Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction

Yibo He, Qinghua Zhang*, Xiaoli Zhan, Dang-guo Cheng, Fengqiu Chen

College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form 19 January 2016
Accepted 22 January 2016
Available online xxx

Keyword:
Ionic liquid
Friedel–Crafts alkylation
SBA-15
1-dodecene

ABSTRACT

Friedel–Crafts alkylation of benzene with 1-dodecene, which is an important reaction of synthetic detergent, was studied via ionic liquid [bmim][TFSI]/$AlCl_3$ (1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide/$AlCl_3$) immobilized on SBA-15 catalysts. XRD, BET, TEM, TG, ammonia TPD investigations were used to search insight into catalyst characteristic. The immobilized catalysts preserved ordered structure and presented high specific surface areas. The utilization of active sites was significantly improved by immobilization. Based on ammonia TPD, immobilized catalysts exhibited higher Lewis acidity than aluminum chloride grafted SBA-15. TG indicated that thermal stability of ionic liquid has been improved by immobilization. The influences of various reaction conditions including reaction time, benzene/1-dodecene ratio were studied. Immobilized ionic liquids have better performance of no matter 1-dodecene conversion or 2-linear alkyl benzene (2-LAB) selectivity, than bulk ionic liquid catalysts or aluminum chloride grafted mesoporous materials. 2-LAB selectivity can be increased from about 35% with bulk ionic liquid to more than 60% with immobilized catalysts. Under optimal condition, 2-LAB selectivity reached as high as 80%. The immobilized catalysts could be reused. And at 3th cycle of catalysts, 1-dodecene conversion could still reach more than 50%. The role of deactivation was proposed based on TEM, BET and TG investigations. By-products as oligomer, produced by oligomerization of olefin, blocked or covered the pores, led to deactivation of catalysts.

1. Introduction

Friedel–Crafts alkylation of benzene with 1-dodecene is an important reaction of synthetic detergent, which is essential to human [1,2]. It is an electrophilic substitution of hydrogen in aromatic compounds, catalyzed by Lewis acid. Generally, it is known that synthetic detergent made from linear alkyl benzene (LAB) has better biodegradability than that made from branched alkyl benzene (BAB). The phenyl group position of LAB has an effect on its surface-active properties and biodegradability of linear alkyl benzene sulfonate (LAS). Among the isomers of LAB, 2-LAB exhibits the highest biodegradability, making it a dominant detergent intermediate [3,4]. LAB is produced industrially over HF or $AlCl_3$ homogenous catalysts, which has serious disadvantages including environmental contamination, difficult separation and low 2-LAB selectivity. The 2-LAB selectivity catalyzed by homogeneous catalysts $AlCl_3$ or HF is in the ranges from 26–33% [1] and 14–20% [5,6]. Moreover, homogeneous system is one of main reasons to environment contamination and difficult separation. The most effectual method to solve these problems is introducing heterogeneous catalyst [7]. While the recently announced "Detal^{TM}" process, which was developed by UOP as the first fixed-bed catalyst alkylation technology requires benzene/1-dodecene ratio as high as 30:1 [1]. Aluminum chloride grafted catalysts is the other one of heterogeneous catalysts for this reaction. Aluminum chloride can be grafted on the surface of such solid to produce Lewis acidic sites, which Friedel–Crafts alkylation needed [8–11]. Bordoloi et al. has synthesized AlMCM-41/beta zeolite and discussed the shape selective synthesis of LAB [12]. Some other modification of zeolites such as desilicated zeolites, 10-ring zeolites (TUN, IMF, etc.) and alkaline-modified mordenite were also widely reported [13–15].

In recent years, ionic liquids have attracted much interest for their unique properties such as non-volatility, non-flammability, high chemical and thermal stability [16,17]. Some of ionic liquids can provide Lewis or Brønsted acidic sites. It is reported that hygroscopic ionic liquid catalysts like [cation][HSO_4], [bmim][Al_2Cl_6Br], [bmim][$FeCl_4$], [Et_3NHCl][$FeCl_3$] and [Et_3NHCl][$AlCl_3$] would result in high acitivity [18–22]. A novel ionic liquid [bmim][TFSI]/$AlCl_3$ catalyst has been developed in our previous work, which has better properties of stability and durability due to the existing of per-

---

* Corresponding author.
E-mail address: qhzhang@zju.edu.cn (Q. Zhang).

http://dx.doi.org/10.1016/j.cattod.2016.01.045
0920-5861/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

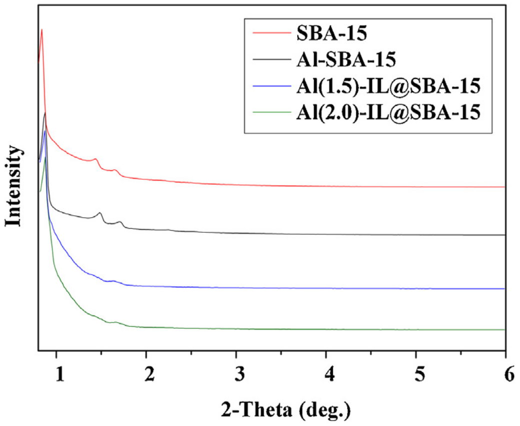


Fig. 1. X-ray diffraction of different catalyst samples.

fluoroalkyl groups [23]. But ionic liquid catalyst amount used in reaction still as high as 5% to 10%, even 20% [24,25].

Indeed, many reports have become available, describing the use of the ionic liquids immobilized on various supports for synthesis of diphenylmethane, synthesis of dimethyl carbonate and epoxidation [26–28]. German researchers reported an immobilized ionic liquid catalyst for alkylation [29]. And no leaching ionic liquid in reaction mixture was found in that research. The immobilization process transferring the desired catalytic properties of the liquids to solid catalysts could combine the advantages of ionic liquids with those of heterogeneous support materials. It overcomes some shortcomings and extends the application of ionic liquid, significantly [30–33].

In this work, highly ordering mesoporous material SBA-15 has been synthesized. Aiming at declining in the ionic liquid catalyst amount, ionic liquid [bmim][TFSI]/$AlCl_3$ was immobilized on SBA-15. XRD, BET, TEM, TG analysis were carried out to investigate the structure of catalysts. Ionic liquids thermal stability and ionic liquids loading amount of immobilization catalysts were measured by TG analysis. TEM gave insight into nano-scale structure of catalysts. Ammonia TPD was used to measure Lewis acidity of catalysts. And the effects of various reaction condition, which were on the synthesis of LAB, were discussed. Moreover, the role of catalysts deactivation was proposed based on TEM, BET and TG investigation.

2. Experiment

2.1. Materials

Ionic liquid 1-butyl-3-methylimidazolium bromide ([bmim]Br), bistrifluoromethanesulfonimidate (LiTFSI) and triblock copolymers Pluronic® P123 ($EO_{20}PO_{70}EO_{20}$) were obtained from Aladdin Reagents Co., Ltd. Anhydrous aluminum chloride, chloroform and other reactants or feedstock were purchased from Sinopharm Chemical Reagent Co., Ltd. Before use, liquid reagent should be refluxed using calcium hydride to remove water, then purified by distillation under nitrogen. Solid material and ionic liquid were dried for 24 h.

2.2. Catalysts preparation

SBA-15 mesoporous materials used in this work was synthesized in a typical method [34,35]. 4 g of Pluoronic® P123, water and HCl (0.28 M) were stirred at 35 °C for 16 h. The appropriate amount of tetraethylorthosilicate (TEOS, 8.5 g) was then added dropwise to the surfactant solution, followed by stirring for 24 h. The resulting gel was introduced into a Teflon lined stainless steel autoclave and heated at 100 °C for two days. The products were filtered, washed with warm distilled water and finally dried at 100 °C, followed by calcination in air at 500 °C, then kept under dry argon.

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. Adding CH_2Cl_2, LiBr was precipitated and separated by filtration. The filtrate was evaporated to dryness then the [bmim][TFSI] obtained [36]. 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 [23]. The ionic liquid [bmim][TFSI]/$AlCl_3$ was denoted as Al(1.5)-IL. The number in brackets demonstrated the molar ratio of $AlCl_3$: [bmim][TFSI].

As previously reported, the air present in the cavities of porous materials can be completely removed through evacuation under vacuum conditions, so that filling the cavities with ionic liquid becomes relatively easy [37]. 1 g of SBA-15 was placed in a two-neck flask, one of the necks was equipped a liquid addition injector, the other was connected to a vacuum equipment. The flask with mesoporous materials was heated at 185 °C for 4 h under vacuum conditions to draw out the gas inside the SiO_2. Then 0.5 g of ionic liquid [bmim][TFSI]/$AlCl_3$ dissolved in CH_2Cl_2 was transferred into

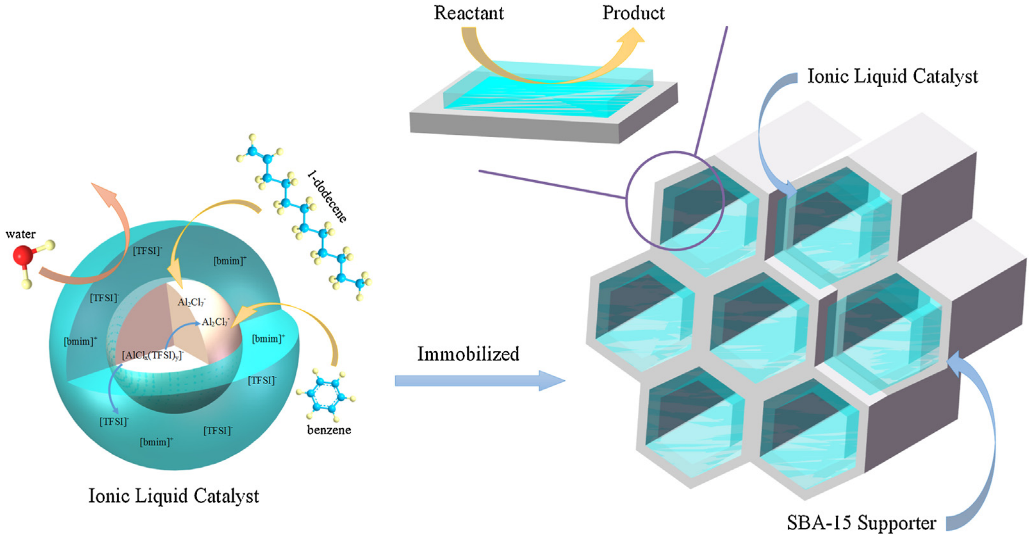


Fig. 2. Illustrations to the ionic liquid catalyst & immobilized catalyst system.

Table 1
N_2 adsorption–desorption isotherms analysis of different samples.

Samples	BET surface area (m^2/g)	Volume of pores (cm^3/g)	Average pore diameter (nm)
SBA-15	751.1	1.24	6.65
Al(1.5)-IL@SBA-15	322.8	0.61	5.51
Al(2.0)-IL@SBA-15	224.0	0.33	5.56
Al(1.5)-IL@SBA-15 AR	33.2	0.06	3.96
Al(2.0)-IL@SBA-15 AR	7.7	0.03	2.34

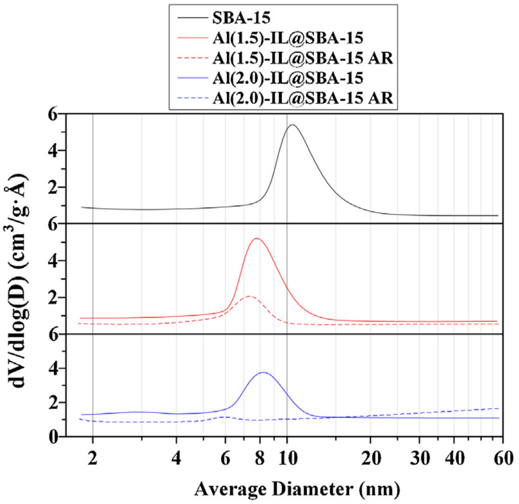


Fig. 3. Average diameter of pore size of different catalyst samples.

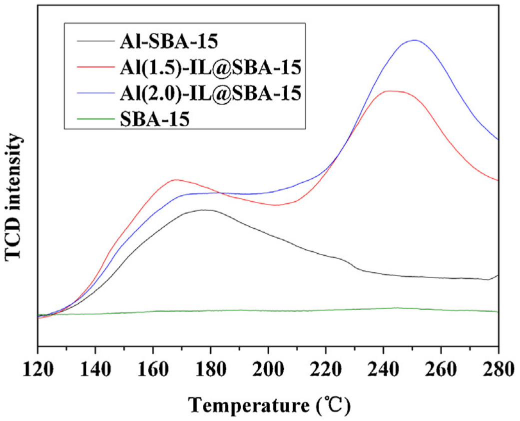


Fig. 4. Ammonia TPD analysis of different catalysis samples.

the flask through a syringe, and the mixture was refluxed for 6 h at 60 °C to fill the pores with ionic liquids. The solvent was distilled out and the resulting mixture was cooled for 3 h at room temperature. The immobilized samples were separated and further purified through three cycles of washing with CH_2Cl_2, to completely remove the [bmim][TFSI]/$AlCl_3$ adsorbed on the surface. Then, immobilized catalysts were dried for 12 h at 50 °C (denoted as Al(1.5)-IL@SBA-15 or Al(2.0)-IL@SBA-15) [38]. Aluminum chloride grafted SBA-15 was synthesized in a reported method (denoted as Al-SBA-15) [39].

2.3. Characterization

N_2 adsorption–desorption isotherms analysis of the catalysts were measured using N_2 as a sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP2020). The phase identification of catalysts was carried out by powder X-ray diffraction (XRD) on XRD 6000 (Shimadzu) equipped with Cu Kα radiation at 40 kV and 30 mA. Temperature-programmed desorption (TPD) of ammonia was performed in AutoChem II 2920, equipped with a thermal conductivity detector (TCD). The thermal stabilities were measured using a TA-Q500 thermogravimetric analyzer (TGA). Transmission electron microscope (TEM) images were obtained with Tecnai G2 F20 S-TWIN. Materials and products of reaction were investigated by gas chromatography (GC). GC was equipped with HP-5 column (30 m).

2.4. Friedel–Crafts alkylation reaction

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 centrifugation. The organic layer was washed with water, dried over Na_2SO_4 and analyzed by GC. The catalyst separated by centrifugation was washed by benzene, then was used for recycling experiments.

Conversion of 1-dodecene and LAB selectivity were calculated as follows:

$$\text{dodecene conversion} = 1 - \frac{\text{dodecene}_{\text{unreacted}}}{\text{dodecene}_{\text{feed}}} \times 100\%$$

$$\text{LAB}_{\text{i}}\text{selectivity} = \frac{\text{LAB}_{\text{i}}}{\sum_{2}^{6}\text{LAB}_{\text{i}}\ \text{isomers}} \times 100\%$$

3. Results and discussion

3.1. Characterization

X-ray diffraction (XRD) patterns of SBA-15, and catalysts with different Al-IL were shown in Fig. 1. In the case of SBA-15, the three typical peaks were observed in the region of $2\theta < 5°$, which can be indexed as the (1 0 0), (1 1 0) and (2 0 0) reflections of ordered mesoporous structure. XRD peak intensity of Al(1.5)-IL@SBA-15 and Al(2.0)-IL@SBA-15 was decreased and became broader, as compared with that of SBA-15 [40]. It was even decreased as compared with that of Al-SBA-15, it resulted from the disturbs on the structure order, which was a consequence of the surface modification. Though the peak intensity was decreased after immobilization, the diffraction peaks could still be detected even after immobilization, which indicated that ordering mesoporous structure was partial preserved [32,41,42].

In previous reports, ionic liquids [bmim][TFSI]/$AlCl_3$ catalyst has been proved to have properties of stability and durability. Fig. 2 demonstrates the illustrations to the ionic liquid catalysts and immobilized catalysts system. As shown in Fig. 2, fluoro ionic liquid mixed with the active sites, and filled in their surroundings. The ionic liquid catalyst was immobilized on SBA-15, and covered the internal surface of mesoporous pores, as shown in Fig. 2. Reactants like benzene and olefin could diffuse through the layer of ionic liquid and contact with active sites [23].

The results of catalysts surface properties investigation are given in Table 1. The specific surface areas of SBA-15 mesoporous material, which was synthesized in a typical method, was estimated

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

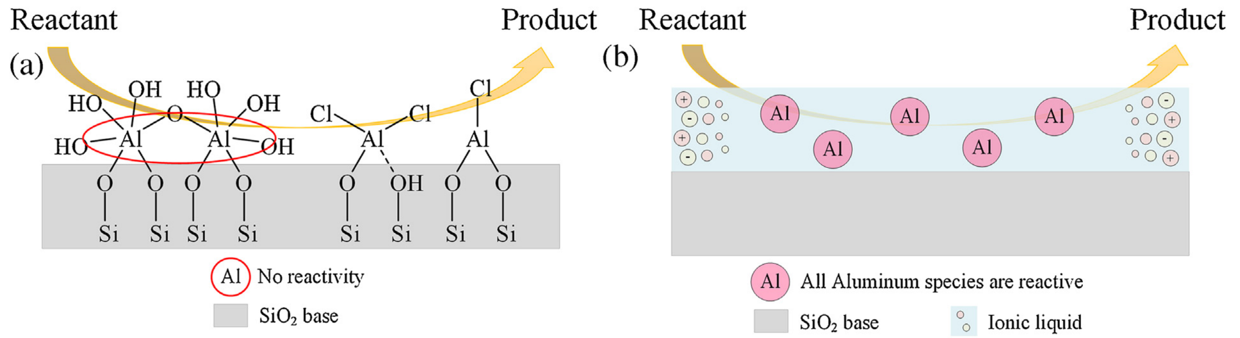


Fig. 5. Illustrations to (a) Al-SBA-15 (b) Al-IL@SBA-15 samples.

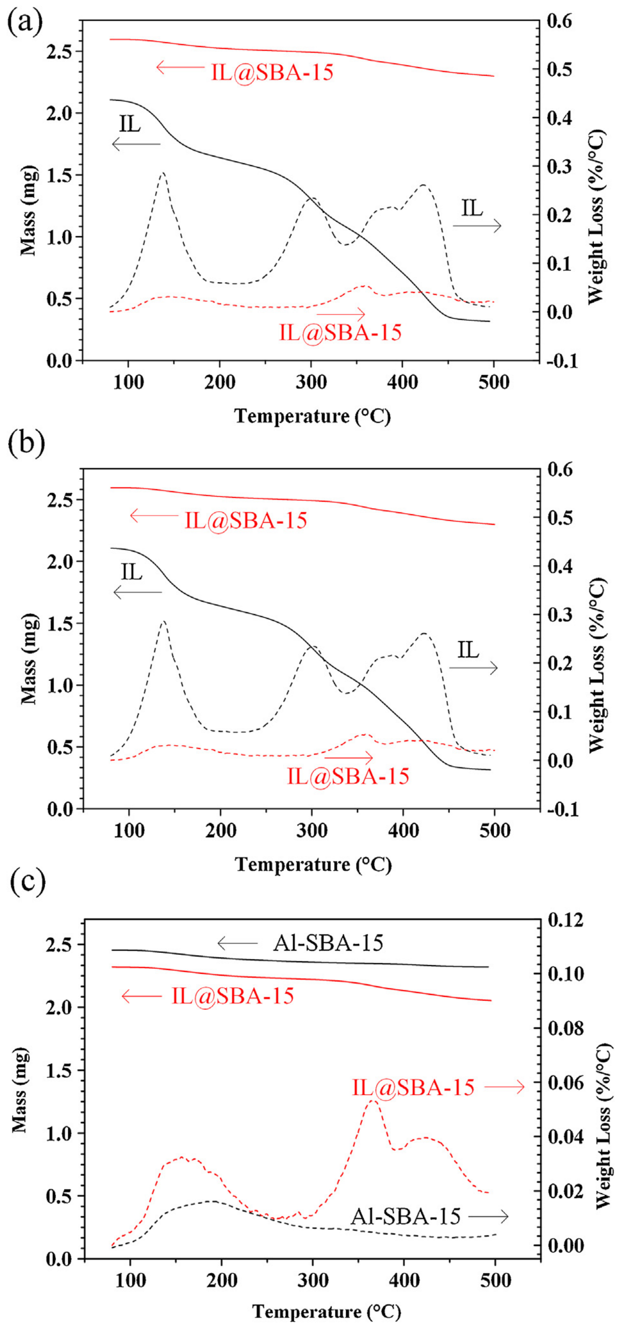


Fig. 6. TG analysis of (a) Al(1.5)-IL@SBA-15 (b) Al(2.0)-IL@SBA-15 (c) Al-SBA-15 samples.

as 751 m^2/g. After immobilization of ionic liquid catalyst, the specific surface areas, volume of pores and average pore diameter all decreased. The pore diameter of immobilized catalysts became narrower because the internal surface of the pore was covered by ionic liquid. It also led to decreasing of the volume of pores and average pore diameter. This led to decreasing of the specific surface areas and volume of pores. While adding the Al species content in ionic liquid, the specific surface areas was declined slightly. In this case, ionic liquid may not only cover the internal surface of the pores, but also fill the pores. When deactivation of catalysts occurred after reaction was conducted several times (denoted as Al(1.5)-IL@SBA-15 AR & Al(2.0)-IL@SBA-15 AR, mark “AR” mean “After Reaction”), the specific surface areas, volume of pores and average pore diameter declined significantly. It may be caused by blockage of pores, which resulted from oligomerization of olefin. Despite the specific surface areas, and volume of pores were greatly reduced compared with parent SBA-15, the data might not as accurate as other samples, it still indicated qualitatively the decline tendency of BET surface.

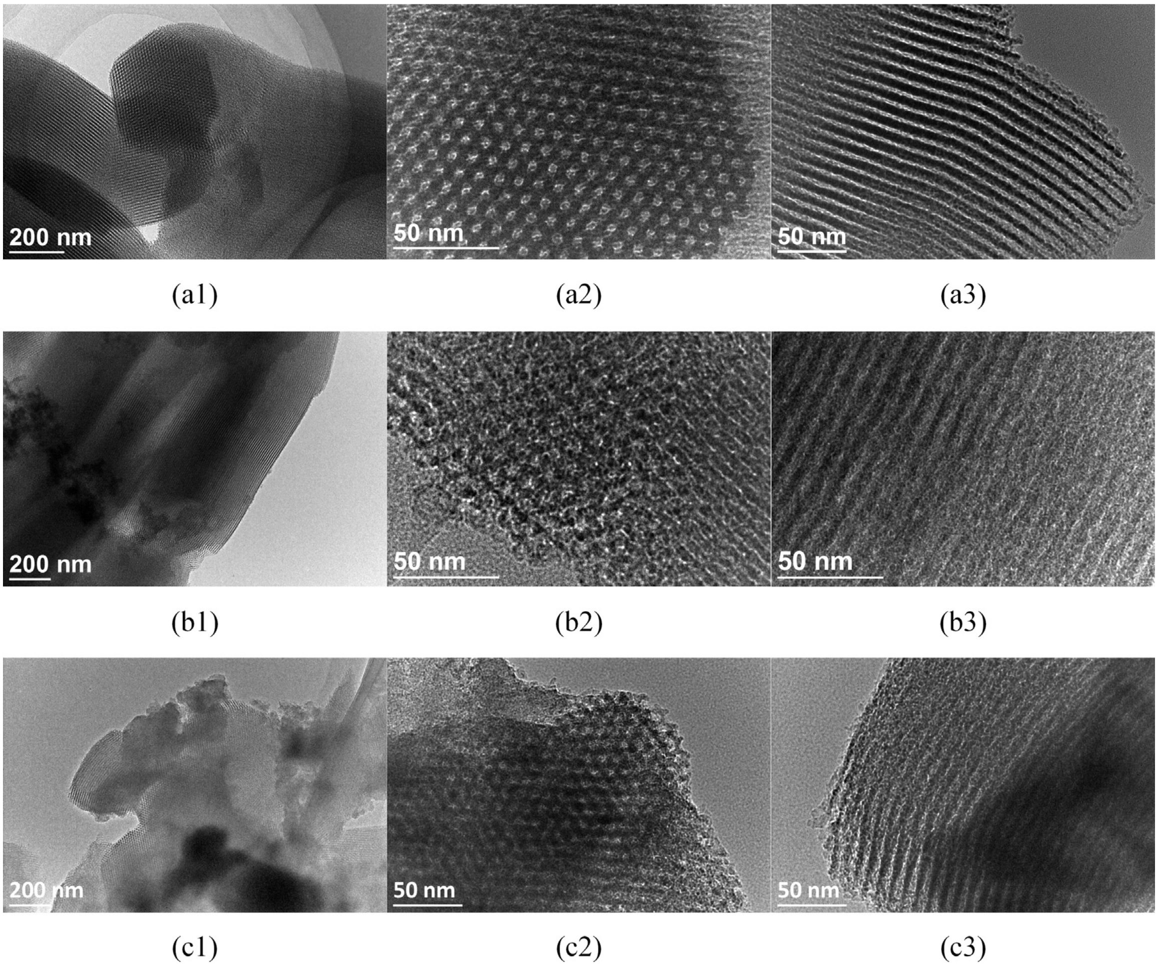
Fig. 3 gives the average diameter of pore size distribution of different catalyst samples before and after immobilization. The average pore size of parent SBA-15 was slightly larger than that of other samples after surface modification. The pore diameter of immobilized catalysts became narrower because ionic liquid covered the surface of the pore. Immobilization of ionic liquid may also cause some damages and partially collapsed of pore structure. The coverage or the filling enlarged the thickness of pores wall, reduced the specific surface and volume of pores. While partially damage or collapse increased volume of pores. As a result, pore size distribution became wider after surface modification. But in this case, the effect of pore coverage greatly exceeded the effect of pore collapse. That was the reason why decreasing of pore volumes and becoming lower of the distribution peaks of SBA-15 were observed for immobilized ionic liquid catalysts.

The density of acid sites was determined by ammonia thermosdesorption (ammonia TPD). Fig. 4 shows the parent SBA-15, the ammonia TPD of aluminum chloride grafted mesoporous material and other two Al-IL supported mesoporous materials. Desorption curves of supported Al-IL mesoporous material presented two important peaks at 170 °C, and 250 °C, while aluminum chloride grafted mesoporous material presented only one, the parent SBA-15 almost showed no peaks between test temperature. Peaks around 200 °C and 250 °C are attributed to Lewis acid type [8,43]. In this case, higher content of Al species in Al-IL led to higher density of acid sites, because Lewis acid sites were produced by tetrahedral 4-coordinate Al species. Comparing with two ionic liquid supported SBA-15, peak presented by Al-SBA-15 was very weak at 250 °C, and peak around 170 °C also was weaker than SBA-15 supported Al-IL neither. It can be explained by higher Al atom utilization of SBA-15 immobilized Al-IL. Moreover, as our previous report, ionic

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

Table 2
Calculation results of TG analysis.

Sample	~200 °C weight loss	200–500 °C weight loss	Total weight loss
Al-IL	22.08%	62.95%	85.02%
Al(1.5)-IL@SBA-15	2.75%	8.77%	11.52%
Al(2.0)-IL@SBA-15	2.69%	8.74%	11.43%



(a1) (a2) (a3)

(b1) (b2) (b3)

(c1) (c2) (c3)

Fig. 7. TEM images of (a) SBA-15 (b) SBA-15 immobilized ionic liquid (c) immobilized catalysts after deactivation.

liquid catalysts had higher stability than $AlCl_3$. Dubé reported that $AlCl_3$ supported catalysts may loss Lewis sites when exposed to ambient air moisture, resulted in declining of the signal in ammonia desorbed [8]. Due to the stability of ionic liquid, the density of Lewis acid sites can be kept for SBA-15 immobilized Al-IL. However, decomposition might be happened for ionic liquid when temperature was excessively high, thus the temperature in ammonia TPD was limited to 280 °C.

As shown in Fig. 5, when $AlCl_3$ was grafted onto SBA-15 material, partial Al atoms could connect more than 3 O atoms. It resulted in octahedral 6-coordinated Al species, which have no reaction activity [8,44]. On the contrary, all ionic liquid surrounding Al species kept reactivity [23,45,46]. In this opinion, SBA-15 immobilized ionic liquid catalysts had higher atom utilization ratio than that of $AlCl_3$ grafted, and more satisfied the green chemical feature.

Besides XRD profile, thermal gravimetric analysis of the catalysts gave qualitative information about the success of the immobilization. As shown in Fig. 6, atmospheric water, which was absorbed during the handling of hygroscopic species, was eliminated about 150 °C. The following step was the decomposition of the salt and finally a stable residue was obtained. Between 250 °C to 500 °C, weight loss in composite material was due to the decomposition of different species in ionic liquid. In Fig. 6, TGA curve of immobilized catalysts were similar to that of Al-IL, but the temperature of each main mass-loss stage became higher after immobilization. Similar curves were evidence of successful immobilization of ionic liquid. It has been reported that the confinement in the nano-pores led to a compression of molecular size and an increase in the melting point [47]. Therefore, immobilization on SBA-15 contributed to enhancing the thermal stability of ionic liquid catalysts. Comparing with IL@SBA-15, TG profile of Al-SBA-15 sample presented a similar peak, which indicated atmospheric water, below 200 °C. However, peaks could hardly be found after 300 °C for Al-SBA-15. It is because that almost no organic content existed in Al-SBA-15 sample.

The calculation results of TG analysis were demonstrated in Table 2. Ionic liquid lost about 22% weight before 200 °C due to its hygroscopicity. Between 200 °C to 500 °C, samples lost their residual organic component. Therefore, calculating weight loss between 200 °C to 500 °C would result in the quantitative loading of ionic liq-

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

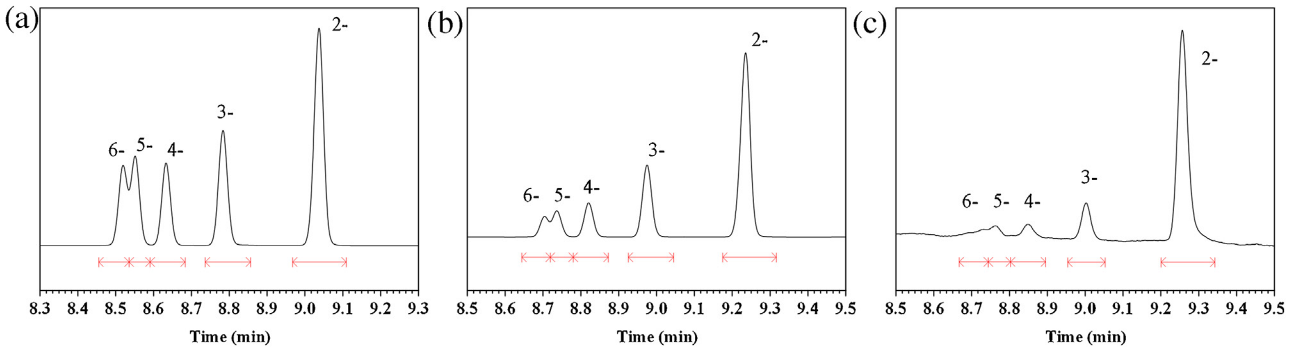


Fig. 8. GC spectrum examples of Friedel–Crafts alkylation products of benzene with 1-dodecene.

Table 3
The results of the benzene alkylation with 1-dodecene over various catalysts.

Catalyst	Catalyst amount	Conversion	Selectivity				
			2-LAB	3-LAB	4-LAB	5-LAB	6-LAB
Al(1.5)-IL	0.5%	0.0%	–	–	–	–	–
Al(2.0)-IL	10%	98.9%	32.7%	19.0%	15.1%	17.2%	16.1%
$AlCl_3$@SBA-15	5%	97.2%	49.0%	21.3%	14.1%	8.7%	6.9%
Al(1.5)-IL@SBA-15	2%	36.1%	67.6%	18.3%	6.8%	4.4%	3.0%
Al(1.5)-IL@SBA-15	5%	98.2%	60.0%	20.3%	8.7%	6.3%	4.6%
Al(2.0)-IL@SBA-15	5%	99.4%	57.5%	20.7%	9.1%	7.5%	5.2%
Al(1.5)-IL@SBA-15	10%	99.2%	59.5%	18.9%	8.1%	6.4%	7.1%

uids. And according to the calculating, two ionic liquid immobilized catalyst samples lost about 8.7% weight, it demonstrated that they have similar ionic liquid capacity, though Al species of these two samples were different.

The ordered mesostructure of parent mesoporous material, immobilized catalysts and catalysts after deactivation can be further confirmed by TEM analysis. In Fig. 7, x1 (a1, b1, c1) demonstrated the panorama of mesoporous material, x2 (a2, b2, c2) presented the direction along and x3 (a3, b3, c3) presented perpendicular to the pore axis. The TEM images of SBA-15 synthesized before are given in Fig. 7(a1–3). All of them showed clear pore and pore wall, demonstrated highly ordered hexagonal array of SBA-15. After ionic liquid immobilization, pore and pore wall, which are shown in Fig. 7(b1–3), cannot be identified as clear as before. However, combining the XRD results with TEM observations, it was clear that the immobilized sample retained its structural integrity and the parallel alignment of channels were essentially unchanged after successive ionic liquid loading process. These observations also suggested that the successful modification of inner pore of ionic liquids on their surface. TEM images of immobilized catalysts after deactivation are shown in Fig. 7(c1–3), some shadow can be seen clearly in these images, which came from oligomer, produced by oligomerization of olefin. After reaction cycled several times, oligomer accumulated and its molecular weight increased, then the active sites were encapsulated and pores were blocked. As results, the specific surface areas of catalysts decreased, reactivity was lost gradually.

3.2. *Alkylation results*

The GC spectrum examples of alkylation products of benzene with 1-dodecene are shown in Fig. 8. Different peaks appeared in Fig. 8 indicated different isomers of LAB. These spectrum peaks are assigned as 6-LAB, 5-LAB, 4-LAB, 3-LAB and 2-LAB with increasing retention time, respectively. LAB selectivity were calculated based on the integral area of different isomers of LAB with the formula mentioned before. In Fig. 8(a)–(c), 2-LAB selectivity in the cases were about 35%, 60% and 80% respectively. It can be obviously seen

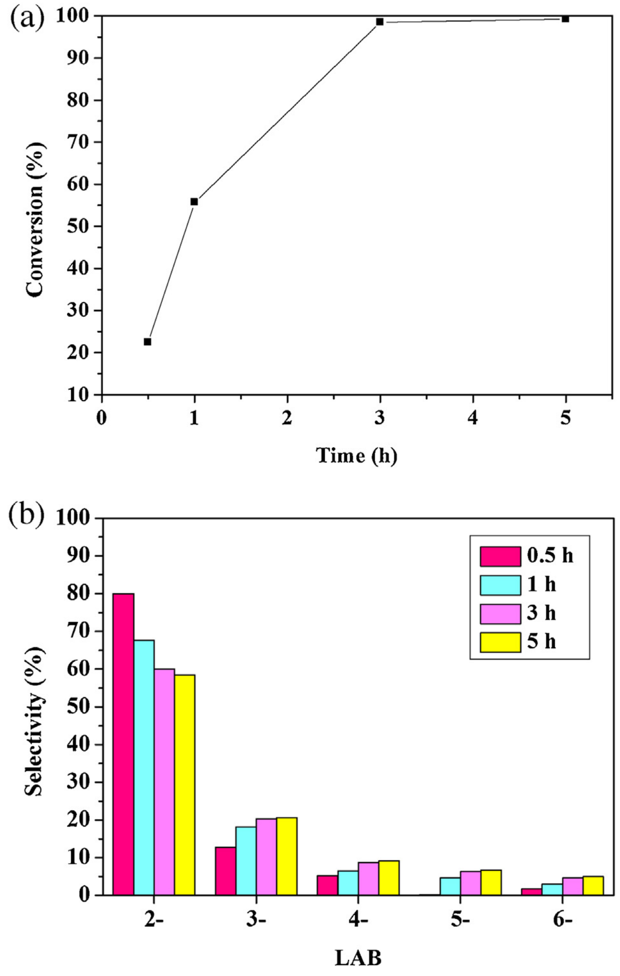


Fig. 9. The influences of reaction time for the alkylation reaction (a) 1-dodecene conversion (b) the distribution of product.

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

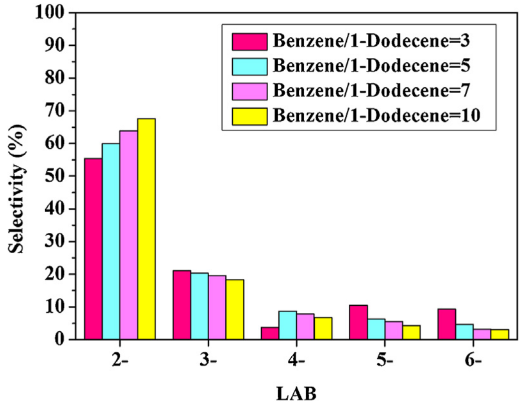


Fig. 10. The influences of benzene/1-dodecene (molar ratio) for the alkylation reaction on the distribution of product.

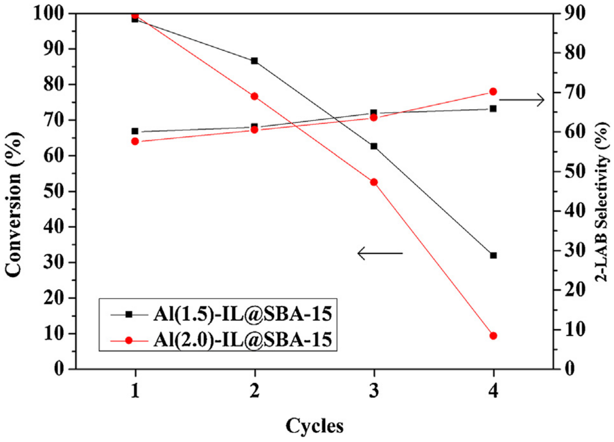


Fig. 11. The reusability of the immobilized ionic liquid catalysts.

that 2-LAB selectivity with immobilized ionic liquid catalyst (more than 60%, Fig. 8(b)) was higher than that with Al-IL catalyst (about 35%, Fig. 8(a)). Under certain conditions, 2-LAB selectivity reached about 80% (Fig. 8(c)).

The results of the benzene alkylation with 1-dodecene over various catalysts at benzene/1-dodecene (molar ratio = 5), 35 °C are present in Table 3. Al(1.5)-IL and Al(2.0)-IL were liquid catalysts. The reaction highly conducted when add 10 wt% catalysts. It indicated that the reaction can conduct quickly, and the catalyst amount can be lower than 10 wt%. In this case, mole of Al species in Al(2.0)-IL was much higher than that of Al(1.5)-IL@SBA-15, due to the existing of silica in Al(1.5)-IL@SBA-15. When mole of Al species were equal, reaction with Al(1.5)-IL@SBA-15 (5 wt%) conducted while reaction with Al(1.5)-IL did not. With the same amount of Al species, immobilized catalysts dispersed active sites better than ionic liquid, due to the highly specific surface areas of supporter. While reaction could only conduct on the surface of ionic liquid droplet with ionic liquid heterogeneous catalysts. Thus higher efficiency could be reached for immobilized catalysts. With solid catalysts, 2-LAB selectivity was lower for reaction with no ionic liquid, Al(2.0)-IL, than others. The distribution of product was tend toward high substituent formation. Ionic liquid may have the ability to maintain 2- isomer stable, and inhibit the isomerization. Higher catalyst amount resulted in more active sites, led to stronger interaction between the reactants and active sites, higher concentration of carbenium ion, and lower 2-LAB selectivity. But proper amount of catalyst led to economic reaction rate. 5 wt% was chosen as a proper ratio of catalysts for the reaction. Aluminum species were the active sites in the alkylation reaction. Adding the Al species content in Al-IL of Al-IL@SBA-15 also caused increasing of the concentration of active sites, and decline the 2-LAB selectivity. Moreover, excessively high Al species in Al-IL led to the waste of active species.

The influences of reaction time for the alkylation reaction were studied under well-optimized conditions, results are shown in Fig. 9. 1-dodecene could reach its highest conversion within 3 h in the alkylation reaction. When reaction was carried out for 0.5 h, 1-dodecene conversion was only about 23%, while 2-LAB selectivity was as high as 80%. During 0.5 h, only small amount of 1-dodecene changed into carbenium ion, so the concentration of carbenium ion was really low. It resulted in insufficiency of isomerization, and higher 2-LAB selectivity. Longer reaction time gave more feedstock for isomerization, which resulted in the decline of 2-LAB selectivity.

The influences of benzene/1-dodecene (molar ratio) for the alkylation reaction were studied under well-optimized conditions, results are shown in Fig. 10. As the ratio of benzene/1-dodecene increased from 3 to 10, 2-LAB selectivity increased from 55% to nearly 70%, 5-LAB or 6-LAB selectivity decreased from 10% to about 5%. 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 in increase of 2-LAB selectivity. That is why benzene/1-dodecene ratio is as high as 30 in industrial "Detal^{TM}" process. However, a higher benzene/1-dodecene ratio causes a higher cost, which is resulted from surplus benzene separation and recycle.

The reusability is one of the most important properties for catalysts, which was studied in the alkylation reaction under well-optimized conditions. The results are showed in Fig. 11.

The reaction could reach nearly 100% conversion of 1-dodecene when the first cycle of the immobilized ionic liquid catalysts. With recycle time increasing, the reaction rate reduced quickly, but 2-LAB selectivity increase slightly. 2-LAB selectivity with Al(2.0)-IL@SBA-15 was lower than that with Al(1.5)-IL@SBA-15 at first, but it became higher at last. 2-LAB selectivity was negatively associated with 1-dodecene conversion. Lower 1-dodecene conversion gave smaller feedstock concentration for isomerization, which resulted in the decline of 2-LAB selectivity. At the 3th cycle of catalysts, 1-dodecene conversion could still reach more than 50%. Higher Al species content in ionic liquid may enhance the Lewis acidity and reactivity of catalyst, while it declined the reusability. The role of deactivation was proposed based on investigation of TEM and BET, as shown in Fig. 12. The TG analysis of deactivated catalyst is showed in Fig. 13, sample continuous lost weight with temperature rising. The continuous weight loss might be resulted from decomposing of oligomer with different molecular weight.

For active catalyst, the ionic liquid covered the carrier surface. Reactants like benzene and olefin could diffuse through the layer of ionic liquid and contact with active sites. During reaction, by-products as oligomer produced by oligomerization of olefin. With the molecular weight increasing, pores were blocked and active sites were covered, as the shadow in TEM images. The oligomerization prevented the reactants from contacting with active sites, then the deactivation of catalyst occurred.

4. Conclusion

Highly ordering mesoporous material SBA-15, which has the property of high specific surface areas, has been successful synthesized. Based on XRD, BET, TEM, TG analysis, ionic liquid [bmim][TFSI]/$AlCl_3$ was proved to be immobilized on SBA-15, covered the internal surface of the pores. XRD and TEM analysis indicated that the mesoporous structure (the hexagonal arranged pore array) and the high specific surface areas were preserved

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

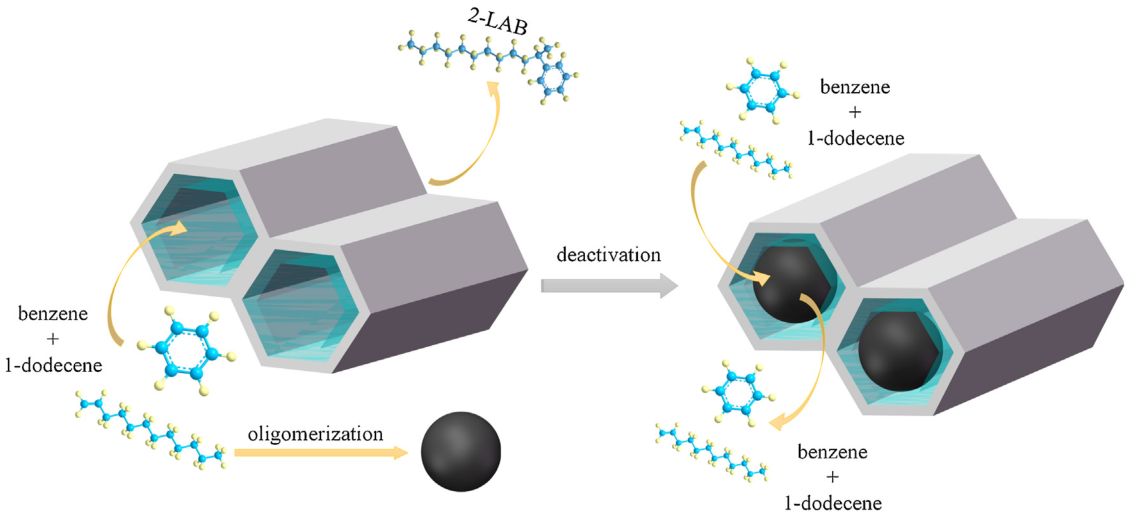


Fig. 12. Illustration to the role of deactivation.

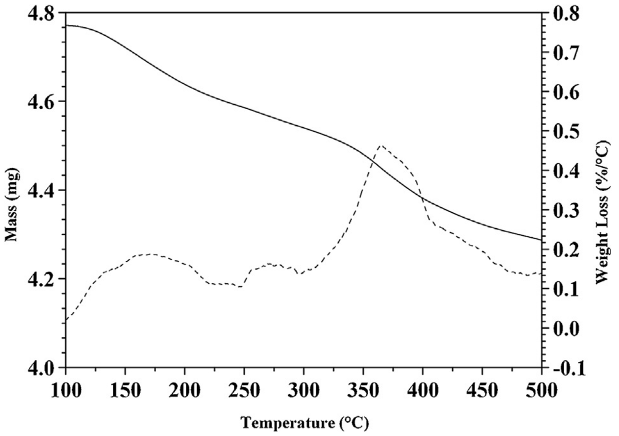


Fig. 13. TG analysis of catalysts sample after deactivation.

after immobilization. Compared to aluminum chloride grafted mesoporous material, SBA-15 immobilized ionic liquids presented higher Lewis acidity according to ammonia TPD analysis. In ammonia TPD analysis, immobilized ionic liquid catalysts presented peaks around 250 °C while Al-SBA-15 showed none. Compared to bulk ionic liquid [bmim][TFSI]/$AlCl_3$, immobilized ionic liquids present higher decomposition temperature and thermal stability. Bulk ionic liquids started to lose organic content from 250 °C. And immobilized catalysts improved this temperature to about 300 °C.

The SBA-15 immobilized ionic liquid catalysts were proved to be active for Friedel–Crafts alkylation of benzene with 1-dodecene. Different catalysts and various parameters were investigated, including reaction time, benzene/1-dodecene, etc. Immobilization of ionic liquid reduced the usage of ionic liquid catalysts due to the dispersion and high contact areas given by SBA-15. Thus, the utilization of active sites was significantly improved by immobilization. Immobilized ionic liquid catalysts gave higher 2-LAB selectivity, due to the ability of maintaining the stability of 2-isomer. Under certain conditions, 2-LAB selectivity was as high as 80%. It is concluded that reaction time and benzene/1-dodecene ratio were important factors for the alkylation. Shorter reaction time and larger benzene/1-dodecene ratio resulted in higher 2-LAB selectivity, which can be explained by carbenium ion concentration. Immobilized ionic liquid catalysts can be reused, and they kept more than 50% reactivity after 3 cycles. The main reason to deactivation was discuss based on TEM, BET and TG investigation. By-products as oligomer, produced by oligomerization of olefin in the reactant, blocked or covered the pores, prevented the reactants from contacting with active sites, and reduced the specific surface areas of catalysts.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (U1362102).

References

[1] A. Aitani, J. Wang, I. Wang, S. Al-Khattaf, T. Tsai, Catal. Surv. Asia 18 (2014) 1.
[2] D.P. Fogliatti, S.A. Kemppainen, T.N. Kalnes, J. Fan, D.R. Shonnard, ACS Sustain. Chem. Eng. 2 (2014) 1828.
[3] T.B. Poulsen, K.A. Jørgensen, Chem. Rev. 108 (2008) 2903.
[4] J.F. Knifton, P.R. Anantaneni, P.E. Dai, M.E. Stockton, Catal. Today 79–80 (2003) 77.
[5] S. Sivasanker, A. Thangaraj, J. Catal 138 (1992) 386.
[6] G.D. Yadav, N.S. Doshi, Org. Process Res. Dev. 6 (2002) 263.
[7] J.N. Armor, Catal. Today 163 (2011) 3.
[8] D. Dubé, S. Royer, D. Trong On, F. Béland, S. Kaliaguine, Microporous Mesoporous Mater. 79 (2005) 137.
[9] A. El Maatougui, J. Azuaje, E. Sotelo, O. Caaman˜o, A. Coelho, ACS Comb. Sci. 13 (2011) 7.
[10] W. Chen, S. Huang, Q. Zhao, H. Lin, C. Mou, S. Liu, Top. Catal. 52 (2009) 2.
[11] V.R. Choudhary, K. Mantri, J. Catal. 205 (2002) 221.
[12] A. Bordoloi, B.M. Devassy, P.S. Niphadkar, P.N. Joshi, S.B. Halligudi, J. Mol. Catal. A: Chem. 253 (2006) 239.

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045

[13] W. Aslam, M.A.B. Siddiqui, B. Rabindran Jermy, A. Aitani, J. Čejka, S. Al-Khattaf, Catal. Today 227 (2014) 187.
[14] M. Kubů, N. Žilková, S.I. Zones, C. Chen, S. Al-Khattaf, J. Čejka, Catal. Today (2015).
[15] J. Lin, J. Wang, J. Wang, I. Wang, R.J. Balasamy, A. Aitani, S. Al-Khattaf, T. Tsai, J. Catal. 300 (2013) 81.
[16] K. Matuszek, A. Chrobok, F. Coleman, K.R. Seddon, M. Swadźba-Kwaśny, Green Chem. 16 (2014) 3463.
[17] P. Cui, G. Zhao, H. Ren, J. Huang, S. Zhang, Catal. Today 200 (2013) 30.
[18] H. Xin, Q. Wu, M. Han, D. Wang, Y. Jin, Appl. Catal. A: Gen. 292 (2005) 354.
[19] G. Qi, F. Jiang, X. Sun, S. Zhao, Sci. China Chem. 53 (2010) 1102.
[20] C.Z. Qiao, Y.F. Zhang, J.C. Zhang, C.Y. Li, Appl. Catal. A: Gen. 276 (2004) 61.
[21] P. Wasserscheid, M. Sesing, W. Korth, Green Chem. 4 (2002) 134.
[22] L.Y. Piao, X. Fu, Y.L. Yang, G.H. Tao, Y. Kou, Catal. Today 93–95 (2004) 301.
[23] Y. He, C. Wan, Q. Zhang, X. Zhan, D. Cheng, F. Chen, RSC Adv. 5 (2015) 62241.
[24] J.H. Kim, J.W. Lee, U.S. Shin, J.Y. Lee, S. Lee, C.E. Song, Chem. Commun. (2007) 4683.
[25] P.H. Tran, P.E. Hansen, H.T. Nguyen, T.N. Le, Tetrahedron Lett. 56 (2015) 612.
[26] G. Wang, N. Yu, L. Peng, R. Tan, H. Zhao, D. Yin, H. Qiu, Z. Fu, D. Yin, Catal. Lett. 123 (2008) 252.
[27] D. Kim, D. Lim, D. Cho, J. Koh, D. Park, Catal. Today 164 (2011) 556.
[28] K. Yamaguchi, T. Imago, Y. Ogasawara, J. Kasai, M. Kotani, N. Mizuno, Adv. Synth. Catal. 348 (2006) 1516.
[29] C. DeCastro, E. Sauvage, M.H. Valkenberg, W.F. Hölderich, J. Catal. 196 (2000) 86.
[30] R. Skoda-Földes, Molecules 19 (2014) 8840.
[31] F. Shi, Q. Zhang, D. Li, Y. Deng, Chem. Eur. J. 11 (2005) 5279.
[32] N. Jiang, H. Jin, Y. Mo, E.A. Prasetyanto, S. Park, Microporous Mesoporous Mater. 141 (2011) 16.
[33] B. Zou, Y. Hu, D. Yu, J. Xia, S. Tang, W. Liu, H. Huang, Biochem. Eng. J. 53 (2010) 150.
[34] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[35] M. Ogura, K. Inoue, T. Yamaguchi, Catal. Today 168 (2011) 118.
[36] H. Srour, H. Rouault, C.C. Santini, Y. Chauvin, Green Chem. 15 (2013) 1341.
[37] S. Chen, Y. Liu, H. Fu, Y. He, C. Li, W. Huang, Z. Jiang, G. Wu, J. Phys. Chem. Lett. 3 (2012) 1052.
[38] C. Li, Y. Wang, X. Guo, Z. Jiang, F. Jiang, W. Zhang, W. Zhang, H. Fu, H. Xu, G. Wu, J. Phys. Chem. C 118 (2014) 3140.
[39] R. Kumar, A. Kumar, A. Khanna, Reaction kinetics, Mech. Catal. 106 (2012) 141.
[40] H. Ma, J. He, D.G. Evans, X. Duan, J. Mol. Catal. B: Enzym. 30 (2004) 209.
[41] H. Zhao, N. Yu, J. Wang, D. Zhuang, Y. Ding, R. Tan, D. Yin, Microporous Mesoporous Mater. 122 (2009) 240.
[42] C. Yuan, Z. Huang, J. Chen, Catal. Commun. 24 (2012) 56.
[43] S. Zhai, W. Wei, D. Wu, Y. Sun, Catal. Lett. 89 (2003) 261.
[44] X. Zhao, J. Mol. Catal. A: Chem. 191 (2003) 67.
[45] V. Ladnak, N. Hofmann, N. Brausch, P. Wasserscheid, Adv. Synth. Catal. 349 (2007) 719.
[46] Q. Zhang, S. Zhang, Y. Deng, Green Chem. 13 (2011) 2619.
[47] Y. Wang, C. Li, X. Guo, G. Wu, Int. J. Mol. Sci. 14 (2013) 21045.

Please cite this article in press as: Y. He, et al., Synthesis of efficient SBA-15 immobilized ionic liquid catalyst and its performance for Friedel–Crafts reaction, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.01.045