5 h, and then stored in a glove box. The glass (80–100 mesh) and activated carbon (50–80 mesh, surface area ≥ 900 m^2/g) were dried at 200 °C for 5 h, and the MCM-41 MS (surface area ≥ 800 m^2/g, pore volume ≥ 0.7 cm^3/g, average pore diameter = 3.5 nm) and SBA-15 MS (surface area ≥ 650 m^2/g, average pore diameter = 8 nm) were calcined at 500 °C for 5 h before use. The preparation of catalyst (SILG) made by covalent bond grafting method was according to Ref. [25]. The acidic SILCs were prepared by a wet impregnation on the different pretreated supports with chloroaluminate IL. Typically, dichloromethane was used to dilute the acidic IL during the wet impregnation process. Homogeneous penetration of the catalyst into the pores was ensured through rigorous stirring at 500 rpm for 2 h, and then the solvent was removed by vacuum (10^{-2} to 10^{-3} mbar, 60 °C, 3 h). The dry SILCs obtained were stored in a glove box atmosphere prior to use. The actual concentration of the IL in the silica supported catalysts was measured by analyzing the Al content via inductively coupled plasma atomic emission spectrometry (ICP-AES). The calculated and experimental values were compared in Table 1, and the relative errors between the calculated values and the measured values were less than 5%.

Table 1
Content of Al determined by ICP-AES.

Catalyst[a]	Al content (wt.%)	
	Calculated	Experimental
IL/silica (10 wt.%)	1.22	1.26
IL/silica (20 wt.%)	2.45	2.57
IL/silica (30 wt.%)	3.67	3.79
Pure IL	12.23	12.81

[a] IL:BMImCl/$AlCl_3$ = 1/2.

2.2. Catalysts characterization

The phase transitions of catalysts were performed with a Mettler-Toledo DSC822e calorimeter and calibrated using indium and zinc. The DSC data were evaluated using the Mettler-Toledo STARe software version 7.01. The samples (10–20 mg) were sealed in a 40 μL aluminum pan using an empty pan as reference. DSC traces were typically scanned from −120 to 200 °C at a speed of 10 °C min^{-1}, and then followed by a cooling process at the same speed.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB 210 instrument with Mg-Kα source (1253.6 eV) and calibrated vs. the C 1s peak at 285.0 eV. A thin IL layer and catalysts were deposited on a polycrystalline gold substrate.

Infrared (IR) analyses were performed at room temperature with a Thermo Nicolet 5700 Fourier transform IR (FTIR) spectrophotometer in the region from 400 to 4000 cm^{-1}. FTIR spectra of adsorbed pyridine (Py) were obtained from KBr plates prepared in an inert atmosphere. The samples adsorbed Py were prepared in the following method: the catalysts were placed in a vacuum desiccator with a Py reservoir, and the system was evacuated to generate a Py atmosphere inside; then the catalyst was kept in the Py environment at room temperature for 2 h. The catalyst was removed from the desiccator and placed under vacuum for at least 3 h to remove excess pyridine at 10^{-2} to 10^{-3} mbar and 70 °C.

The Al concentrations in the samples were determined by ICP-AES, using an IRIS Advantage ER/S machine. The ^{29}Si solid state cross-polarization and magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were recorded on a Bruker Avance II WB 400 spectrometer.

2.3. Reaction procedures

The continuous gas phase experiments were carried out at atmospheric pressure in a fixed bed reactor (8 mm in diameter and 10 cm in length). Catalyst (1 g) was placed into the reactor in a glove box, and the reactant containing isobutene was continuously fed using gas mass flow controllers (Seven Star D08-2D/M). Mass balance greater than 95% was used to calculate the conversion of butene and the selectivity of product. The conversion of butenes from the isobutene/feed mixture was monitored via an online GC equipped with a flame ionization detector (FID) (Agilent 6820, n-octane was used an internal standard) after a stabilization time of 1 h on stream. Qualitative analyses of products were examined by a HP 6890/5973 GC-MS, and quantitative analyses were carried out by a GC-FID (Agilent 6820). The detailed analysis conditions were described as follows: the injector and detector temperatures were 260 and 300 °C, respectively; the column temperature was increased stepwise to 260 °C, holding at 40 °C for 1 min, increasing to 60 °C at 2 °C min^{-1}, holding at 60 °C for 5 min, increasing to 150 °C at 1 °C min^{-1}, increasing to 200 °C at 2 °C min^{-1}, holding at 200 °C for 2 min, increasing to 260 °C at 2 °C min^{-1}, and holding at