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ARTICLE

Durability Enhanced Ionic Liquid Catalyst for Friedel-Craft Reaction between Benzene and 1-Dodecene: Insight of Catalyst Deactivation

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Friedel-Craft alkylation of benzene with 1-dodecene, which is an important reaction of synthetic detergent, was studied using the catalyst of [bmim][TFSI]/AlCl$_3$ (1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide/AlCl$_3$). These ionic liquid catalysts show biphasic behaviors at specific condition. Active site species and Lewis acidity were determined by NMR and acetonitrile probe FT-IR. NMR spectroscopy investigations indicated that "Coordinated" and "uncoordinated" [TFSI]$^-$ existed in the ionic liquid catalyst system sumultaneity, while tetrahedral 4-coordinate Al$_2$Cl$_7$$^-$ was the main active specie for Friedel-Craft alkylation. The complexation [AlCl$_x$(TFSI)$_y$]$^-$ tend to decompose and release 4-coordinated Al$_2$Cl$_7$$^-$ and [TFSI]$^-$. The phase behaviors study of the ionic liquid [bmim][TFSI]/AlCl$_3$ demonstrated that the upper phase could be used as an efficient heterogeneous catalyst when AlCl$_3$/IL≥1.5. Due to the presence of anion [TFSI]$^-$ around active sites, especially [TFSI]$^-$ at "uncoordinated" state, ionic liquid formed a stable and hydrophobic chemical environment, which enhanced catalysts durability. The influence of various reaction conditions including catalyst reusability on the alkylation reaction was studied, and the potential reasons to catalyst deactivation were discussed. The highest 2-LAB selectivity was more than 50% when 1-dodecene conversion was nearly 100%. Comparing with liquid or solid acid catalyst, ionic liquid catalysts have many advantages in perspectives concerning energy and environmental.

1 Introduction

Synthetic detergents made from branched alkyl benzene (BAB) have been widely applied in all sorts of areas in our daily life.[1-4] However, the increasing usage of detergent leads to branched alkyl benzene sulfonate (BAS) accumulation and environment contamination. Generally, it is generally known that synthetic detergent made from linear alkyl benzene (LAB) has better biodegradability than that made from BAB or natural soap.[5] The phenyl group position of LAB has an effect on its surface-active property and biodegradability of linear alkyl benzene sulfonate (LAS). Among the isomers of LAB, 2-LAB exhibits the highest biodegradability, making it dominant detergent intermediate.[6-8]

HF or AlCl$_3$ was commonly used as a homogenous catalyst in the industrial production of LAB. This kind of catalysts showed serious problems including environment contamination, equipment corrosion, difficult separation, and low 2-LAB selectivity. The 2-LAB selectivity catalysed by AlCl$_3$ or HF is in the ranges from 26~33%[1, 2] and 14~20%.[9, 10] While the recently announced Detal™ process, which developed by UOP as the first fixed-bed catalyst alkylation technology requires benzene/1-dodecene ratio as high as 30:1. In recent years,

ionic liquids have attracted much interest for their unique properties such as non-volatility, non-flammability, high chemical and thermal stability.[11-15] The use of ionic liquid catalysts like [cation][HSO$_4$], [bmim][Al$_2$Cl$_6$Br], [bmim][FeCl$_4$], [Et$_3$NHCl][FeCl$_3$] and [Et$_3$NHCl][AlCl$_3$] would result in high activity. These kinds of ionic liquid catalysts could not be reused for many times because of their moisture sensitivity.[16-20] Improving the durability of ionic liquid could promote its efficiency and reduce the cost. Researchers became more interested in developing stable and durable ionic liquid catalysts.[21-24] Perfluoroalkyl groups have properties of stability and hydrophobicity. Fluoro-ionic liquids are considered to be catalysts with high catalytic activity, good chemical stability and durability.

In this work, ionic liquid was prepared from 1-butyl-3-methylimidazolium bromide ([bmim]Br), lithium bis((trifluoromethyl)sulfonyl)imide (LiTFSI) and AlCl$_3$. The Lewis acidity of the catalysts was investigated by acetonitrile probe FT-IR spectroscopic. Species of ionic liquid catalysts were demonstrated by NMR spectroscopy. The effects of various reaction conditions on the synthesis of LAB were investigated. Moreover, the potential reasons to catalyst deactivation were discussed.

2 Experiment

2.1   Materials and pre-treatment:

Ionic liquid [bmim]Br, lithium salt LiTFSI were obtained from Aladdin Reagents Co., LTD. Anhydrous aluminum chloride, acetonitrile and chloroform were purchased from Sinopharm Chemical Reagent Co., LTD. Before use, liquid reagent should be refluxed using calcium hydride to remove water, then

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purified by distillation under nitrogen, solid material and ionic liquid was dried for 24 h.

2.2 Catalyst preparation and alkylation reaction:

Ionic liquid [bmim]Br was heated gently at 80 °C. The lithium salt LiTFSI was added to the melt under N_2 and stirred for 24 h. The result product was dissolved in CH_2Cl_2. LiCl was precipitated and separated by filtration. The filtrate was evaporated to dryness then the [bmim][TFSI] obtained.[25] The ionic liquid [bmim][TFSI] was heated to 80 °C, and $AlCl_3$ was slowly dissolved in [bmim][TFSI] with stirring for 6 h to ensure complete mixing. Separation of different layers was promoted by centrifugation, then different layers of the ionic liquids obtained by decantation.

The alkylation reaction was conducted in a 150 ml flask with a magnetic stirrer. Catalyst was added into the flask quantitatively, followed by benzene and 1-dodecene. After the completion of the reaction, the organic layer containing the products and reactants unreacted was separated by decantation. The organic layer was washed with water, dried over Na_2SO_4 and analyzed by gas chromatography. For the recycling experiments, the ionic liquid was extracted three times with cyclohexane, then the experiment was repeated as described above.

2.3 Analysis:

FT-IR spectra was obtained by Nicolet 5700 Fourier Transform Infrared Spectrometer, and analyzed by Nicolet OMINC 8.2 software. IR test samples were prepared by mixing ionic liquid catalyst and acetonitrile at the molar ratio of 1:1. The samples were diluted with chloroform appropriately, injected to a liquid pool with KBr windows, tested directly by Nicolet 5700 Fourier Transform Infrared spectrometer. ^{12}C-NMR, ^{19}F-NMR, ^{27}Al-NMR analysis were carried out by Agilent DD2-600 nuclear magnetic resonance spectrometer. Materials and products of reaction were investigated by gas chromatography (GC). GC was equipped with HP-5 column (30 m). The initial column temperature maintained at 110 °C for 3 min, raised at the rate of 15 °C/min and maintained at 300 °C for 9 min. The injection temperature was at 300 °C.

3 Result and discussion

3.1 Catalyst

3.1.1 Phase behaviors of catalyst

[bmim][TFSI]/$AlCl_3$ mixtures show biphasic behavior under some specific composition ranges. Many kinds of ionic liquids show these biphasic behaviors.[26-28] Wasserscheid *et al.* indicated that most of [cation][TFSI]/$AlCl_3$ ionic liquids showed biphasic behavior. Typically, a certain amount of $AlCl_3$ can be homogeneously dissolved in this kind of ionic liquids up to the lower limit of biphasic regime. With further addition of $AlCl_3$, phase separation began. Rocher *et al.* also investigated biphasic behavior of some ionic liquids at low $AlCl_3$ mole fraction (<0.5). However, few researchers have discussed the relationship between the reaction activity and the compounds structure of two-phase above. The catalysts used in this work were of relatively high $AlCl_3$ mole fraction than that of references before. Figure 1 shows the experimental phenomena of biphasic behavior. At $AlCl_3$/IL=1.0, the mixture formed a bi-phase, containing a light brown upper layer, and a turbid lower layer. At $AlCl_3$/IL=1.5, the upper layer turned opaque, and the color became darker, the lower layer turned transparent and clear. The volume of the lower phase decreased with the further addition of $AlCl_3$. Exceeding the upper limit of the bi-phase regime ($AlCl_3$/IL=3), the system

started to become monophasic again. All these bi-phase systems became monophasic when heated at or above 80 ºC.
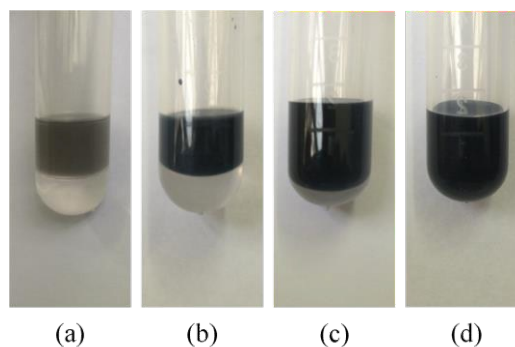
Figure 1. Phase behavior phenomena of [bmim][TFSI]/$AlCl_3$. (a)$AlCl_3$/IL=1.0, (b)$AlCl_3$/IL=1.5, (c)$AlCl_3$/IL=2.0, (d)$AlCl_3$/IL=3.0
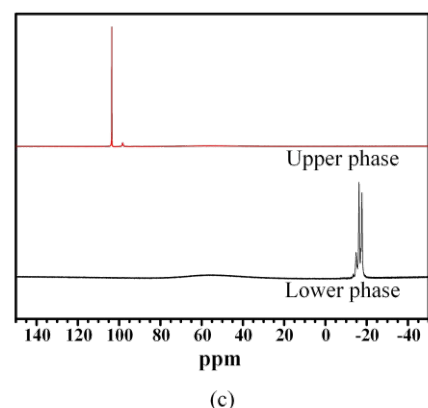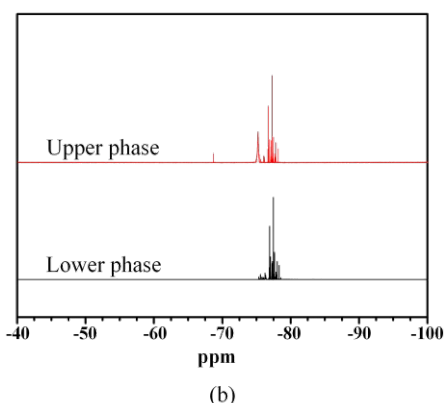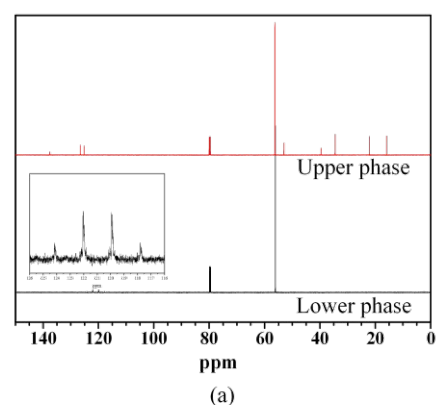
Ionic liquids like $AlCl_3$/IL have been used as catalyst for Friedel-Crafts alkylation reaction.[29-31] The upper phase and lower phase were used as catalyst directly for alkylation reaction of benzene and 1-dodecene respectively. Only the upper phase demonstrated catalysis activity when ratio of $AlCl_3$/IL≥1.5. The result shows that adding $AlCl_3$ to [bmim][TFSI] induced different structure of coordination compounds, which indicated that, different $AlCl_3$ content produces different structure of coordination compounds, which was related to the reaction activity. Among these coordination compounds, catalytic activity was shared within some coordination compounds, while some still remained inactive. Not considering the case of biphasic behaviors, while direct application of this ionic liquid as catalyst will result in inaccurate measurement of the catalyst and a waste of the ionic liquid.[32] It is necessary to obtain deeper understanding of compound structures and Lewis acidity changing in biphasic behavior.

3.1.2 NMR analysis

The upper and the lower layer of the catalyst system were studied by ^{12}C-NMR, ^{19}F-NMR and ^{27}Al-NMR spectroscopy to gain insights into the catalysis active species at $AlCl_3$/IL=1.5. Figure 2 (a) shows ^{12}C-NMR spectra for the upper and the lower phase of an example. Resonances at δ=56 ppm, δ=80 ppm are the peaks of solvent. The resonances, which were observed at 15.9 ppm, 22.0 ppm, 34.5 ppm, 39.6 ppm, 53.0 ppm, 125.0 ppm, 126.6 ppm, 137.6 ppm were attributed to [bmim]$^+$. Interestingly, no [bmim]$^+$ signal can be found in the lower phase. Resonances around 120~122 ppm were indications of [TFSI]$^-$. Two CF_3 quartets were observed in ^{12}C-NMR spectra. The two quartets were attributed to "coordinated" and "uncoordinated" [TFSI]$^-$.[27] [TFSI]$^-$ at "uncoordinated" state formed a chemical environment, which was stable and hydrophobic. Compared with [bmim]$^+$ resonances in the upper phase, [TFSI]$^-$ resonances were too small to distinguish.

Figure 2 (b) shows ^{19}F-NMR spectra for the upper and lower phase. [TFSI]$^-$ resonances were observed clearly in both the upper and lower phase. It was showed that all [bmim]$^+$ concentrate in the upper phase, there was no [bmim]$^+$ in the lower phase. However, [TFSI]$^-$ existed in both the upper phase and lower phase. ^{27}Al-NMR spectroscopy has been widely used to discuss the chemical speciation of aluminum. 4-coordinate (tetrahedral) and 6-coordinate (octahedral) were detected

both liquid phase respectively.[28] A sharp resonance signal, discovered at 104 ppm in Figure 2 (c), was attributed to the presence of tetrahedral $AlCl_4^-$ and $Al_2Cl_7^-$. Resonances around -15~20 ppm were indications of octahedral aluminum species $[Al(TFSI)_3]$ among which several isomers were found in Figure 2 (c). A small resonance was also apparent at $\delta=98$ ppm, which was identified to be a product of the reaction with residual water. Little resonances at $\delta=-3$ ppm and $\delta=94$ ppm, assigned to $[AlCl_2(NTf_2)_2]^-$ and $[AlCl_3(NTf_2)]^-$ species, appeared to exist stably only at the high temperature. The addition of $AlCl_3$ to [bmim][TFSI] led to complexation with [TFSI] first, then disproportionation of the $[AlCl_x(TFSI)_y]^-$ complexes generated $Al(TFSI)_3$ and $AlCl_4^-$.[33] And $[AlCl_x(TFSI)_y]^-$ may tend to decompose and release $AlCl_4^-$ and [TFSI]$^-$ in the system to maintain the balance of ionic content.

NMR spectroscopy investigations indicated that tetrahedral 4-coordinate species was active site for Friedel-Crafts alkylation [TFSI]$^-$ which existed in the upper layer that formed stable and hydrophobic chemical environment. As shown in Figure 3, fluoro hydrophobic groups mixed with the active sites, and filled in their surroundings of them. It makes the active sites not easy to be contacted by the moisture of reactants. However, the hydrophobic groups produced no limitation to the transportation and diffusion of the reactants. Reactants like benzene and olefin could diffuse through the layer of fluoro-ionic liquid and contact with active sites. Thus, fluoro groups formed stable and hydrophobic chemical environment and the ionic liquid catalyst had good water-resisting property and high reactivity.

(a)

(b)

(c)

Figure 2. the upper and lower phase at $AlCl_3/IL=1.5$, (a) ^{12}C-NMR, (b) ^{19}F-NMR, (c) ^{27}Al-NMR
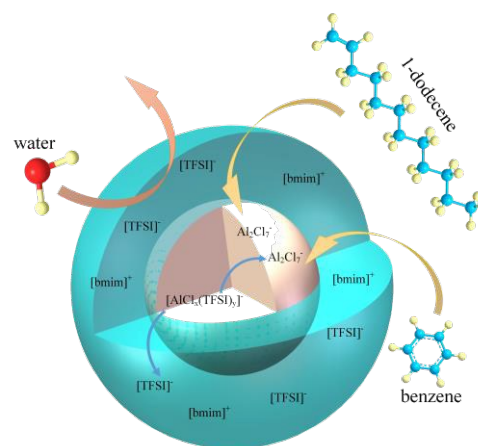
Figure 3. Illustration to the ionic liquid catalyst system

3.1.3 Lewis Acidity of Ionic Liquids

Acetonitrile probe FT-IR was performed to measure the Lewis acidity of ionic liquids, and the results are displayed in Figure 4.[34] The region from around 2252 cm^{-1} and 2293 cm^{-1} are signals of –CN stretching vibrations of acetonitrile, while ionic liquid catalyst showed no signal in regions ranging from 2500 to 2000 cm^{-1}. Once the acetonitrile mixed with Lewis acidic sites, which came from ionic liquid catalyst, the –CN stretching vibration bands shifted to higher wavenumber. The magnitude of shift could be contributed to the strength of the Lewis acidic sites.[16]
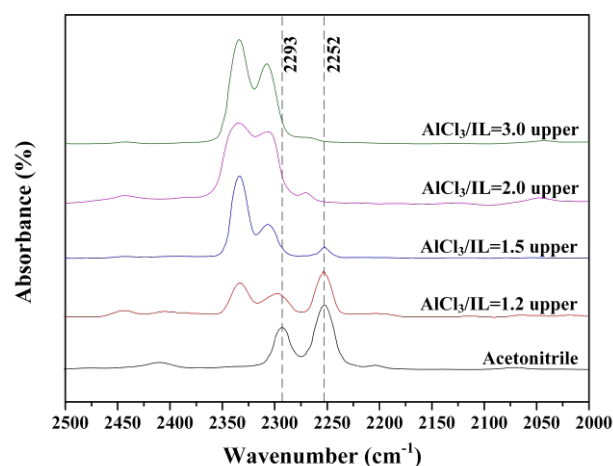
Figure 4. FT-IR of the mixture of acetonitrile and the ionic liquid catalyst

A new absorbance peak around 2330 cm^{-1} indicated the existence of Lewis acidic sites when the acetonitrile is mixed with ionic liquid catalyst. At $AlCl_3/IL=1.2$, though ionic liquid system showed no catalytic activity, but still showed Lewis acidity. At this ratio of $AlCl_3/IL$, signal at 2252 cm^{-1} and 2293 cm^{-1} became weaker, and signal at 2293 cm^{-1} shifted to higher slightly. With more $AlCl_3$ addition into ionic liquid system, the magnitude of bands at 2293 cm^{-1} shifting became larger, the intensity of bands at 2330 cm^{-1} became stronger while that of 2252 cm^{-1} became weaker. At $AlCl_3/IL=2.0$, bands at 2252 cm^{-1} shift magnitude, and the intensity of bands at 2310 cm^{-1} became stronger compared with that at $AlCl_3/IL=1.5$. With the increasing addition of $AlCl_3$, the intensity of shifted -CN stretching vibrations of acetonitrile became weaker, thus indicating the Lewis acidic strength of the ionic liquid catalyst system increased with $AlCl_3$ addition. At low $AlCl_3$ concentration ($AlCl_3/IL\leq2.0$), the Lewis acidic strength increased significantly, while the Lewis acidic strength does not go on increase obviously at high $AlCl_3$ concentration ($AlCl_3/IL > 2.0$).

3.2 Alkylation of benzene with 1-dodecene
#### 3.2.1 The effect of various reaction conditions

The influences of benzene/1-dodecene (molar ratio) for the alkylation reaction were studied at cata. =0.9 wt%, $AlCl_3/IL=2.0$, 35 °C, results is showed in Figure 5 (a) and (b).

(a)

(b)
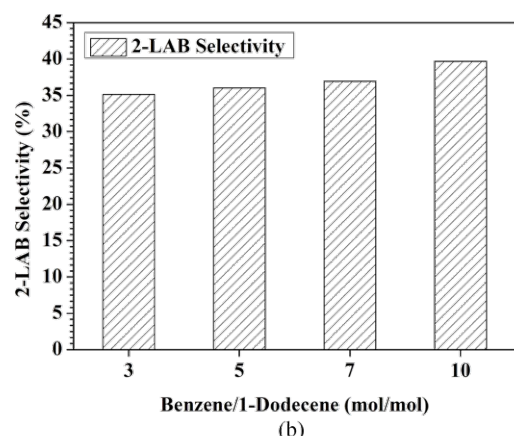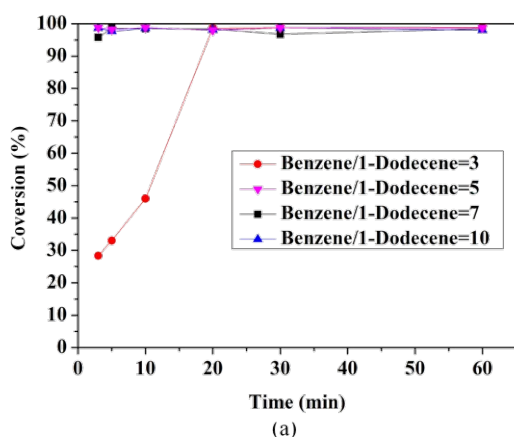
Figure 5. The effect of benzene/1-dodecene ratio on (a) conversion of 1-dodecene, (b) 2-LAB selectivity

Alkylation reaction was conducted quickly so that 1-dodecene could reach its highest conversion within a short time. As the ratio of benzene/1-dodecene increased, 2-LAB selectivity increased from 35% to about 40%. With the same Lewis acidity, increasing the ratio of benzene/1-dodecene indicated the carbenium ion concentration diluted. The reduced carbenium ion concentration could inhibit the hydrogen shift reactions and isomerization, resulting increased of 2-LAB selectivity. This is why benzene/1-dodecene ratio is as high as 30 in industrial "Detal™" process.[35, 36] However, a higher benzene/1-dodecene ratio causes a higher cost, which is resulted from surplus benzene separation and recycle.

The influence of catalyst amount and catalyst type in the reaction system is showed in Figure 6 at $AlCl_3/IL=1.5$, 35 ºC, benzene/1-dodecene=1.5. As showed in Figure 6, the amount of ionic liquid catalyst affected not only the conversion of 1-dodecene but also the selectivity of 2-LAB. Reaction was faster over $AlCl_3$ than that of $AlCl_3/IL$ for reasons of that more contact between reactant and catalyst was realized by a homogeneous reactions system. Although the reaction was faster catalyzed of $AlCl_3$, homogeneous reaction system led to a recycle difficulty. Therefore, as heterogeneous reaction catalyst, $AlCl_3/IL$ was much more favourable.
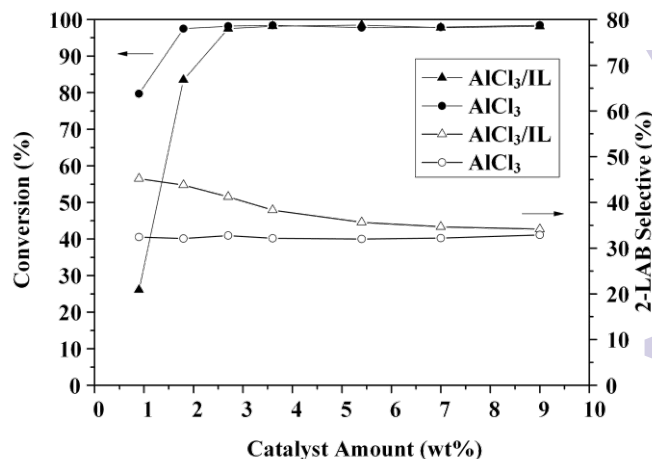
Figure 6. The effect of catalyst amount

The selectivity of 2-LAB remained at about 30% when the reaction catalyzed by $AlCl_3$. At low concentration (< 4.0 wt%) of ionic liquid catalyst, selectivity of 2-LAB reached over 40%, with the increased concentration of the ionic liquid catalyst, 2-LAB selectivity was levelled down to that of $AlCl_3$. Obviously, increased concentration of the ionic liquid catalyst caused an enhanced interaction between the reactants and the Lewis acidic species and an increasing concentration of carbenium ion. As a result, with the addition of the ionic liquid catalyst, the reaction process was much faster, yet resulted in a lower 2-LAB selectivity. Therefore, to obtain an ideal product quality, amount of the ionic liquid catalyst should be lower than 4.0 wt%.

The ionic liquid catalyst systems contained different proportion of $AlCl_3$ were applied in alkylation reaction at benzene/1-dodecene=1.5, 35 ºC, as shown in Figure 7.
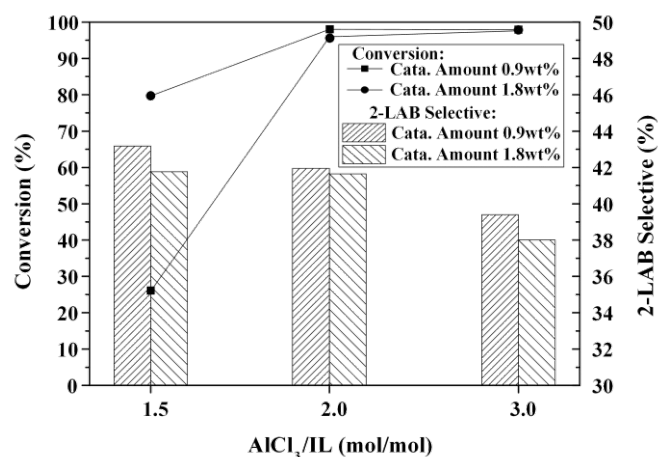
Figure 7. The effect of $AlCl_3$/IL

Aluminum species were the catalysis active centres in the alkylation reaction. The content of $AlCl_3$ influenced reaction significantly. As demonstrated in Figure 7, at the same the ionic liquid catalyst amount, a higher content of $AlCl_3$ in the ionic liquid catalyst resulted in a faster reaction rate but a lower 2-LAB selectivity. Obviously, when $AlCl_3$/IL was infinite, namely large enough, the reaction results were the same with that catalyzed by merely $AlCl_3$. Meanwhile, doubling the ionic liquid catalyst caused the increase of the reaction rate and decrease of 2-LAB selectivity.

For Friedel-Craft alkylation reaction, Lewis acid strength and Lewis acidic density significantly affected reaction. More $AlCl_3$ content in the ionic liquid catalyst induced higher Lewis acidity, namely Lewis acid strength. More amount of the ionic liquid catalyst in reaction system induced more catalysis active sites, namely Lewis acidic density. Higher Lewis acidity and larger Lewis acidic density increased the reaction rate, but decreased the 2-LAB selectivity. When Lewis acidity and acid sites were infinite, the reaction results were the same with that catalyzed by merely $AlCl_3$. Therefore, to obtain an ideal product quality, catalyst amount and catalyst composition should be controlled in a reasonable range.

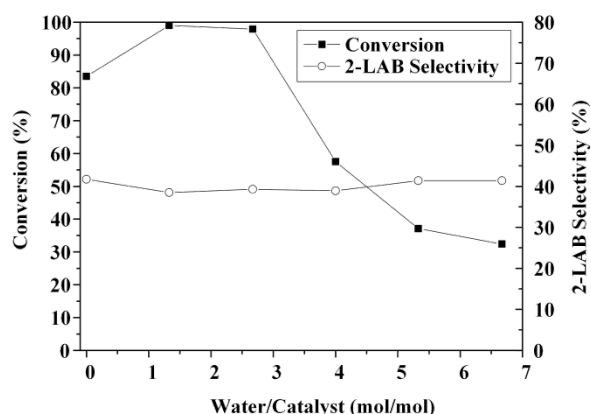### 3.2.2 Water-resisting property and reusability

Figure 8. The effect of moisture in reaction

The influence of the moisture to the reaction system is showed in Figure 8. Due to the high moisture sensitivity of $AlCl_3$, it is important to investigate the effect of the moisture on the ionic liquid catalyst. As showed in Figure 8, strict dried condition was not optimal. A small amount of moisture in the system had a positive effect on the activity of the ionic liquid catalyst. Slight moisture may cause the generation of H^+ in the system, which would accelerate the reaction. However, with the further increased moisture in the system, the activity of the ionic liquid catalyst decreased due to the decomposition of the Lewis acidic species, while 2-LAB selectivity increased slightly. This also might be ascribed to the concentration reduce of the activity species, and the carbenium, and then the isomerization was inhibited. It was worth noting that the ionic liquid catalyst could maintain a high reactivity, when the mole of moisture was larger than catalyst itself. It meant that the ionic liquid catalyst [bmim][TFSI]/$AlCl_3$ had a good water-resisting property.
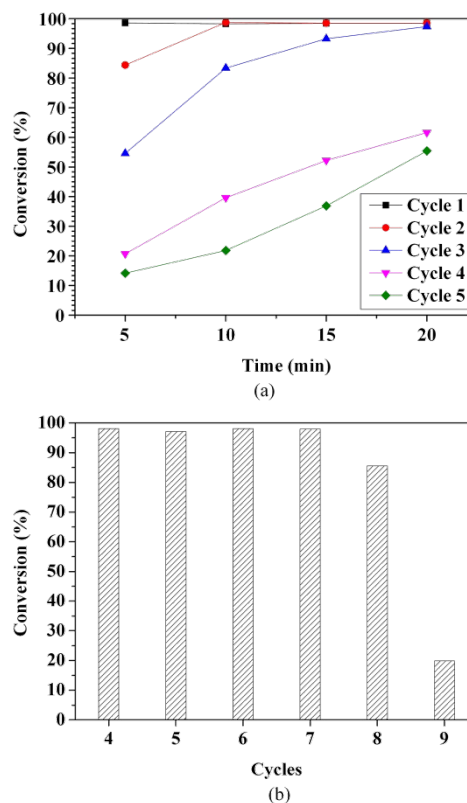

Figure 9. (a) The reusability of the ionic liquid catalyst before 5 cycles, (b) The reusability of the ionic liquid catalyst for 12 h per cycle

The reusability is one of the most important properties for the ionic liquid catalyst, which was studied in the alkylation reaction at benzene/1-dodecene=5, $AlCl_3$/IL=2.0, cata.=9.0 wt%, 35 ºC. As shown in Figure 9 (a), the reaction carried out quickly with the fresh ionic liquid catalyst. With recycle time increasing, the reaction rate reduced slowly. At the 5th cycle of catalyst, 1-dodecene conversion could still reach 50% within 20 min. In order to obtain a deeper understanding of the reusability of the ionic liquid catalyst, the reaction time was extended to 12 h, the reaction results are shown in Figure 9 (b) and Table 1. Conversion of 1-dodecene could reach nearly 100% in 12 h when catalyst recycling less than seven times. Increasing the recycle times, catalyst activity decreased significant. Conversion of 1-dodecene could only reach 20% after reaction for 12 h, while 2-LAB selectivity increased

slightly with the increasing of the recycle times. It might be caused by Lewis acidity changes.

Table 1. The reusability data of the ionic liquid catalyst for 12 h from 4th to 9th cycle.

Cycles	4	5	6	7	8	9
Conversion (%)	98.1	97.2	98.1	98.0	85.5	19.9
2-LAB Selectivity (%)	43.2	43.5	44.0	43.9	45.5	46.0

Acetonitrile probe FT-IR showed how the Lewis acidity changed, as shown in Figure 10. As the recycle times increased, intensity of absorbance peak around 2330 cm^{-1} became weaker while that of –CN stretching vibrations band at 2253 cm^{-1} became stronger which meant the decrease of the Lewis acidic density. Besides, shifting of band around 2330 cm^{-1} and band around 2310 cm^{-1} proved the decrease of the Lewis acidic strength.
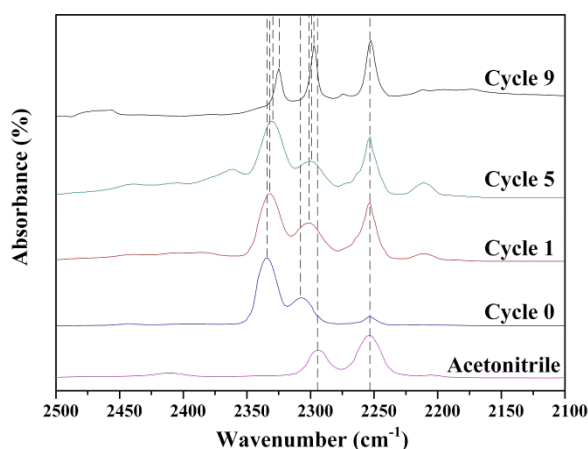
Figure 10. FT-IR of the mixture of acetonitrile and different cycle of the ionic liquid catalyst
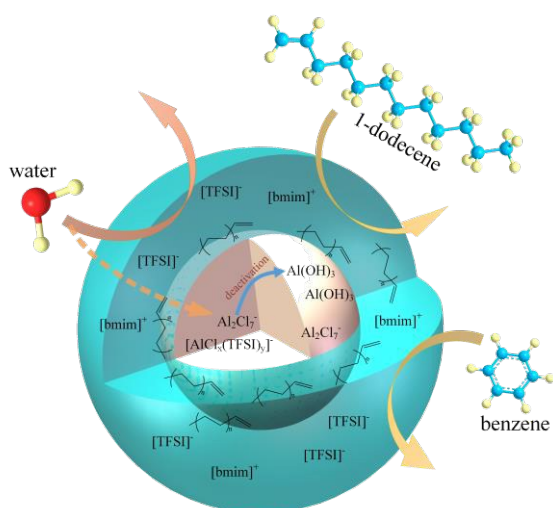
Figure 11. Illustration to the ionic liquid catalyst system after several times cycles

When the catalyst gradually lost reactivity, the situation of the catalyst was predicted and the case was showed in Figure 11. As a side-reaction, oligomer would be produced by polymerization of 1-dodecene. With the increased molecular weight of oligomer, the diffusion of the reactant will be more difficult. Thus the by-product might accumulate around the active sites, and encapsulate them in the end. As a result, reactants could not pass through and contact with the existing active sites. The acetonitrile probe FT-IR investigation also proved the catalyst acidity after deactivation. Another possible reason to catalyst deactivation was the moisture in tiny quantities passing through the hydrophobic group, and contacting with active sites, leading to hydrolysis of active sites.[37, 38]

4   Conclusions

The phase behaviors of [bmim][TFSI]/AlCl$_3$ was investigated, the upper phase of [bmim][TFSI]/AlCl$_3$ could be used as the heterogeneous ionic liquid catalyst when AlCl$_3$/IL≥1.5. Based on ^{19}F-NMR and ^{12}C-NMR investigations, no [bmim]$^+$ signals can be found in the lower phase, [TFSI]$^-$ existed in both phase at "coordinated" and "uncoordinated" state. "Uncoordinated" state [TFSI]$^-$ formed a stable and hydrophobic chemical environment, enhanced catalyst durability and water-resisting property of catalyst. ^{27}Al-NMR investigation showed that 4-coordinate (tetrahedral) aluminum species concentrated in the upper phase and 6-coordinate (octahedral) aluminum species concentrated in the lower phase. Catalysis activity of the ionic liquid catalyst was attributed to the presence of tetrahedral 4-coordinate Al$_2$Cl$_7^-$.

Acetonitrile probe FT-IR investigation showed the relationship between Lewis acidity, density, and reaction. Various parameters were investigated, including benzene/1-dodecene ratio, amount of the ionic liquid catalyst, AlCl$_3$/IL, moisture, recycle times. It is concluded that larger catalyst amount and higher AlCl$_3$ content, would result in the increase of Lewis acid density and Lewis acidity, causing a faster alkylation reaction and a lower 2-LAB selectivity, which can be explained by carbenium ion concentration. Benzene/1-dodecene ratio also significantly affected the reaction. Two potential reasons to deactivation were discussed. By-products as oligomer accumulated around and encapsulated the active sites would prevent reactants from contacting with active sites. Another possible reason to catalyst deactivation was the moisture in tiny quantities passing through the hydrophobic group, and contacting with active sites, leading to hydrolysis of active sites.

References

1. A. Aitani, J. Wang, I. Wang, S. Al-Khattaf and T. Tsai, *CATAL SURV ASIA*, 2014, **18**, 1-12.
2. G. D. Yadav and M. I. N. I. Siddiqui, *IND ENG CHEM RES*, 2009, **48**, 10803-10809.
3. D. P. Fogliatti, S. A. Kemppainen, T. N. Kalnes, J. Fan and D. R. Shonnard, *ACS SUSTAIN CHEM ENG*, 2014, **2**, 1828-1834.
4. J. L. G. de Almeida, M. Dufaux, Y. B. Taarit and C. Naccache, *Journal of the American Oil Chemists' Society*, 1994, **71**, 675-694.
5. A. M. Nielsen, L. N. Britton, C. E. Beall, T. P. McCormick and G. L. Russell, *ENVIRON SCI TECHNOL*, 1997, **31**, 3397-3404.
6. T. B. Poulsen and K. A. Jørgensen, *CHEM REV*, 2008, **108**, 2903-

2915.

7. R. Kumar, A. Kumar and A. Khanna, *Reaction Kinetics, Mechanisms and Catalysis*, 2012, **106**, 141-155.

8. M. Horňáček, P. Hudec, K. Velebná and P. Lovás, *CATAL COMMUN*, 2015, **64**, 1-5.

9. S. Sivasanker and A. Thangaraj, *J CATAL*, 1992, **138**, 386-390.

10. G. D. Yadav and N. S. Doshi, *ORG PROCESS RES DEV*, 2002, **6**, 263-272.

11. K. Matuszek, A. Chrobok, F. Coleman, K. R. Seddon and M. Swadźba-Kwaśny, *GREEN CHEM*, 2014, **16**, 3463.

12. M. Nayeri, M. T. Aronson, D. Bernin, B. F. Chmelka and A. Martinelli, *SOFT MATTER*, 2014, **10**, 5618.

13. Z. S. Qureshi, K. M. Deshmukh, K. P. Dhake and B. M. Bhanage, *RSC ADV*, 2011, **1**, 1106-1112.

14. K. Qian, Y. Q. Deng, *Journal of Molecular Catalysis. A, Chemical*, 2001, **171**, 81-84.

15. C. Qiao, Y. Cai and Q. Guo, *Frontiers of Chemical Engineering in China*, 2008, **2**, 346-352.

16. H. L. Xin, Q. Wu, M. H. Han, D. Z. Wang and Y. Jin, *Applied Catalysis A: General*, 2005, **292**, 354-361.

17. G. Qi, F. Jiang, X. Sun and S. Zhao, *Science China Chemistry*, 2010, **53**, 1102-1107.

18. C. Z. Qiao, Y. F. Zhang, J. C. Zhang and C. Y. Li, *Applied Catalysis A: General*, 2004, **276**, 61-66.

19. P. Wasserscheid, M. Sesing and W. Korth, *GREEN CHEM*, 2002, **4**, 134-138.

20. L. Y. Piao, X. Fu, Y. L. Yang, G. H. Tao and Y. Kou, *CATAL TODAY*, 2004, **93-95**, 301-305.

21. C. M. S. S. Neves, M. G. Freire and J. A. P. Coutinho, *RSC ADV*, 2012, **2**, 10882-10890.

22. Y. Zhang, A. Zhu, Q. Li, L. Li, Y. Zhao and J. Wang, *RSC ADV*, 2014, **4**, 22946.

23. S. Shahriari, L. C. Tomé, J. M. M. Araújo, L. P. N. Rebelo, J. A. P. Coutinho, I. M. Marrucho and M. G. Freire, *RSC ADV*, 2013, **3**, 1835-1843.

24. R. Gusain, R. Singh, K. L. N. Sivakumar and O. P. Khatri, *RSC ADV*, 2014, **4**, 1293-1301.

25. H. Srour, H. Rouault, C. C. Santini and Y. Chauvin, *GREEN CHEM*, 2013, **15**, 1341-1347.

26. N. Brausch, A. Metlen and P. Wasserscheid, *CHEM COMMUN*, 2004, 1552.

27. T. Rodopoulos, L. Smith, M. D. Horne and T. Rüther, *Chemistry - A European Journal*, 2010, **16**, 3815-3826.

28. N. M. Rocher, E. I. Izgorodina, T. Rüther, M. Forsyth, D. R. MacFarlane, T. Rodopoulos, M. D. Horne and A. M. Bond, *Chemistry - A European Journal*, 2009, **15**, 3435-3447.

29. L. Schilder, S. Maaß and A. Jess, *IND ENG CHEM RES*, 2013, **52**, 1877-1885.

30. J. E. Martyn, American Chemical Society, Editon edn., 2002, vol. 818, pp. 90-105.

31. V. I. Pârvulescu and C. Hardacre, *CHEM REV*, 2007, **107**, 2615-2665.

32. V. Ladnak, N. Hofmann, N. Brausch and P. Wasserscheid, *ADV SYNTH CATAL*, 2007, **349**, 719-726.

33. P. Eiden, Q. Liu, S. Zein El Abedin, F. Endres and I. Krossing, *Chemistry - A European Journal*, 2009, **15**, 3426-3434.

34. Y. Yang and Y. Kou, *CHEM COMMUN*, 2004, 226.

35. P. G, *UOP Technology and More Newsletter*, 2011.

36. C. J, C. M and V. B, *Presented at the Middle East Petrotech*, 2012.

37. J. Lin, J. Wang, J. Wang, I. Wang, R. J. Balasamy, A. Aitani, S. Al-Khattaf and T. Tsai, *J CATAL*, 2013, **300**, 81-90.

38. A. R. A. S. Deshmukh, V. K. Gumaste and B. M. Bhawal, *CATAL LETT*, 2000, **64**, 247-250.