

Review

Research progress in ionic liquids catalyzed isobutane/butene alkylation[☆]Panxue Gan, Shengwei Tang^{*}

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ABSTRACT

The complicated reaction mechanism and the character of competitive reactions lead to a stringent requirement for the catalyst of C₄ alkylation process. Due to their unique properties, ionic liquids (ILs) are thought to be new potential acid catalysts for C₄ alkylation. An analysis of the regular and modified chloroaluminate ILs, novel Brønsted ILs and composite ILs used in isobutane/butene alkylation shows that the use of either ILs or ILs coupled with mineral acid as homogeneous catalysts can help to greatly adjust the acid strength. By modifying the structural parameters of the cations and anions of the ILs, the solubility of the reactants could also be adjusted, which in turn displays a positive effect on improving the activity of ILs. Immobilization of ILs is an effective way to modulate the surface adsorption/desorption properties and acid strength distribution of the solid acid catalysts. Such a process has a tremendous potential to reduce the deactivation of catalyst and enhance the activity of the solid acid catalyst. The development of novel acid catalysts for C₄ alkylation is a comprehensive consideration of acid strength and its distribution, interfacial properties and transport characteristics.

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1. Introduction

Strong acid catalyzed isobutane/butene alkylation is an important petroleum process to produce high octane number gasoline, which has the characteristics of low contents of sulfur, aromatics and alkenes, and is commonly used as an excellent additive in global gasoline pool. Out of total global gasoline consumption, approximately 13%–15% consists of alkylation gasoline. Alkylation gasoline has a production rate of about 100 million tons per year [1]. However, with the increase of vehicle ownership, phasing out of methyl *tert*-butyl ether (MTBE), expanding use of ethanol-gasoline blends and the ever growing environmental requirements of motor gasoline, the production and demand for alkylation gasoline show an increasing trend with every passing year [2,3].

Nowadays, sulfuric acid (H₂SO₄) and hydrofluoric acid (HF) have widely been used in commercial alkylation process to synthesize high-grade petrol via the addition reaction of light alkanes and alkenes. In such a process, the miscibility of the acid and hydrocarbon and the mass transfer of these two phases have significant influences on the reaction efficiency, the yield of target product and the catalyst lifetime [4]. The acid soluble oil (ASO) and a large quantity of waste acid were produced in H₂SO₄ process as byproducts. It is very costly to regenerate the waste acid [5]. In contrast to the H₂SO₄ process, the catalyst consumption of hydrogen fluoride process is relatively lower (less than 1 kg·t⁻¹ alkylate). However, there has been much concern

about the toxicity of HF along with its volatility and corrosiveness. Although the HF units are easier to expand and have lower maintenance and operational costs than the corresponding H₂SO₄ units [6], yet the fundamental problem of being environment-unfriendly still remains unchanged. So, solid acid is thought to be a potential alternative to replace the traditional acids in catalyzed alkylation processes [7,8]. The solid acid catalyst shows good catalytic activity and selectivity for alkylate under certain conditions as well as in a commercial process. However, the use of solid acid can only be commercialized unless the problems, such as rapid deactivation and regeneration of the solid acid, could be solved effectively [9,10].

The reaction mechanism of C₄ alkylation is complicated due to a number of competing reactions simultaneously existing in the process [11,12]. The selectivity of alkylate depends on the formation of carbocation and the protonation of the alkenes. The protonation of the alkenes depends on the acidity of the catalyst, while the concentration of the carbocation depends on the solubility of isobutane in the acid phase [1,13]. Obviously, these two characteristics play a vital role in the alkylation process. Corma *et al.* [14] have reported that H₀ in the range of −8.1 to −12.7 is beneficial to alkylation. The lower acidity favors the alkene polymerization, while higher acidity aggravates the cracking of alkylate. Because of the reaction between H₂SO₄ and the organics [15], the acid strength of H₂SO₄ is decreased gradually, which in turn affects the selectivity and yield of alkylate and also produces a lot of waste acid as a byproduct.

The solubility of the reactants in the acid phase has significant influence on the reaction direction and reaction extent of alkylation. In the commercial H₂SO₄ or HF process, the difference in polarity of the isobutane and butene leads to the difference of dissolubility in catalyst phase. As a result, the local I/O (isobutane to olefin) ratio in the reaction region

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is significantly lesser than the required for the desired reaction and therefore, a number of side-reactions are favored due to the excess of olefin. As a crucial step in C_4 alkylation process, the rate of hydride transfer between C_8 -carbenium ion and isobutane is around 3–4 orders of magnitude lower than the alkene polymerization or addition [16,17]. Therefore, in the presence of excessive alkenes, the catalyst deactivation and low selectivity caused by the polymerization are difficult to be avoided.

Room temperature ionic liquids (RTILs) are molten salts ($T_m < 100^\circ\text{C}$) and consist of larger organic cations and smaller inorganic anions. The asymmetry in the structure results in their low melting points. It is widely accepted that the physicochemical properties of the ILs, such as melting point, density, viscosity, solubility, and acid strength, can be adjusted by modifying the structure and combination of the cations/anions [18–21]. Due to the possibility of controlling the acidity and the dissolution properties of the catalytic system, acidic ILs are thought to be a potential alternative to replace the traditional acids [22–24]. With these excellent features, it has extensively been investigated and successfully applied in many different chemical reaction processes such as esterification [25], Friedel–Crafts alkylation [26] and isomerization [27].

Acidic ILs have received extensive research attention due to their unique physicochemical properties. This review is designed to summarize and analyze the research progress catalyzed by ILs, which usually are used as catalysts or co-catalysts for C_4 alkylation. With a deep analysis of the role of ILs, we can better understand the fundamental catalysis principles and indicate the developmental direction of the exploring of novel catalysts, which could commercially be used in C_4 alkylation process.

2. Pure Ionic Liquid (IL) Systems

2.1. Chloroaluminate(III) ILs

Chloroaluminate ILs have comparative Lewis acid strength with anhydrous AlCl_3 and are widely investigated as acid catalyst in a lot of important reactions. They also show remarkable catalytic activity in C_4 alkylation process [28]. A strengthened acidity is helpful to increase the hydride transfer rate between the TMP^+ (TMP represents Trimethylpentanes) and isobutane and to inhibit both the isomerization of TMP^+ and the trend to form heavy ends, such as C_{12} and C_{16} . So the catalyst acidity has significant impact on the catalyst life, selectivity and yield for C_8 -alkylate [29,30]. A proper and stable catalyst acidity is crucial for the process to obtain a long catalyst life and a high yield of target product.

Chauvin *et al.* [29] have reported the formation of stable molten salt mixture $[\text{BMIm}]\text{Cl}/\text{AlCl}_3$ ($[\text{BMIm}]\text{Cl}$, 1-butyl-3-methylimidazolium chloride) at room temperature by adding AlCl_3 to the $[\text{BMIm}]\text{Cl}$. The acidity of the molten salt mixture can be adjusted by changing the content of AlCl_3 in the mixture. As the AlCl_3 content increases, so does the strength of the acid. Therefore, altering the composition of ILs is an effective way to adjust the acid strength [31,32]. This unique characteristic arouses extensive research on the application of chloroaluminate ILs in C_4 alkylation [31,32]. The catalytic activity of $[\text{BMIm}]\text{Cl}/\text{AlCl}_3$ in the alkylation of isobutane with 2-butene was studied by Chauvin *et al.* [29]. A TMP yield of 88.6% was achieved. Yang *et al.* [33] established an IR spectroscopy method to study the acidity of $[\text{BMIm}]\text{Cl}/\text{AlCl}_3$ by using pyridine as IR spectroscopic probe and the catalytic activity of $[\text{BMIm}]\text{Cl}/\text{AlCl}_3$ in the isobutane–butene alkylation was also investigated.

The acidity and catalytic activity of Chloroaluminate ILs, $\text{Et}_3\text{NHCl}-\text{AlCl}_3$ (triethylamine hydrochloride–aluminum chloride), in the alkylation of isobutane with 2-butene was studied by Liu *et al.* [34]. When the molar ratio $\text{AlCl}_3/\text{Et}_3\text{NHCl}$ of $\text{Et}_3\text{NHCl}-\text{AlCl}_3$ varies from 1.5 to 2.0, the main existence form of the anion is changed from $[\text{AlCl}_4]^-$ to $[\text{Al}_2\text{Cl}_7]^-$, which leads to an increase in the acidity from -12.1 to -13.1 and an increase in the mass fraction of C_8 -alkylate from 39.8% to 46.5% [34]. It is obvious that the addition of AlCl_3 significantly

improves both the Lewis acidity and the catalytic activity, whereas the quality of alkylate is also improved at the same time.

A number of studies focused on the mechanism of acidity adjustment. The Lewis acid–base properties of these ILs are determined by the chloroaluminate species. With the help of ^{27}Al NMR and FT-IR, the main existence forms of the anions in chloroaluminate ILs are: $[\text{AlCl}_4]^-$, $[\text{Al}_2\text{Cl}_7]^-$ and $[\text{Al}_3\text{Cl}_{10}]^-$. These forms have been confirmed by a number of published studies [34–36]. Cui *et al.* proved that the Lewis acidity of $\text{Et}_3\text{NHCl}-\text{AlCl}_3$ is attributed to $[\text{AlCl}_4]^-$, $[\text{Al}_2\text{Cl}_7]^-$ and $[\text{Al}_3\text{Cl}_{10}]^-$ [36]. The AlCl_3 composition in ILs has a significant effect on the existence form of the anions. When the molar ratio of $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$ is less than 0.5, the anion is $[\text{AlCl}_4]^-$ and the IL is basic. With the increasing content of AlCl_3 , $[\text{Al}_2\text{Cl}_7]^-$ is the another existence form of anion and the IL is acidic. And when the molar ratio of $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$ arrives 0.66, one of the existence forms of anion is $[\text{Al}_3\text{Cl}_{10}]^-$ (as can be seen in Table 1).

Table 1

The anion forms of ionic liquid $[\text{EMIm}]\text{Cl}-\text{AlCl}_3$ at different $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$ ratios (reproduced from ref. [22]).

Acidity	$x^{[\text{a}]}(\text{AlCl}_3) = 0-0.5$	$x^{[\text{a}]}(\text{AlCl}_3) = 0.5-0.67$	$x^{[\text{a}]}(\text{AlCl}_3) = 0.67-0.75$
	Basic	Acidic	Strong acidic
Type-I	Cl^-		
Type-II	$[\text{AlCl}_4]^-$	$[\text{AlCl}_4]^-$	
Type-III		$[\text{Al}_2\text{Cl}_7]^-$	$[\text{Al}_2\text{Cl}_7]^-$
Type-IV			$[\text{Al}_3\text{Cl}_{10}]^-$

Note: [a] is the molar ratio of $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$.

Viscosity is a fundamental physicochemical property of the liquid catalyst. It has a dramatic influence on the mixing of the reactant and the catalyst phase or the interphase mass transfer, then it plays a vital role on the reaction efficiency and target product yield. Viscosities of the ILs are strongly dependent upon the compositions. Some works are concerned with the relationships between the viscosity of acidic ILs and the structure or compositions. With longer chains in cation, the resulting ILs become more and more viscous. The van der Waals interactions and hydrogen bonding are the sources of the high viscosities [37]. For an IL with the form of $[\text{AMIm}]\text{X}$ -type ($[\text{AMIm}] = 1\text{-alkyl-3-methylimidazolium}$, $\text{X} = \text{anion}$), the effect of anionic species on the viscosity is much stronger than that of the alkyl chain length [38]. The viscosity is also strongly dependent upon the mole fraction of AlCl_3 in the IL. Among the Cl^- , $[\text{AlCl}_4]^-$ and $[\text{Al}_2\text{Cl}_7]^-$ anions, Cl^- allows the strongest hydrogen bonding while $[\text{Al}_2\text{Cl}_7]^-$ results in the lowest [39]. So, a higher AlCl_3 content not only increases the acidity, but also helps to reduce the viscosity. It is beneficial for the hydrocarbon dispersion in the acid phase, which helps to enhance the mass transfer and the reaction rate in this system. This eventually improves the quality of alkylate.

Since the reaction region of the alkylation lies mainly in the interface, therefore the solubility of the reactants in the catalyst phase exhibits a significant impact on the selectivity of the resultant product [40,41]. However, because of the differences in the polarities of isobutane and butene, the rate of alkene polymerization is far more than the corresponding hydride transfer between C_8^+ and isobutane, which deactivates the catalyst and reduces the selectivity of the objective product [42]. By increasing the solubility of isobutane in the acid phase, it is likely to improve the local I/O ratio. This not only intensifies the formation of C_8 -alkylate, but also extends the catalyst life time [30].

It has been reported that by increasing the alkyl chain length of the cation, the solubility of isobutane in the acid phase also increases, which in turn increases the local I/O ratio. With a longer alkyl chain, it is possible to modulate the physical properties of ILs from being hydrophilic to hydrophobic [43]. As a result, one could predict or tune the dissolution properties by modifying the cation with different alkyl substituents.

Yoo *et al.* [30] conducted a detailed study of the alkylation of isobutane and 2-butene in IL media using [AMIm] halide–aluminum chloride. The study encompassed various alkyl groups and halides on IL's cation and anion respectively. For the same halide anion, ILs with longer alkyl chains were more reactive (1-octyl-3-methylimidazolium [OMIm]), which could be attributed to the higher solubility of the isobutane in the ILs. But it should be noted that the ratio of TMP/DMH (DMH represents dimethylhexanes) was kept almost constant by simply changing the alkyl chain length. If cation is kept constant and anion is varied from Cl^- to Br^- , a strong Lewis acid $[\text{Al}_2\text{Cl}_6\text{Br}]^-$ forms, which could react with hydrogen atom of the imidazolium ring in the 2-position, and hence results in the formation of a Brønsted acid [44]. Compared to the H_2SO_4 process, [OMIm]Br- AlCl_3 was more active. However, the selectivity to TMPs was almost one third of the H_2SO_4 process [30].

In an earlier study, Evering and Roebuck [45] discovered that the mixtures of aluminum chloride–ether complexes are highly active to C_4 alkylation process, where the activity was attributed to the higher solubility of isobutane in ether. With this in mind, Lu *et al.* [46] synthesized a series of acidic chloroaluminate ILs functionalized with ether group, which show a remarkable impact on the alkylation process. With the adjustment of the Lewis acidity and isobutane solubility improvement in ionic liquid by the ether group, 1-methoxyethyl-3-methylimidazolium bromide aluminum chloride ([MOEMIm]Br/ AlCl_3) was the best catalyst among all the investigated ones. The selectivity of C_8 in alkylate reached 66.6% under optimized conditions ($x_{\text{AlCl}_3} = 0.75$, I/O = 10, $T = 308\text{ K}$).

Though chloroaluminate ILs have been shown plausibility, the selectivity and alkylate quality was seldom greater than those obtained in the commercial alkylation processes. Additionally, chloroaluminate ILs are extremely oxophilic [47], forming adducts with C–O functionalities and sensitive to traces of water for the release of HCl. Moreover, the change in acidity during alkylation process and the inability to restore its original value has inhibited the commercial application of the chloroaluminate ILs in alkylation processes.

2.2. Modified chloroaluminate ILs

It is difficult to have a balance among the requirements of acid strength, dissolution characteristics and interfacial characteristics in C_4 alkylation process. In case of chloroaluminate ILs as main catalysts, the addition of different organic or inorganic additives is beneficial to modify the catalyst's physicochemical properties, due to which better performance can be obtained.

A representative work is the composite ILs chloroaluminate ILs + CuCl with a successfully industrial application at a $100\text{ kt}\cdot\text{a}^{-1}$ plant. A composite ionic liquid (CIL) developed by China University of Petroleum shows good catalytic performance for isobutane alkylation. The first commercial $100\text{ kt}\cdot\text{a}^{-1}$ CILA plant was successfully commissioned in 2013 in Shandong by Deyan Chemical Co. Ltd., China. This plant includes four sections namely feed treatment, staged reactors, reactor refrigeration, and product treatment. In addition, this plant also has CIL handling facilities to enable the removal of solids and regeneration of CIL. It is said that: the olefin conversion was 100%, the alkylate yield was 80% of the feed, the average RON of alkylate was 96.8, the catalyst consumption per ton alkylate was 5 kg, the energy consumption per ton alkylate was 150 kge. It is also said that, in comparison to HF and H_2SO_4 plants, the CILA plant has better safety and environmental benefits and has been running stably for two years.

In an earlier research, Huang *et al.* [48] have reported that when CuCl is added to $\text{Et}_3\text{NHCl}\cdot\text{AlCl}_3$, side reactions such as cracking, polymerization, and isomerization can be inhibited by the interactions between CuCl and $[\text{AlCl}_4]^-$ or $[\text{Al}_2\text{Cl}_7]^-$. However, the mechanism of the process is still unknown. With the help of ESI-MS and ^{27}Al NMR, Liu *et al.* [49] confirmed that a composite anion $[\text{AlCl}_4\text{CuCl}]^-$ was formed. As an excellent acceptor of carbenium-ion, $[\text{AlCl}_4\text{CuCl}]^-$ composite anion should be preferred for increasing the hydride transfer rather than the chain

propagation step which causes the formation of C_{12}^+ and C_{16}^+ from C_8^+ . Carbenium-ion chain mechanism showed that most of the light by-products of alkylation could be considered as a result of β -scissions of C_{12}^+ or C_{16}^+ [42]. Compared to the H_2SO_4 process, the TMP yield reached 92% in alkylate. After this, the same researchers systematically investigated the changes of composition, acid strength and product distribution due to the addition of different additives in ionic liquids of [BMIm]Cl- AlCl_3 and $\text{Et}_3\text{NHCl}\cdot\text{AlCl}_3$ [50]. As reported, the C_8 selectivity is probably determined by the composition of the modified IL catalyst rather than the acid strength. The complexation of transition metal with 2-butene can increase the isobutane-to-butene ratio during the alkylation reaction [51], which results in a better selectivity of objective product. Hence, the composition change of the modified IL should be responsible for these better results.

It should be noticed that a change in the mole fraction of AlCl_3 in the IL only affects the number of acid sites and the acidity of ILs; it does not have any impacts on the properties of the acid sites. For this reason, Zhang *et al.* did not obtain a significant improvement on the catalytic behavior of the ILs in isobutane/2-butene alkylation just by changing the mole fraction of AlCl_3 [52]. However, when aromatic compounds are added to $\text{Et}_3\text{NHCl}\cdot\text{AlCl}_3$ IL, the Lewis acid sites could be modified through π -complexation between the Lewis acid sites and the π -cloud of the aromatic ring [45,52]. Additionally, the alkyl carbenium could also be stabilized by the interaction of carbenium and aromatic ring, which inhibited the further occurrence of the secondary reaction. Furthermore, when a substituent group of the added aromatics (having an electron-donating group) was incorporated, the Lewis acidity was crippled by the π -complexation of the Lewis acid sites with π -cloud of the aromatic ring, whereas the existence of the electron withdrawing group functionalized the other way around.

Evering *et al.* [45] reported that inhibitors, which are aromatics or metal halides added in the AlCl_3 -ether, are more inclined to behave as basic and the combination of H^+ with aromatics is strong. In such a case, a carbenium ion with lower acid strength was formed as seen in Fig. 1.

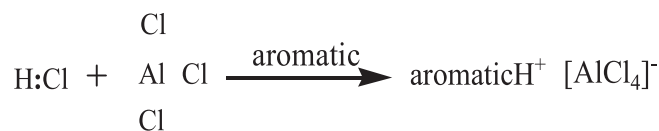


Fig. 1. Mechanism of inhibition through the formation of less acidic species (adapted from Ref [45]).

The carbenium ion mechanism is widely accepted by researchers, whereas the protonation of the alkene is the initial step of the alkylation reaction [42,53]. With suitable promoters combined with [BMIm]Cl- AlCl_3 ionic liquid, the yields of TMP and RON may have comparable values to compete with both H_2SO_4 and HF processes [54,55]. The active species (*tert*-butyl cation) of alkylation reaction are directly generated as a result of the introduction of *tert*-butyl halide as a promoter [55], instead of hydride shift between the protonated 2-butene and isobutane, which implies that the reaction pathway has been changed. Compared to the H_2SO_4 process, when *tert*-butyl bromide was added after 5 min, the conversion of the 2-butene was almost 100%, while under other conditions it was only slightly higher than 30%. However, because of the limitation of hydride transfer between C_8^+ and isobutane, the selectivity for TMP still remains low, even though the apparent reaction rate has been improved by around 1–2 orders of magnitude. There is a great deal of consensus on the fact that the Lewis acid chloroaluminate ILs are extremely sensitive to moisture and traces of water for the release of HCl through an irreversible hydrolyzation process [47]. However, there is little clear quantitative understanding of how the hydrolysate influences the composition and physicochemical properties of the chloroaluminate ILs. The released HCl dissolves in IL and interacts

with Lewis acid species, and the H^+ can be released entirely without the solvation effect, so that the IL probably becomes a superacid. It was verified in an acidity measurement of chloroaluminate IL by a UV spectroscopy method. When anhydrous HCl was filled in chloroaluminate IL, the acid strength was stronger than that of 100% H_2SO_4 . It showed a character of superacid [56]. Ferdinand Pöhlmann *et al.* [57] reported that the [BMIm]Cl- $AlCl_3$ IL keeps a constant catalytic activity by filling anhydrous HCl continuously. The deactivated chloroaluminate IL can also be regenerated by the introduction of anhydrous HCl, which currently is a common method used to regenerate and improve the chloroaluminate IL catalyst [57–59]. When HCl or trace water was filled in chloroaluminate IL, a Brønsted acid species $[Al_2Cl_7OH]^-$ was detected. It is probably the reason for the formation of superacid. The plausible mechanism can be described as seen in Fig. 2.

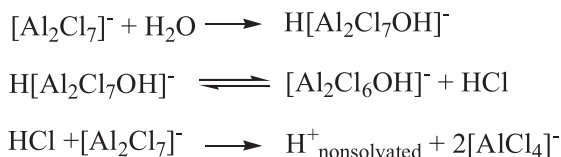


Fig. 2. Reaction pathway for the generation of superacid in Lewis acidic ILs (adapted from Ref [54]).

Hence, water seems to be a promising additive to tune the acidity of $AlCl_3$ -based ILs. In the case of [OMIm]Br- $AlCl_3$ and [(HO₃SBu)MIm]HSO₄ (1-(4-sulfbutyl)-3-methylimidazolium hydrogensulfate), Bui *et al.* [54] investigated the influence of water as additive. Due to the interaction of H_2O and $[Al_2Cl_7]^-$, H^+ was released. When [(HO₃SBu)MIm]HSO₄ was used, the proton located in $-SO_3H$ group also reacted with $AlCl_3$ to form a superacid (see Fig. 3). But it should be emphasized that the concentration of water cannot exceed $0.12 \text{ mg} \cdot \text{g}^{-1}$ in the feed stream. Also, for a higher acidity, the formation of much heavier end (C_9^+) is favored.

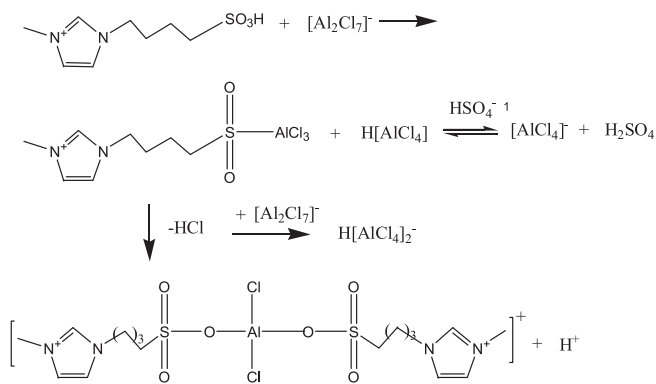


Fig. 3. Formation of superacidic species by the reaction of $AlCl_3$ and sulfonic acid group (adapted from Ref [54]).

The selectivity of C_8 and TMPs can significantly be improved by the use of modified chloroaluminate ILs. In fact, selectivity higher than the traditional H_2SO_4 and HF processes can be achieved. However, the sensitivity to moisture still remains to be solved. Additionally, it is unfavorable for controlling the reaction process, where the catalytic process is complicated due to the additives. In some extreme cases, the catalyst may be deactivated due to the precipitation of the $CuCl$ [60].

3. Brønsted Acid ILs

The chloroaluminate ILs performed commendably in C_4 alkylation process. With adjustment of the amount of $AlCl_3$ and reasonable choice

of the auxiliaries, the selectivity for C_8 and catalytic activity can significantly be improved. However, in the presence of traces of water, there is a dramatic change in the acidity [54]. There are a variety of novel ILs which have emerged with the development of various applications of the ILs. Therefore, it is becoming a new field to develop novel ILs for the application in the C_4 alkylation, which would have a strong acidic character and would demonstrate stability to moisture. H_2SO_4 or HF used in the traditional alkylation process belongs to Brønsted acids. The reason for using H_2SO_4 or HF is that the use of Brønsted acid favors the formation of target alkylate rather than the unsaturated compounds [42,61,62]. So, researchers tend to find alternative Brønsted acid ILs to replace the chloroaluminate ILs that have previously been used in C_4 alkylation. Cole *et al.* [63] reported the synthesis of a series of Brønsted ILs in 2002 for the first time. The cation of the ILs was modified with sulfonic group and proved catalytic activity in several classical acid-promoted organic reactions. These Brønsted ILs possess not only strong acidity but also enough stability to moisture or water. Due to these superior characteristics, these Brønsted ILs have been applied in many chemical processes [64,65].

3.1. Pure Brønsted IL

Tang *et al.* [66] synthesized a series of ILs. Some of these included 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-amide ([HMIm][Tf₂N]), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIm][HSO₄]), 1-octyl-3-methylimidazolium hydrogen sulfate ([OMIm][HSO₄]), 3-methyl-1-(3-sulfobutyl)-imidazolium hydrogen sulfate ([MBSIm][HSO₄]), 3-methyl-1-(3-sulfobutyl)-imidazolium trifluoro methylsulfonate ([MBSIm][OTf]) and 3-methyl-1-(3-sulfopropyl)-imidazolium trifluoro methylsulfonate ([MPBSIm][OTf]). These ILs have been used as C_4 alkylation catalysts both in pure form and coupled with H_2SO_4 or TFOH (trifluoromethanesulfonic acid). The results showed that pure Brønsted ionic liquid with dual-acidic group exhibited comparable value of TMP/DMH. However, some of these ILs, which have single $-SO_3H$ group, did not provide satisfactory results for the very low conversion. Additionally, in comparison to pure H_2SO_4 or TFOH and IL/acid systems, all of these ILs perform poorly. Liu Ying *et al.* [67] have synthesized a series of ILs modified by $-SO_3H$ group and have also investigated their catalytic activity towards C_4 alkylation. For the same cation, anions were varied from [Tf₂N]⁻ to [HSO₄]⁻ and then to [OTf]⁻. The conversion of 2-butene and selectivity for C_8 remained below 60% and 40% respectively, while both C_8^- and C_{12}^- appeared in alkylate due to lower acidity ($H_0 > -8.2$). When $-SO_3H$ group was grafted onto the cation, the acidity was enhanced and a better selectivity for C_8 was observed.

Olah and coworkers [68] found that anhydrous HF forms remarkably stable solutions with pyridine and its analogs to give pyridinium poly (hydrogen fluoride) (see Fig. 4), which performs as an IL. Two different kinds of amine-(HF)_n ILs and HF immobilized on solid polymeric amines ionic solid were synthesized with 70%–95% HF contents. The pyridinium poly (hydrogen fluoride) PPHF, poly ethylenimine (hydrogen fluoride) PEIHF and poly(4-vinylpyridinium) poly(hydrogen fluoride) PVPHF systems were successfully used for isobutane-isobutylene/butane alkylation. It is interesting to note that the acidity of the onium-poly (hydrogen fluoride) complexes depends on their composition, while the equilibrium and the catalytic activity are affected by the free HF in the solution. Additionally, these novel catalysts significantly reduce the volatility of HF through complexation. This modification plays an important role in commercial HF process to minimize the environmental hazards without weakening the activity for alkylation [69].

3.2. Composite Brønsted ILs

As has been mentioned earlier, the acid strength of pure Brønsted ILs was too low to catalyze the C_4 alkylation, which results in a bad quality alkylate. Wasserscheid and coworkers [70] investigated the catalytic

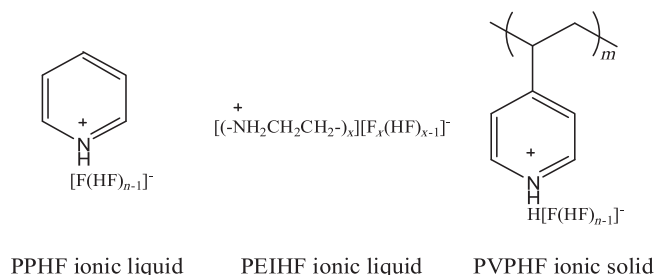


Fig. 4. Structures of HF equivalent amine-poly-(hydrogen fluoride) complexes. (Adapted from Ref [68]).

activity of IL/ H_2SO_4 mixtures, which have been used to catalyze the Friedel–Crafts alkylation of benzene with 1-decene. The results clearly demonstrate an interplay of acidity and solubility effects caused by the IL additive. In some cases, low amounts of IL additive result in a dramatic improvement of product yield [66,71].

Tang *et al.* [66] reported a new process for isobutane/1-butene alkylation by using certain acid imidazolium ILs coupled with strong acids such as H_2SO_4 and TFOH. The use of different types of substituted 3-methyl-imidazolium ILs and binary mixtures were investigated, and a significant change was observed due to the addition of small amount of IL. Since its discovery, the concept has attracted the attention of many researchers [71–73].

Zhang's group systematically investigated the binary mixtures of strong acids and additives in isobutane alkylation [71,73,74]. Xing *et al.* [72] synthesized a series of imidazolium-based ILs ([CnMIm]– SbF_6 ; $n = 4, 6, 8$) and pyridine-based ILs ([CnPy]– SbF_6 ; $n = 2, 4, 6, 8$). The catalytic activity of these ILs coupled with TFOH was investigated for isobutane/1-butene alkylation. These ILs contain $[\text{SbF}_6]^-$ as anion and performed well when coupled with TFOH. However, when [BMIm][OTf] was used, no alkylate was observed. This may be caused by the lower acidity of [BMIm][OTf] (50 wt%)/TFOH (50 wt%) system. According to Kim [75], the better catalytic activity of the ILs containing $[\text{SbF}_6]^-$ may be attributed to the formation of strongly acidic salt $[\text{CF}_3\text{SO}_3\text{H}_2][\text{SbF}_6]$ through anion exchange between [BMIm][SbF_6] and TFOH. When the alkyl chain length of [CnPy][SbF_6] ILs was changed, the yield of alkylate increased as the length of the alkyl group increased from 2 to 6 and then decreased for $n = 8$. This may be attributed to the higher solubility of isobutane in the ILs or its solution, where higher hydride transfer from the isobutane to C_8 carbonium was achieved. This resulted in higher generation of desired C_8 alkylate and a suppression of side reaction.

On the study of [BMIm][SbF_6]/ H_2SO_4 binary mixtures, it was observed that the deactivation of H_2SO_4 was dramatically inhibited by the addition of traces of ILs (0.5 wt%) [71]. The phenomenon was explained by a mild change in the acidity of the [BMIm][SbF_6]/ H_2SO_4 system. In comparison to pure H_2SO_4 process, the system resulted in inhibited formation of ASO, which was very important to preserve the catalytic activity [59,76].

As has been mentioned earlier, the C_4 alkylation is not only influenced by the acid strength, but also by the solubility of the hydrocarbon in the acid phase. There are many studies on the solubility of hydrocarbons in different ILs [50,77–79], and the reaction was obviously affected by the solubility parameters. Recently our group has reported the solubility parameters of three different ILs and the values were used to qualitatively explain the difference of the solubility of isobutane in different ILs [79]. Therefore, both the acid strength of the ionic liquids and the dissolution characteristic should be taken into account for such systems.

For the same anions, the solubility of isobutane in ILs follows the order of: ammonium > imidazolium > phosphonium [80]. Anion of ILs also plays an important role in the solubility of hydrocarbons in the ILs [81]. Cui *et al.* [82] synthesized a series of ammonium-based ILs (AMILs) so as to increase the solubility of isobutane in the acid phase.

They studied the catalytic activity of TFOH coupled with AMILs in the alkylation of isobutane and 1-butene. The efficiency of TFOH was dramatically enhanced by the addition of AMILs. The anion of IL also has an obvious impact on the alkylate quality for the solubility differences of reactants in the catalyst phase. Compared with the catalyst of TFOH and the ILs with anion $[\text{OTf}]^-$, a higher I/O ratio was probably obtained in the mixture of TFOH coupled with the ILs containing anion $[\text{HSO}_4]^-$, then a higher alkylate quality was observed.

Inspired by the discussion mentioned in composite chloroaluminate ILs, Liu *et al.* synthesized a series of dual acidic ILs, (3-sulfonic acid)-propyl-triethylammonium metal chloride salt $[\text{HO}_3\text{SC}_3\text{NET}_3]\text{Cl-MCl}_x$ ($\text{MCl}_x = \text{AlCl}_3, \text{FeCl}_3, \text{CuCl}, \text{ZnCl}_2$), which possess both of the Brønsted and Lewis acid site. These ILs have shown excellent catalytic activity and selectivity in both of the dimerization of fatty acid methyl ester [83] and isobutane/isobutene alkylation [84]. With different Lewis acid MCl_x added, the conversion of isobutene and selectivity of alkylate was higher than the pure $[\text{HO}_3\text{SC}_3\text{NET}_3]\text{Cl}$, which may attributed to the synergetic effect of the both Brønsted acidic sites and stronger acidity of the Lewis acid. The hypothetical mechanism of the synergetic effect of both the Brønsted and Lewis acid site is illustrated in Fig. 5. The IL, $[\text{HO}_3\text{SC}_3\text{NET}_3]\text{Cl-ZnCl}_2$, showed the best catalytic performance of all the investigated ILs, where the TMP/DMH > 75, with conversion of isobutene 100%. Additionally, the existence of air and moisture seems to have no obvious impact on the stability of these ILs, except for the $[\text{HO}_3\text{SC}_3\text{NET}_3]\text{Cl-AlCl}_3$, which is sensitivity to trace of water.

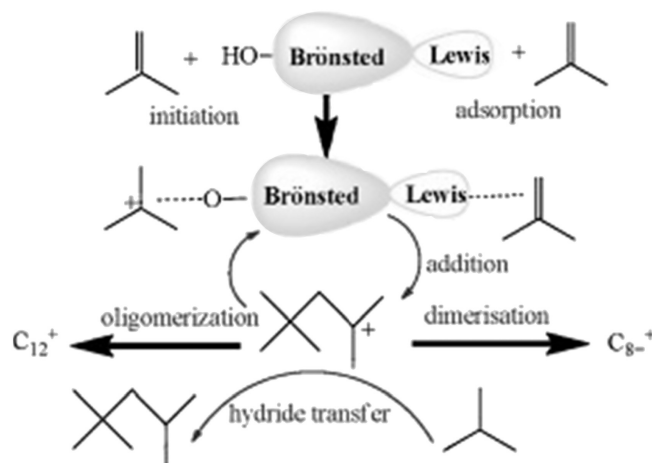


Fig. 5. The mechanism of C_4 alkylation reaction in the presence of the B-L acidic IL. (Reproduced from Ref [84]).

From the above discussion, it is clear that the Brønsted ILs are more resistant to moisture in air than chloroaluminate ILs. However, the acid strength is weaker than the chloroaluminate ILs. Therefore, Brønsted ILs are less likely to catalyze the C_4 alkylation alone. The Brønsted ILs are preferred to act as auxiliaries rather than the main catalysts in the mixtures. Since the physicochemical properties of the catalytic system can be adjusted, therefore the improvement in the catalytic properties is one of the main research directions for the Brønsted ILs for C_4 alkylation.

3.3. Supported ILs phase catalyst (SILPC) systems

Due to the existing problems, such as higher product costs, limited knowledge of the physicochemical properties, product separation, and effective recovery of the catalyst, the commercial application of ILs is still limited. Moreover, contrary to the expectations, the application of a large number of ILs as solvents or catalysts in many catalytic processes may not be 'green'. So, the concept of supported ILs in porous solids through impregnation, immobilization and encapsulation is becoming a hot topic for research and application [85,86].

The SILPC combines the advantages of ILs and heterogeneous catalysis. With the characteristics of designable and excellent solubility of organic and inorganic metallic salts, ILs have been applied as solvents for many polar or ionic catalysts. In such systems, the ILs are dispersed on a supporter. This new concept has successfully been applied in many areas such as I/O regulation [87], carbonylation [88], hydroformylation [89] and Heck's reaction [90]. Furthermore, parameters such as the interaction between the ILs and the species of supporter, active sites, reaction medium, and reactants are different for different ILs. Therefore, the selectivity and catalytic activity of such systems also vary with different ILs. With the interaction of ILs and hydroxyl group, chloroaluminate IL [BMIm]Cl- AlCl_3 and 1-(tri-ethoxy-silyl-propyl)-3-methylimidazolium chloride was successfully immobilized on the surface of the MCM-41 [91,92]. The system performed well in the alkylation of benzene with dodecene. With the same method, Kumar *et al.* dispersed the Lewis acid ILs on the MCM-41(FK 700) supporter by impregnation and immobilization [93] (Fig. 6). The catalytic activity of the immobilized one was higher than the impregnated one. It is also higher than the traditional solid acid catalyst SAC-13 and H-Beta. The reason why the modified catalyst can prolong the catalyst's life should be the existence of $[\text{Al}_2\text{Cl}_7]^-$, which acts as a strong Lewis acid and accelerates the cracking of the heavy ends, thus reducing the coke deposition. Moreover, it should be pointed out that the lifetime of the SILPC is shorter than that of the pure IL system, while the C_8 selectivity is also lower than that of pure IL.

In the commercial mineral acid alkylation process, a very high I/O ratio (the actual I/O ratio may be as high as 1000 in H_2SO_4 system [4]) is used to promote the formation rate of desired products. However, the local I/O ratio in the reaction region on the solid acid strongly depends on the adsorption capacities of reactants. It is difficult to get a high I/O ratio at the acid sites by just increasing the I/O ratio in feed. A preferential adsorption of olefin over alkane on the solid acid catalyst usually takes place in the isoparaffin/olefin alkylation process [94]. Actually, polar reactants are readily adsorbed on the solid acid catalysts due to their intrinsic surface polarity. Low I/O ratio leads to excessive butene existing on the surface of acid sites, which is conducive to the oligomerization, polymerization or addition of butene, and the formation of heavy compounds (C_9+). Then the plugging of pore openings and the cover of active sites by heavy compounds is unavoidable [9].

The adsorption properties of catalyst not only have a significant influence on the reaction efficiency, product yield and catalyst life, but also decide the reaction direction. Liu *et al.* [95] discovered that grafting chloroaluminate IL on different supporter probably leads to different reaction product. When the ILs were supported on glass or activated carbon, the alkylation reaction was taken place. When the support was changed as silica, isobutene oligomerization became the main reaction.

This phenomenon can be attributed to the differences of adsorptive capacity of isobutane and butene on the catalyst. Therefore, it is of great significance to seek for an effective way to modulate the adsorption capacities of reactant on the solid acid catalysts.

Generally, the adsorption capacities of reactants on the catalyst active sites mainly depend on the physicochemical property and surface features of the catalysts. The pore size also has been found to affect the adsorption capacity through steric hindrances [96]. It is an efficient way to improve the local I/O ratio by modulating the surface hydrophobicity through surface modification. Grafting ILs is one of the effective ways to modulate the adsorption properties. The surface character of the SILPC can be customized by a rational design of the ILs structure or the alkyl chain length [97]. Thus the relative adsorption capacity of alkenes and alkanes on the catalyst can be modulated, and the local I/O ratio and hydride transfer ability could significantly be improved. Tang *et al.* [87] obtained an almost stoichiometric adsorption ethane/ethylene ratio on MCM-22 by grafting a dual acidic ionic liquid 3-sulfoethyl-1-(3-propyltriethoxysilane)imidazolium hydrogen sulfate. Shen *et al.* [98–100] studied the catalytic activity of SBA-15/16 supported with ILs in the alkylation of isobutane with 1-butene. They tuned the acid strength by immobilizing propyl-sulfonic, arene-sulfonic or perfluoroalkylsulfonic acid groups and adjust the hydrophilic-hydrophobic nature of the surface by using organosilica or by capping the surface OHs of silica. Acid functionalized mesoporous organosilica and silanized silica has a hydrophobic surface and leads to a higher paraffin concentration in the pore system. They show a better catalysis than the catalysts with hydrophilic surface. A three-dimensional mesopore solid acid is superior to one-dimensional ones both in butene conversion and TMP selectivity for the low diffusion resistance and resisting deactivation by pore plugging. Materials modified with perfluoroalkylsulfonic acid groups exhibit the best catalytic activity for its strong acidity. They suggested that strong acid sites like perfluoroalkylsulfonic acid groups, three-dimension mesopores structure and hydrophobic surface should be desired for an alkylation catalyst.

Traditional solid acid catalysts performed as high efficiency catalysts for alkylation at the initial stage, while rapid deactivation occurred as the reaction proceeded further for the coke deposition. As described above, the adsorption properties of components on the catalyst, the acid strength, the distribution of acid sites with different acidity and the resistance of mass transfer all have a significant influence on the reaction efficiency, the selectivity of target product and catalyst lifetime. As the suggestion of Shen *et al.* [99] a good catalyst for the C_4 alkylation process need a balance on the acidity, surface property and transfer property, so as to get a high local I/O ratio, a proper acid strength and a low resistance of transfer, and then to intensify the reaction with a high reaction efficiency, high yield of objective product and a long catalyst lifetime.

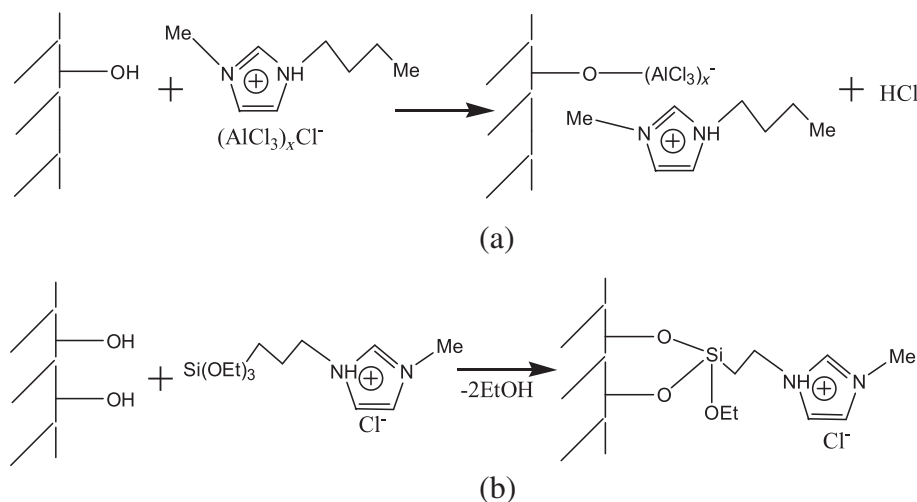


Fig. 6. (a) Immobilization by impregnation. (b) Immobilization by grafting. (Adapted from Ref [93]).

Only fragmentary researches about the application of SILPC on C_4 alkylation process were reported [93,95,98–100]. A lot of work is needed to explore the catalytic activity, catalysis mechanism, deactivation mechanism and regeneration technology. However, we believe that the ionic liquids will play an important role in the exploring of new solid acid catalyst of C_4 alkylation process for its unique character.

4. Summary and Future Prospect

The complicated reaction mechanism and the character of competitive reactions lead to a stringent requirement for the catalyst of C_4 alkylation process. The catalyst should keep a proper acid strength and relatively centralized distribution so as to provide enough acid sites with desired acidity. Lower acid strength favors the butene oligomerization to form heavy compounds while higher acid strength favors the cracking to form light components. A rapid decrease of acidity leads to a short catalyst lifetime. Meanwhile, the catalyst should have excellent interfacial properties and transport characteristics so as to provide an ideal I/O ratio in the reaction region.

Chloroaluminate(III) ILs can provide an adjustable acidity and tunable miscibility with hydrocarbons. However, the oxophilic character and water sensitivity impede its application. Addition of organic or inorganic additives into chloroaluminate ILs brings a synergistic catalytic effect to intensify the hydride transfer and inhibit the side reactions, and then to improve the alkylation process with a higher selectivity of C_8 and TMPs than the traditional H_2SO_4 and HF processes. The catalyst can be regenerated and the acidity of catalyst can be kept at a constant by supplementing HCl. It should be a good candidate for the catalyst of C_4 alkylation. The feasibility of the application in C_4 alkylation process has been proved in a $100\text{ kt}\cdot\text{a}^{-1}$ plant by China University of Petroleum. However, we should pay close attention to the separation of additives, the escape of HCl released from the catalyst deactivation, and the precipitation of additives, such as CuCl. The results of long-term operation of the CIL in the commercial plant will provide enough information about the application prospect of CIL in C_4 alkylation process.

The acidity and dissolution property of Brønsted acidic ionic liquids also are adjustable. Brønsted acidic ionic liquids are insensitive and stable to water. And it can provide proton H^+ directly to favor the formation of target alkylate. However, the acid strength is not strong enough to get a good quality alkylate product. The Brønsted ILs are good auxiliaries of strong Brønsted acid to get an adjustable dissolubility, an appropriate acidity and an improved mass transfer. So, synergistic catalytic effect should be expected by mixing Brønsted ILs with strong inorganic acid, such as H_2SO_4 , HF, etc. The IL/acid composite system would be the most potential catalyst to replace the traditional inorganic mineral acid system. Some good research results are obtained in the lab. However, the feasibility needs to be verified in a commercial plant. And further researches are necessary to obtain the fundamental information, such as the catalysis mechanism, deactivation mechanism, regeneration technology, transfer properties, etc.

Supporting acidic ILs on solid acid can effectively modulate the surface hydrophobicity and then to adjust the adsorption property. A stoichiometric I/O ratio on the acid sites is probably obtained by tailoring the structure of ionic liquids. SILPC is probably a potential substitute catalyst of the mineral acid. However, the supporting of IL leads to a decrease in specific surface area, pore volume and pore size. A mesoporous or macroporous solid acid is an ideal support to prepare SILPC. The acidity of acidic ILs is different with that of solid acid. The SILPC have at least two kinds of acid sites with different acid strengths. It probably has a significant influence on the catalytic activity and product selectivity. Now, only few works on the research of SILPC in C_4 alkylation were reported. An in-depth and systematic theoretical research on the fundamental physicochemical properties of these systems is necessary to explore new SILPC.

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