



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.

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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 ($\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 1$ 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 m²/g, pore volume = 0.74 cm³/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 m²/g) were dried at 200 °C for 5 h, and the MCM-41 MS (surface area ≥ 800 m²/g, pore volume ≥ 0.7 cm³/g, average pore diameter = 3.5 nm) and SBA-15 MS (surface area ≥ 650 m²/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

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/AlCl₃ = 1/2.

compared in Table 1, and the relative errors between the calculated values and the measured values were less than 5%.

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 ²⁹Si 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 as 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

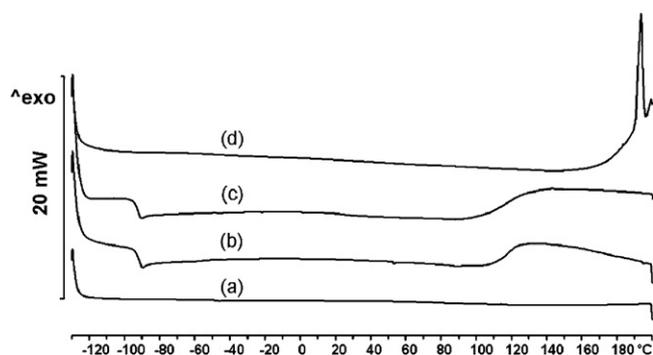


Fig. 1. DSC curves of the studied catalysts: (a) silica, (b) IL (BMImCl/AlCl₃ = 1/2), (c) IL/glass carrier (10 wt.%), and (d) IL/silica (10 wt.%).

260 °C for 10 min. Qualitative analysis was performed according to the holding time of the peak by the area normalization method [19]. In this study, the selectivity of dimers, trimers and tetramers was described in wt.%. The contribution of pentamers or higher oligomers was negligible in this work since their concentrations were less than 0.5 wt.%.

3. Results and discussion

3.1. Characterization of catalysts

Considering that the silica supports are available low-cost materials in comparison with other supports and the IL/silica catalysts have an active effect for isobutene oligomerization, therefore we mainly investigated the properties and performance of IL/silica catalysts hereinafter.

3.1.1. DSC analysis

The thermal behaviors of chloroaluminate ILs (BMImCl/AlCl₃ = 1/2) on different supports were analyzed and compared by DSC technique. As seen in Fig. 1, phase behavior was not detected for the isolate silica support at the range from -120 to 200 °C (curve a). And the chloroaluminate IL displayed a glass transition and thermal decomposition at -92 and 110 °C, respectively (curve b), in agreement with previous result [30]. After the IL was supported on a glass carrier, no obvious change was observed compared with the ILs in curve c, which suggested that ILs were physically absorbed on the carrier surface. If the support was replaced with the silica, however, the thermal properties of IL/silica (10 wt.%) significantly changed in comparison with the pure IL. No glass transition was obtained in curve d, suggesting that a strong chemical interaction took place between the support and ILs. Furthermore, the chemical interaction further enhanced the catalyst thermal stability up to 170 °C.

3.1.2. XPS characterization

The chemical state and surface composition of the chloroaluminate IL (BMImCl/AlCl₃ = 1/2) and the IL/silica catalyst (30 wt.%) were analyzed by XPS. Fig. 2a gave an overview scan of the catalyst. The survey spectrum showed that aluminum, silicon, chlorine, carbon, nitrogen and oxygen were detected at the surface of the catalyst, which included the main component elements of the IL and the support. Fig. 2b and c show the high resolution spectrum for Al 2p region on pure IL and IL/silica, and the binding energy for Al 2p were at 75.3 and 74.8 eV, respectively. The data indicated that the binding energy of the Al 2p in the catalyst decreased 0.5 eV compared with the pure IL, which could be due to the chemical environmental change, that is, the increase of corresponding electron density. As the ILs were immobilized on the supports, the Cl–Al bond rupture

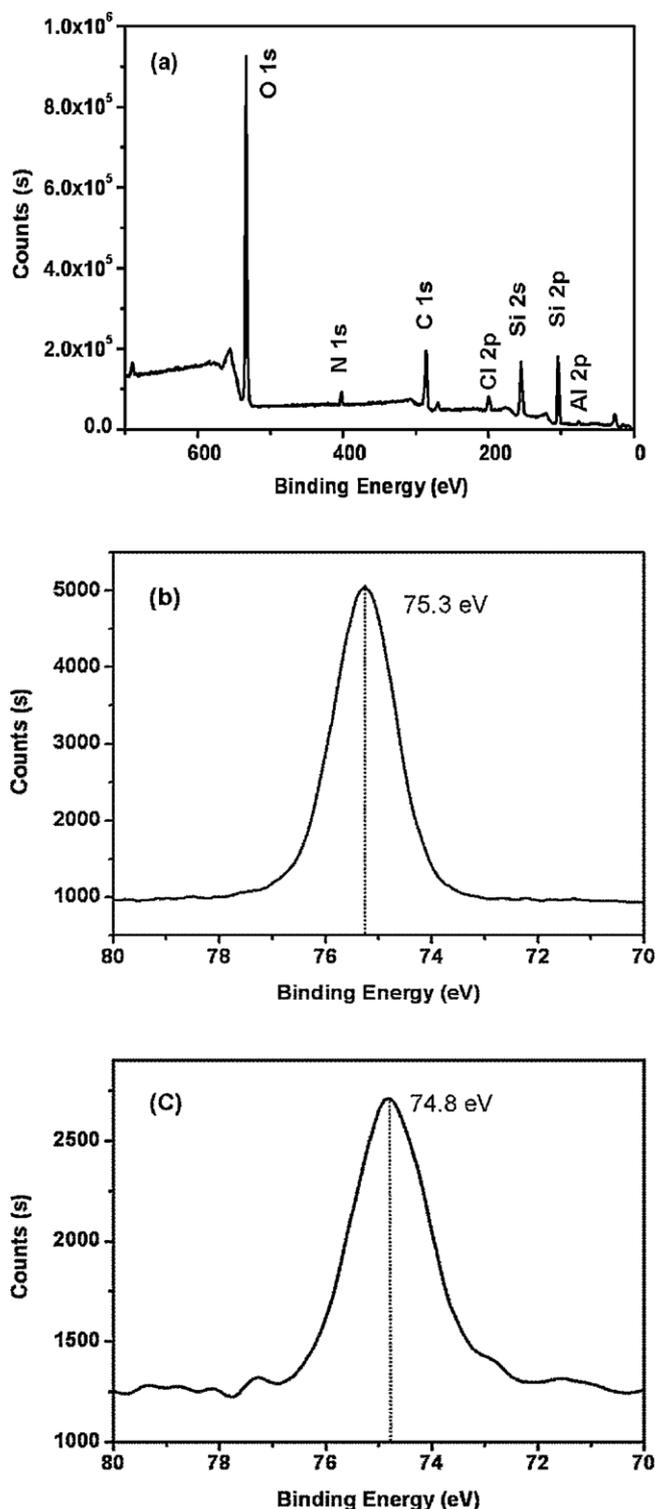


Fig. 2. XPS survey spectrum of (a) IL (BMImCl/AlCl₃ = 1/2)/silica (30 wt.%), (b) Al 2p region on pure IL, and (c) Al 2p region on IL/silica (30 wt.%).

and the O–Al bond formation led to the increased electron density [31]. In addition, the relative elemental concentrations at the sample surface could also be obtained from the XPS analysis results. For the catalyst IL/silica (30 wt.%), the value of atomic ratio of Cl:Al measured by XPS is 2.07, indicating that more O–Al bonds were formed on the catalyst surface [32].

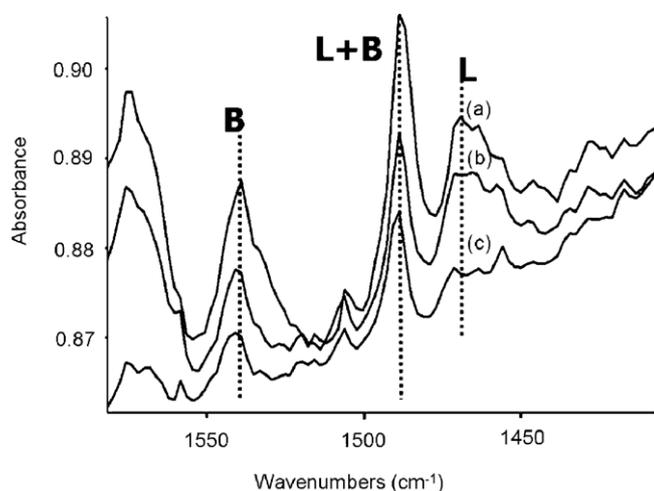


Fig. 3. Infrared spectrum of IL (BMImCl/AlCl₃ = 1/2)/silica catalysts with different load capacity after pyridine adsorption: (a) IL/silica (30 wt.%), (b) IL/silica (20 wt.%), and (c) IL/silica (10 wt.%).

3.1.3. Infrared examination

The Lewis and Brønsted acid sites could be analyzed using the FTIR spectrum of adsorbed pyridine [33], so Py-IR spectroscopy was employed to investigate the acidity nature of catalysts with different loadings (BMImCl/AlCl₃ = 1/2). As shown in Fig. 3, three evident absorptions could be detected on these catalysts at the range from 1550 to 1450 cm⁻¹. The IR peak at 1540 cm⁻¹ involved a C–N⁺–H bending vibration and was usually used as a fingerprint for the pyridinium ion, which was ascribed to the protonation of pyridine with Brønsted acid sites [33]. The IR peak at 1460 cm⁻¹ was attributed to the adsorption of pyridine coordinated on Lewis acid sites [34]. The peak at 1490 cm⁻¹ was associated to the vibration of the pyridinic ring on both Brønsted and Lewis acid sites and could not be used to distinguish between the two types of acid sites [35]. The IR absorptions indicated both Brønsted and Lewis acid sites existed on the surface of the catalysts. In addition, Fig. 3 shows that the concentration of both Lewis and Brønsted acid sites decreased as the order of (a) IL/silica (30%) > (b) IL/silica (20%) > (c) IL/silica (10%).

3.1.4. ²⁹Si CP/MAS NMR measurement

Solid-state ²⁹Si nuclear magnetic resonance (²⁹Si NMR) technique employing magic angle spinning (MAS) with cross polarization (CP) was used to characterize the prepared catalysts, which is a sensitive and reliable tool to provide useful structural information on the modified silica surface [36]. Fig. 4 shows the ²⁹Si CP/MAS NMR spectra for the supported catalysts prepared using different methods, together with the spectrum of amorphous silica as a comparison. Three peaks can be observed for the silica sample (Fig. 4a): the resonance peaks at –91, –101 and –110 ppm were assigned to the Q² ((SiO)₂–Si–(OH)₂), Q³ ((SiO)₃–Si–OH) and Q⁴ ((SiO)₄–Si) units of the silica particles, respectively [37]. After immobilized by impregnation method with IL (Fig. 4b), the signals at –91 and –101 ppm assigned to Q² and Q³ were strongly diminished and only a broadening of the peak assigned to Q⁴ could be detected, which indicated that covalent bonds between the Lewis acid anions and silanol groups on the surface of the support were formed in this catalyst (Scheme 1) [38]. As the silica was modified by grafting method (SILG, Fig. 4c), the disappearance of the Q² and Q³ signals and the retention of the Q⁴ signal were also observed. Furthermore, two additional peaks at about –56 and –65 ppm appeared in Fig. 4c, which could be ascribed to T¹ (SiO–SiR(OEt)₂) and T² ((SiO)₂–SiR–OEt), respectively. This proved that the grafting of the organic cation on to the surface has successfully taken place (Scheme 2) [29].

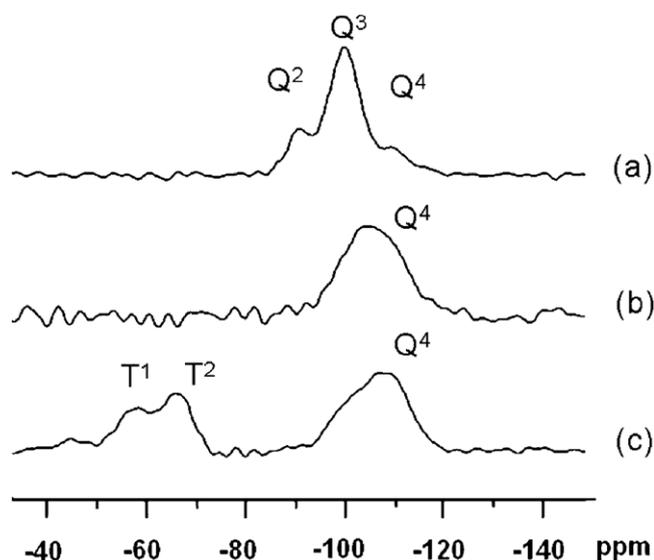
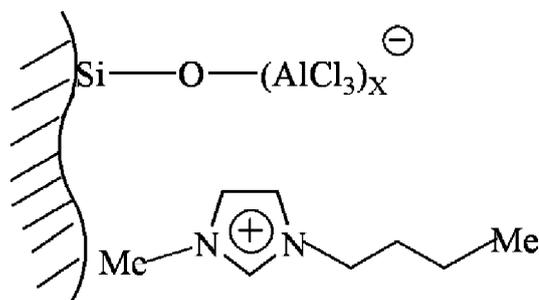


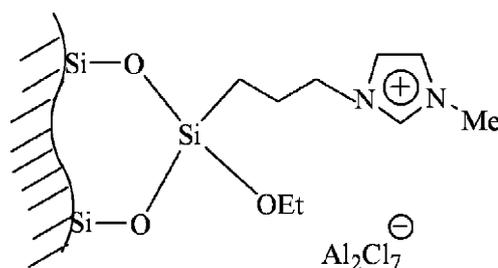
Fig. 4. ²⁹Si CP/MAS NMR spectra for the prepared catalysts and pure silica: (a) pure silica, (b) IL/silica (BMImCl/AlCl₃ = 1/2, 20 wt.%), and (c) SILG.



Scheme 1. The possible structure of immobilized IL on silica.

3.2. Different reaction routes over different supports

All the above prepared SILCs were subjected to the trimerization of using C4 feed to evaluate their catalytic performance. Interestingly, the choice of carrier significantly influenced the selection of the chemical reaction route under the same conditions. As can be seen in Table 2, similar to the case of pure ILs [1], both glass and activated carbon (AC) supported catalyst resulted in only alkanes (Entries 1 and 2), which originated from isobutane/butene alkylation (Scheme 3). However, for the silica supported catalyst, isobutene oligomerization (Scheme 4) was observed under the same experimental conditions, resulting in products of isobutene dimers, trimers and tetramers [39]. Based on the DSC results, the different reaction routes caused by carriers might be correlated to the physical/chemical adsorption. That is the catalytic activity



Scheme 2. Supported acid ionic liquid catalyst by covalent bond grafting method (SILG).

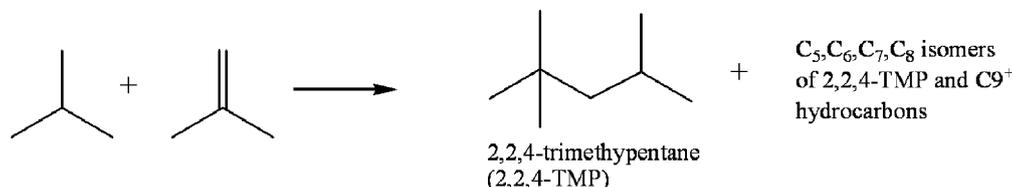
Table 2
Catalytic performance of chloroaluminate IL (BMImCl/AlCl₃ = 1/2) on various supports for butene reaction at the same conditions.^a

Entry	Catalyst (wt.%)	Reaction type	Conversion (%)	Product distribution (wt.%)					
				C ₅ –C ₇	C ₈	C ₉ ⁺	C ₈ ⁼	C ₁₂ ⁼	C ₁₆ ⁼
1	IL/glass (10%)	Alkylation	89.1 ^b	19.0	32.1	48.9	–	–	–
2	IL/AC (30%)	Alkylation	95.0 ^b	25.2	28.6	46.2	–	–	–
3	SILG	Alkylation	93.5 ^b	26.5	23.2	50.3	–	–	–
4	IL/silica (30%)	Oligomerization	93.1 ^c	–	–	–	9.6	76.1	14.3
5	IL/MCM-41 (30%)	Oligomerization	91.4 ^c	–	–	–	10.7	79.4	9.9
6	IL/SBA-15 (30%)	Oligomerization	95.6 ^c	–	–	–	8.8	61.8	29.4

^a Reaction conditions: isobutane/isobutene ratio = 10:1, GHSV = 600 h⁻¹, 25 °C.

^b Conversion of butane.

^c Conversion of isobutene.



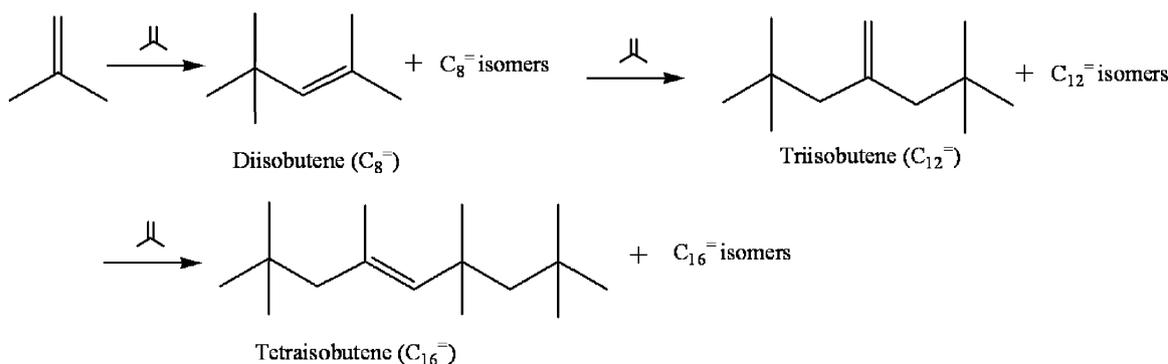
Scheme 3. Isobutane/butene alkylation.

for isobutene oligomerization may be derived from the synergy between Al₂Cl₇⁻ anion and silica. Comparable experiments using other supports including MCM-41 MS and SBA-15 MS possessing Si–OH on the surface [40,41] further confirmed this point (Entries 5 and 6). Based on the XPS data, the reaction between ILs anions (i.e. Al₂Cl₇⁻) and silanol groups leads to formation of covalent Si–O–Al solid acid bridges [34], which were prone to adsorb butenes instead of isobutane on the surface of catalyst, thereby the oligomerization was promoted sequentially. It was reported that codimerization reactions between isobutene and other butenes are always slower than isobutene dimerization, and the trimers are relatively easily produced from the addition of isobutene to dimers [39], thus isobutene is the primary reactant in the feed and other butenes more or less participate in oligomerization. That is the reason that conversion was calculated on isobutene basis. Furthermore, we also synthesized supported acidic IL catalyst by covalent bond grafting method on silica (Entry 3, SILG, Scheme 2) to act on the C₄ fraction. As a result, only alkanes were observed from the products. The Si–OH on the support surface had reacted with silicone coupling agent due to the grafting reaction [25], and the Si–O–Al bridge bond could not be generated. Hence, it would not change the gas absorbability on the surface and the isobutene oligomerization could not be promoted over this catalyst.

3.3. Effects of conditions on the oligomerization of isobutene

3.3.1. Effect of IL loading on the oligomerization of isobutene

The influence of chloroaluminate IL (BMImCl/AlCl₃ = 1/2) loading on the reaction of isobutene trimerization were investigated at 25 °C, and the results were illustrated in Fig. 5. The reactions were conducted with different catalyst loadings ranging from 5 to 30 wt.% with the reactant compositions (isobutane/isobutene ratio = 10:1) at a gas hourly space velocity (GHSV) of 600 h⁻¹. It has been reported that both Brønsted and Lewis acid sites contributed to the isobutene oligomerization [42], so the isobutene conversion was related to the concentration of acid sites. As shown in Fig. 3, the amount of acid sites decreased with the order of IL loading, and this trend coincided with the catalytic performance, including conversion over these catalysts. It was observed that the selectivity of trimers was 76.1% with the 30 wt.% IL loading, and slightly increased when the IL loadings decreased from 30 to 5 wt.%. Besides, the tetramers selectivity also showed increasing trend with decrease of IL loading. The declined slight selectivity of trimers and tetramers with higher IL loading might be due to the steric hindrance caused by the crowded alkyl groups. Because of an amorphous structure, there was not sufficient space to further oligomerization at the high acid site [4]. On the contrary, the selectivity of dimers decreased with the increase of trimers and



Scheme 4. Isobutene oligomerization.

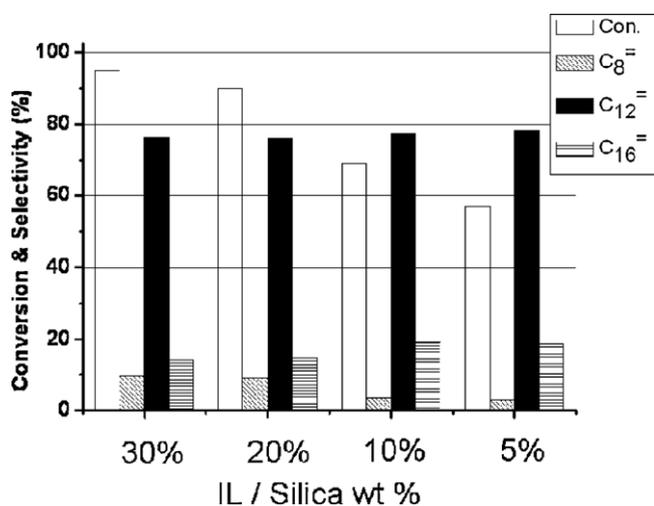


Fig. 5. Effect of IL loading amount on the oligomerization of isobutene (isobutane/isobutene ratio = 10:1, GHSV = 600 h⁻¹, 25 °C).

tetramers. Consequently, the amount of IL loading on silica determined the isobutene conversion in the isobutene oligomerization, and insignificantly influenced the trimer selectivity.

3.3.2. Effect of temperature on the oligomerization of isobutene

The effect of reaction temperature was also investigated using the SILC (IL/silica, BMImCl/AlCl₃ = 1/2, 30 wt.%). Fig. 6 illustrates the data of isobutene conversion and oligomers selectivity at different temperatures. Obviously, as reaction temperature increased, the conversion of isobutene also increased. The isobutene conversion was above 90% even at 10 °C, and then the total conversion was obtained at 50 °C and 70 °C over the tested catalyst. The selectivity of trimers basically increased with the increasing temperature, which was consistent with the previous reported results [19], and it could be up to 91.4% at 50 °C. At the same time, the selectivity of tetramers was contrary to the increasing temperature, and even it could not be detected in the products at 70 °C. The main reason might be due to the fact that cracking reactions occurred at higher temperature and more dimers were generated accordingly [19]. The extent of cracking reactions became severe with increasing temperature, which led to the lower selectivity of trimers at 70 °C than at 50 °C. These results suggested that relatively high reaction

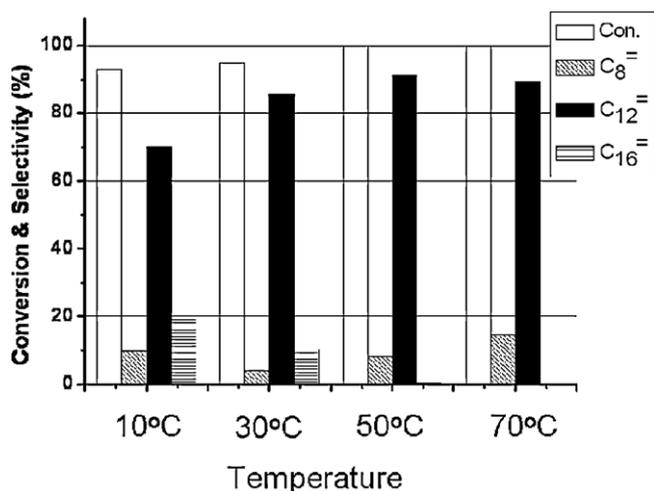


Fig. 6. Effect of temperature on the oligomerization of isobutene (catalyst: IL/silica 30 wt.%, isobutane/isobutene ratio = 10:1, GHSV = 600 h⁻¹).

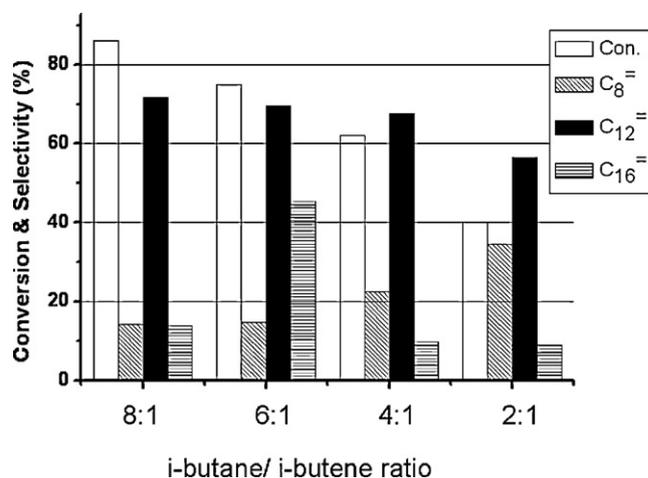


Fig. 7. Effect of isobutene concentration on the oligomerization of isobutene (catalyst: IL/silica 30 wt.%, GHSV = 600 h⁻¹, 10 °C).

temperature favored the conversion of isobutene and enhanced the formation of trimers.

3.3.3. Effect of isobutene concentration on the oligomerization of isobutene

Fig. 7 shows the reaction results over IL/silica catalyst (BMImCl/AlCl₃ = 1/2, 30 wt.%) with the various reactant compositions (isobutane/isobutene ratio) at GHSV of 600 h⁻¹. The sharp decrease in conversion of isobutene with the increased isobutene concentration could be observed in Fig. 7. The trimers selectivity increased with the decrease of isobutene concentration and reached the selectivity of about 71.7% from the reactants containing a low isobutene concentration of 11.1%. Moreover, the higher concentration of isobutene in the reactants was fed, the more dimers were obtained in the products. Because the oligomerization of isobutene could be regarded as a consecutive reaction from monomer to dimers, from dimers to trimers, and trimers to tetramers [43], the kinetic rate constants for oligomers of isobutene decreased with the carbon atom number of the olefin [44]. Therefore, the selectivity of dimer of isobutene increased in the circumstance of high isobutene concentration, whereas the selectivity of trimers and tetramers decreased instead. Therefore, low isobutene concentration in the feed was beneficial to improve the conversion of isobutene and the selectivity of trimers in the gas-phase reaction.

3.3.4. Effect of space velocity (GHSV) on the oligomerization of isobutene

The productivity of a reaction greatly depends on the space velocity. Fig. 8 depicts the general trends of isobutene conversion and trimers selectivity over the catalyst IL/silica (BMImCl/AlCl₃ = 1/2, 30 wt.%) as a function of space velocity (GHSV) at 25 °C. As the space velocity increased, both isobutene conversion and trimers selectivity decreased. The tetramers selectivity changed with process conditions in a similar manner to the trimers selectivity. The lower trimers selectivity at higher GHSV could be related to the low isobutene conversion because the selectivity increased with the isobutene conversion [45]. Similarly, the concentration of dimers in the products increased with decrease of isobutene conversion, which was also due to the consecutiveness of isobutene oligomerization reaction. Based on the above results, selective isobutene trimerization thus should be conducted at low space velocity.

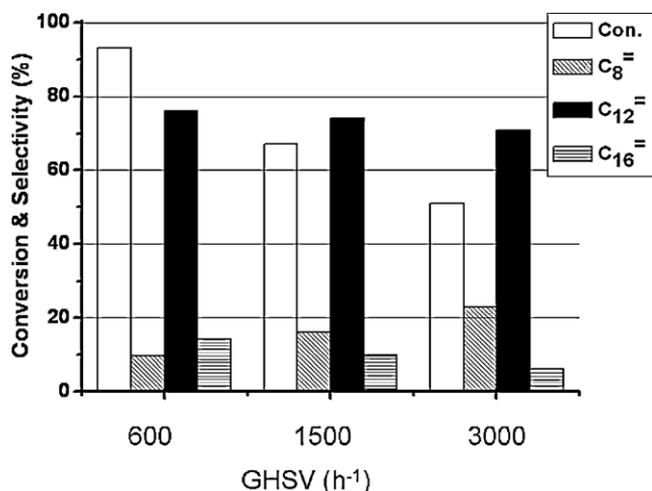


Fig. 8. Effect of space velocity (GHSV) on the oligomerization of isobutene (catalyst: IL/silica 30 wt.%, isobutane/isobutene ratio = 10:1, 25 °C).

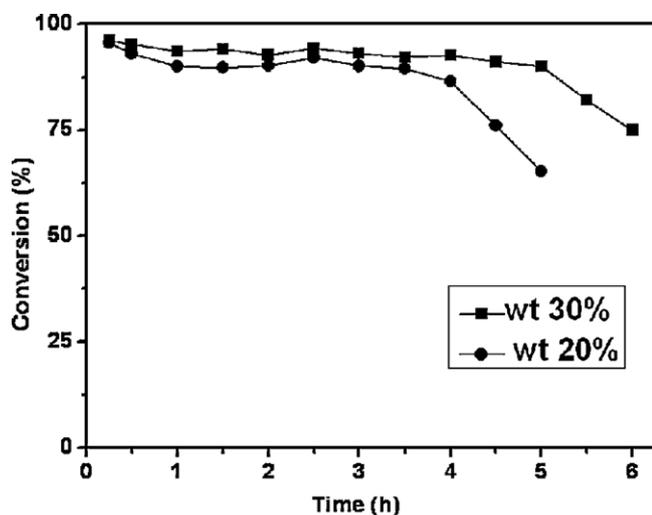


Fig. 9. The conversion of isobutene at different catalyst loadings with time on stream (isobutane/isobutene ratio = 10:1, GHSV = 600 h⁻¹, 25 °C).

3.3.5. Evaluation of the SILCs stability

The stability of the SILCs for isobutene oligomerization was also evaluated. The conversion of isobutene as a function of the time was shown in Fig. 9. After a stabilization time of 1 h on stream, the IL/silica catalyst (BMImCl/AlCl₃ = 1/2, 30 wt.%) showed relatively stable conversion values (about 93%) for 5 h, and then gradually declined to 76%. For the IL/silica catalyst (20 wt.%), after 4 h, the conversion of isobutene began to decrease as the reaction time was prolonged. With regard to deactivation, the catalyst with 30% IL loading showed better stability for oligomerization, which might result from the higher concentration of Lewis acid sites on the catalyst [46]. This deactivation of the catalyst can be attributed to the formed olefins with high molecular weight during the reaction, which blocked active sites on the catalyst and decreased the catalytic activity [47].

4. Conclusions

In conclusion, supported chloroaluminate ILs were prepared and used for the trimerization of isobutene based on C4 mixture at mild conditions. It was interestingly found that the carrier played a crucial role in isobutene trimerization. The catalysts supported on glass or AC carriers induced isobutane/butene alkylation,

whereas the catalyst supported on silica showed catalytic activity for isobutene oligomerization. DSC and XPS characterization results indicated that catalytic activity for isobutene oligomerization might originate from the synergy between Al₂Cl₇⁻ anion and silica. Furthermore, the influences of temperature, reactant concentration, space velocity and loading amount of the IL/silica catalysts for the oligomerization were investigated. Optimized conditions were observed at relatively high temperature, low space velocity, and low isobutene concentration in the feed. Total conversion of isobutene and 91.4% selectivity of trimers were obtained at 50 °C over the IL/silica (30 wt.%) catalyst.

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