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Stability, Deactivation, and Regeneration of Chloroaluminate Ionic Liquid as Catalyst for Industrial C4 Alkylation

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Abstract: Alkylation of isobutane and 2-butene was carried out in a continuous unit using triethylamine hydrochloride (Et_3NHCl)-aluminum chloride ($AlCl_3$) ionic liquid (IL) as catalyst. The effects of impurities such as water, methanol, and diethyl ether on the stability of the catalytic properties and deactivation of the ionic liquid were studied in the continuous alkylation. In the Et_3NHCl-$2AlCl_3$ ionic liquid, only one half of the aluminum chloride could act as the active site. With a molar ratio of 1:1, the active aluminum chloride in the ionic liquid was deactivated by water by reaction or by diethyl ether through complexation while the complexation of aluminum chloride with two molecular proportions of methanol inactivated the active aluminum chloride in the ionic liquid. The deactivation of chloroaluminate ionic liquid was observed when the active aluminum chloride, i.e., one half of the total aluminum chloride in the ionic liquid, was consumed completely. The regeneration of the deactivated ionic liquid was also investigated and the catalytic activity could be recovered by means of replenishment with fresh aluminum chloride.

Keywords: alkylation; isobutane; 2-butene; ionic liquids

1. Introduction

To minimize the negative environmental effects from automobile fuels, increasing regulatory pressure is being imposed on oil refineries to reduce the blending amounts of some components in motor fuel such as aromatic hydrocarbons and methyl tert-butyl ether (MTBE); thus, the alkylation of isobutane and butene is becoming more important in petroleum refinery for producing isooctane, which has high octane numbers, exhibits clean burning characteristics and can be used as the ideal additive for new formula gasoline. However, commercial alkylation is catalyzed by highly corrosive and environmentally detrimental concentrated sulfuric acid (H_2SO_4) or hydrofluoric acid (HF), which has many disadvantages such as acid sludge treatment, cooling and separation problems, high operating cost, and safety problems [1]. Therefore, it is very necessary to develop a new class of catalyst for alkylation of isobutane/butene to replace the conventional catalysts.

Some types of solid acid catalysts such as modified molecular sieves and immobilized heteropolyacids or superacids have been investigated as substitutes for the conventional liquid acids. Some of these solid catalysts show high catalytic activity and selectivity at the beginning of the reaction, but reactivity decays rapidly due to carbon deposition [2]. Alkylation under supercritical conditions exhibits a longer lifetime of the catalyst, compared with the reaction in the liquid or gas phase [3].

Room temperature ionic liquids have been recognized as novel and “green” solvents for synthetic chemistry over recent decades and are receiving increasing attention in the catalysis field worldwide [4]. Alkylation catalyzed by ionic liquids is one of the focuses of catalysis study [5–10] 1-Alkyl-3-methylimidazolium halide-aluminum chloride ionic liquids have been investigated as catalysts for isobutane/2-butene alkylation [11,12] Acidic ionic liquid synthesized by aluminum chloride and triethylamine hydrochloride has also been confirmed to be an excellent catalyst for alkylation. Cu additive was introduced into the ionic liquids in order to improve the selectivity of the objective product, i.e., trimethylpentane (TMP) and distinctly increase the ratio of trimethylpentane/dimethylhexane (DMH) [13–15]. It is well known that the octane number of alkylate is primarily a direct function of the trimethylpentane content and the dimethylhexanes are not desired. The main advantages arising from the use of ionic liquids are a higher alkylate quality than that obtained from conventional liquid acids, very low alkene content in the product, and simple product separation, which thus show promising prospects for ionic liquids as alternatives to conventional liquid acids for alkylation [11,13].

As is now well known in the commercial alkylation unit, the feedstock (i.e., isobutane and butene) usually comes from the MTBE unit, the catalytic cracking process or ethylene plant. It is contaminated with traces of water, methanol and ether inevitably because of the difficulty of separation. These impurities need to be removed as much as possible for commercial alkylation when the mineral acids are used as catalysts. For example, in the H_2SO_4 alkylation process, the contents of water, ether, and methanol in the feedstock must be reduced to a very low level in order to avoid the increase of acid consumption. Although the modified chloroaluminate ionic liquids have exhibited many advantages over mineral acids as described above, the same challenge from impurities could be faced directly in the alkylation process catalyzed by ionic liquids. However, the influences of the impurities in the industrial feedstocks on the stability and lifetime of the very important properties of a catalyst, of the modified chloroaluminate ionic liquid have not been studied up to present. Obviously, these researches could be of great importance for the future potential industrial application of ionic liquids in isobutane/2-butene alkylation. Thus, in the present work, the effects of these impurities on the catalyzing properties of the ionic liquids for alkylation of isobutane with 2-butene were investigated in detail. The regeneration of the deactivated ionic liquid was also studied.

2. Results and Discussion

2.1. Effect of Water

The chloroaluminate ionic liquids are very moisture-sensitive. The water content in the alkylation system therefore probably influences the catalytic properties of the ionic liquids. Thus, in this work, the effects of water on the catalytic performances of the ionic liquid, i.e., the lifetime, the activity, and isooctane selectivity, were investigated in continuous alkylation by means of the study on the mass of a feedstock treated with 1 g ionic liquid and the component of the alkylation products. The water content in the feedstock without dehydrating was 1480 ppmw. The water contents in the other feedstocks were reduced to 850 ppmw, 375 ppmw, and 110 ppmw, respectively. The experimental results are reported in Figures 1–4.

In Figure 1, a marked increase of the mass of the feedstock treated with 1 g ionic liquid with the decrease of water content in the feedstock can be seen. When the content of water in the feedstock decreased from 1480 ppmw to 110 ppmw, the mass of feedstock treated with 1 g ionic liquid increased from 29 g to 338 g before deactivation of the ionic liquid (deactivation was considered when the conversion of 2-butene was lower than 50%). It can also be seen that, in the steady period, the higher water content in the feedstock led to higher conversion of 2-butene. This observation indicated that the activity of the chloroaluminate ionic liquid in the high water content system was stronger than that in the low water content system.

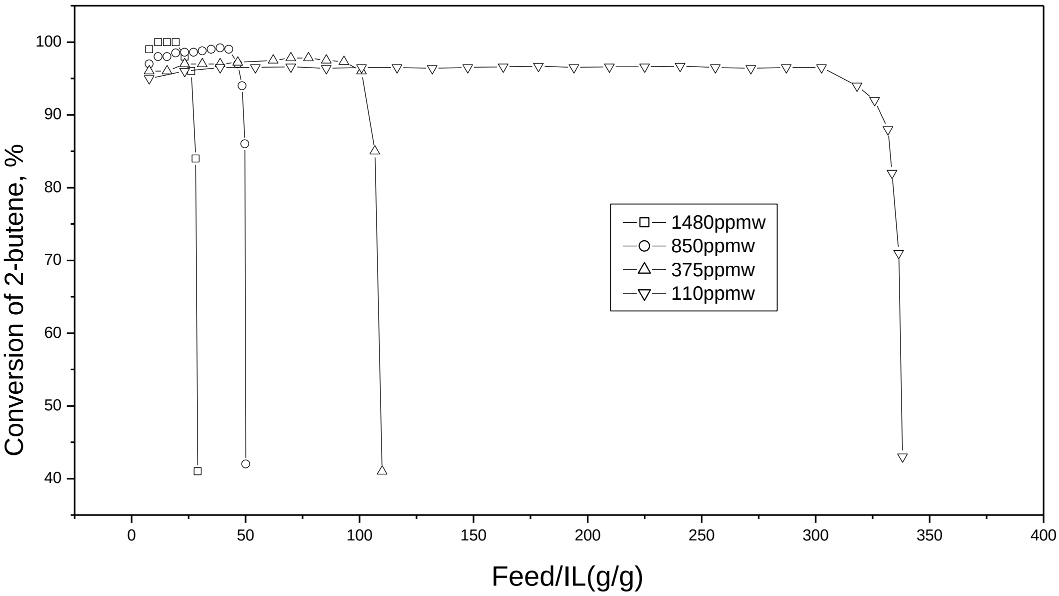

Figure 1. Effects of water content in the feedstocks on the mass of feedstock treated with 1 g ionic liquid, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1.

Figure 2 shows the effect of water content in feedstocks on the isooctane content in alkylates. It can be seen that there is an induction period of the isooctane content in this ionic liquid catalytic system. In the induction period, the isooctane content in alkylates increased with the increase of the mass of the feedstocks treated by 1 g ionic liquid. After the induction period, a steady period of the isooctane content was observed as expected. In the steady period, the isooctane content remained stable to a certain degree. With the deactivation of the ionic liquid, the isooctane content in the alkylates decreased quickly. The water content in the feedstock also affected the lengths of the induction and the steady periods. High water content in the feedstock resulted in a short induction and steady period. In the case of low water content in the feedstock (110 ppmw and 375 ppmw), the isooctane content in the alkylate was over 80% in the steady period, higher than that of the case of high water content in the feedstock (850 ppmw and 1480 ppmw).

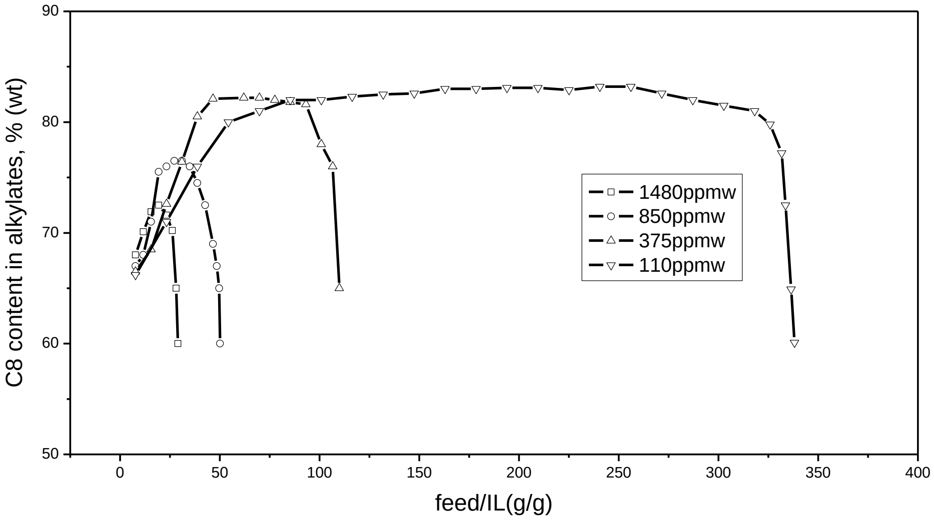

Figure 2. Effects of water content in the feedstocks on the isooctane content in alkylates. The reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1.

In Figure 3, the effects of water content in feedstocks on TMP/DMH in alkylates are reported. As with the isooctane content in Figure 2, a similar trend of TMP/DMH in alkylates is observed. As the amount of the feedstocks treated increased, the ratio of TMP/DMH first increased and then remained stable. Finally, the ratio decreased with the deactivation of the ionic liquid.

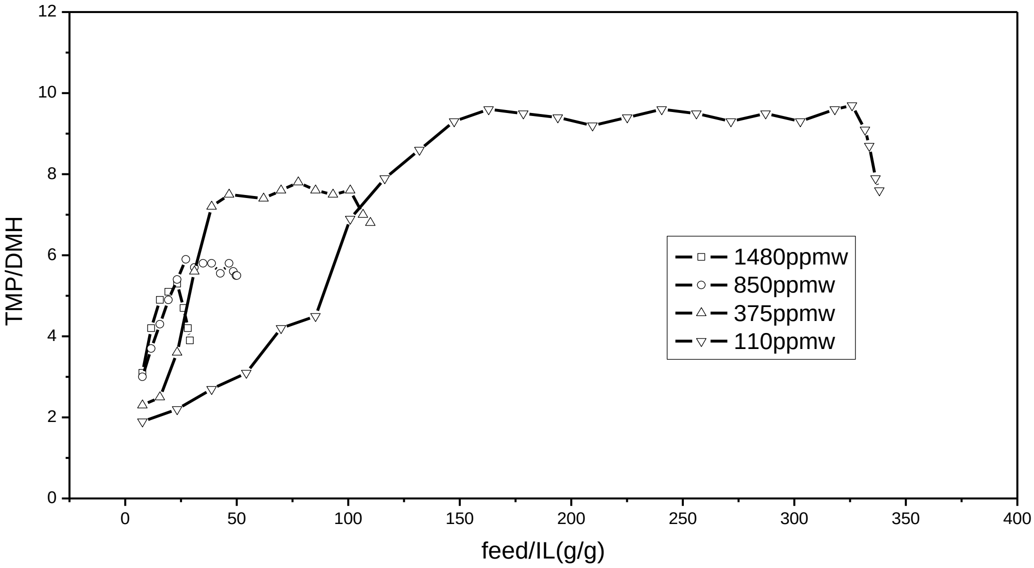

Figure 3. Effects of water content in the feedstocks on trimethylpentane/dimethylhexane (TMP/DMH), the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1.

Figure 4 shows the content of different kinds of hydrocarbons in alkylates in the case when the water content in the feedstock was 110 ppmw. The heavy ends, i.e., C9 and C9+, and the light ends, i.e., C5~C7, exhibited similar trend as the increase of the amount of the feedstock treated. In the whole stage of the alkylation, the content of heavy ends was a little higher than that of the light ends.

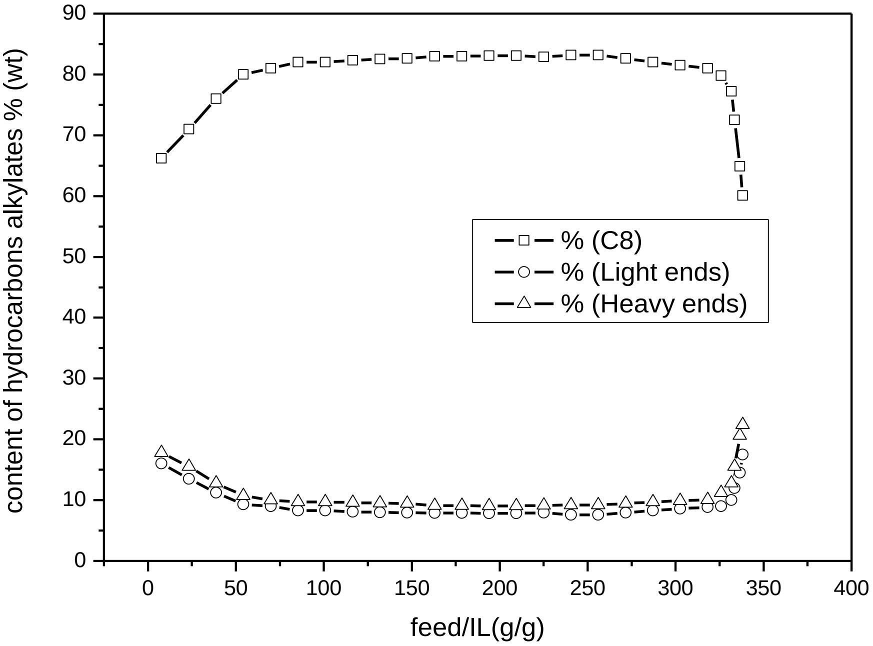

Figure 4. The content of hydrocarbons in alkylate, the water content in feedstock was 110 ppmw, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1.

In this section, the trend of the mass of feedstock treated by 1 g ionic liquid affected by the water content in feedstocks was studied. In order to obtain more detailed information about the deactivation of the chloroaluminate ionic liquids, the amount of water accumulated in the ionic liquid when the ionic liquid was deactivated and the amount of the aluminum chloride in the fresh ionic liquid should be compared.

Table 1 shows the amount of accumulated water in 1 g ionic liquid when the ionic liquid was deactivated. There was 4.805 mmol aluminum chloride in the ionic liquid used in this study. It can be clearly seen that, for different water contents in feedstocks, all the molar quantities of accumulated water in 1 g ionic liquid were approximately about 2.4 mmol, i.e., half of the molar quantity of aluminum chloride in 1 g fresh ionic liquid. Aluminum chloride is very moister-sensitive, the reaction between water and aluminum chloride can be described with the Formula (1) below.

$$AlCl_3 + H_2O \rightarrow AlCl_2(OH) + HCl \tag{1}$$

According to Formula (1) and the above comparison, it was conjectured that the chloroaluminate ionic liquids would be deactivated in the case of loss of one half of the aluminum chloride in the fresh ionic liquid. Besides, all the molar quantities of the accumulated water were a little less than 2.4 mmol. The gap increased as the water content in the feedstock decreased.

Table 1. The amount of accumulated water in the ionic liquid.

Water content in feedstock (ppmw)	1480	850	375	110
Mass of feedstock treated (g/g)	29	50	109	338
Molar quantity of accumulated water in 1 g ionic liquid (mmol)	2.384	2.361	2.271	2.066

It is well known that the chloroaluminate ionic liquid can have a different acidity by variation of the $AlCl_3/Et_3NHCl$ molar ratio [16]. In the ionic liquids with $AlCl_3/Et_3NHCl$ molar ratio <1, the dominant anions are Cl^- and $AlCl_4^-$, and the ionic liquids are basic. In the ionic liquids with $AlCl_3/Et_3NHCl$ molar ratio = 1, there is only $AlCl_4^-$ in the ionic liquid, the ionic liquid is neutral. The basic and neutral ionic liquids have no catalytic activity for the alkylation of isobutane/butene. In the ionic liquids with the $AlCl_3/Et_3NHCl$ molar ratio >1, the dominant anions are $AlCl_4^-$ and $Al_2Cl_7^-$, and the ionic liquids are acidic. The Lewis acidity originates from dissociation of $AlCl_3$ from the dimeric anion, i.e., $Al_2Cl_7^-$ [11]. The Lewis acid site (dissociative $AlCl_3$) can be transformed to a Brønsted acid site by complexation of aluminum chloride, hydrogen chloride, and a certain proton acceptor such as butene or cuprous chloride [17]. The complex acts as an effective catalyst to catalyze the alkylation of isobutane and butene. In this case, hydrogen chloride came from the reaction of water in the feedstock and aluminum chloride as shown in Formula (1).

From the discussion above, it can be deduced that the dissociative $AlCl_3$ would appear only in the case of the $AlCl_3/Et_3NHCl$ molar ratio >1, and the ionic liquid exhibits Lewis acidity and potential catalytic activity for alkylation. In this study, the molar ratio of $AlCl_3/Et_3NHCl$ in the synthesis of ionic liquid is 2:1. Thus, at most half the amount of aluminum chloride can act as the Lewis acid site (co-catalyst) to form the effectively active site. In the acidic ionic liquid, $Al_3OCl_8^-$, $Al_3O_2Cl_6^-$, $Al_2OCl_5^-$, $Al_3Cl_9OH^-$, and $Al_2Cl_6OH^-$ are the most probable oxychlorlaluminate or hydroxychloroaluminate species, from the reaction between water and aluminum chloride [18,19]. The loss of this part of the aluminum chloride would lead to the deactivation of the chloroaluminate ionic liquids. The Formula (1) describes the reaction of the hydrolysis deactivation of active aluminum chloride in the ionic liquids. The other half of the amount of the aluminum chloride only acts as a component of the neutral solvent ($[Et_3NH][AlCl_4]$) and is catalytically inactive for alkylation [20].

From the data in Table 1, it can be seen that the molar quantities of accumulated water are not equal to the amount of aluminum chloride in the ionic liquid. The gap increased with the increased mass of the feedstock treated. This observation suggested that there would be other factors affecting the lifetime of the chloroaluminate ionic liquids. It was without doubt that traces of aluminum chloride dissolved in the hydrocarbons and were carried out of the alkylation system. This part of the aluminum chloride loss was negligible in the case of a low amount of feedstock treated. However, as the amount of feedstock treated increases, it becomes more and more significant. In the case of low butene conversion, the unreacted butene would carry more aluminum chloride because of the chemical interaction between aluminum chloride and butene.

As mention above, the HCl in the catalysis system came from the reaction between water and aluminum chloride. The content of water therefore influences the concentration and the acidity of the effectively catalytic sites. The low water content in the feedstocks leads to proper acidity of the active sites, resulting in relatively high isooctane selectivity and ratio of TMP to DMH. Whereas, the high water content in feedstocks increases the amount of the active sites, leading to high butene conversion relatively.

2.2. *Effect of Methanol*

Methanol is usually present in the feedstock of the industrial alkylation process. A marked exotherm of chloroaluminate ionic liquids was observed after addition of methanol dropwise, indicating a strong chemical interaction. So methanol in the feedstock would also affect the catalytic properties of the chloroaluminate ionic liquids. The effect of methanol therefore was investigated by means of a similar method as in Section 2.1. The water content in the feedstock was 375 ppmw. Methanol was pumped into the feedstock tank by a plunger pump. The methanol contents in this study were 800 ppmw and 1740 ppmw, respectively.

Figure 5 shows the effect of methanol on the amount of feedstock treated by 1 g ionic liquid. With the introduction of methanol into the catalytic system, a decrease of the lifetime of the ionic liquids was observed. When the content of methanol in the feedstock increased from 0 ppmw to 800 ppmw and 1740 ppmw, the mass of feedstock treated by 1 g ionic liquid decreased from 109 g to 70 g and 49 g before deactivation of the ionic liquid (deactivation was also considered when the conversion of 2-butene was lower than 50%). The addition of methanol sped up the deactivation of the ionic liquid. However, at the steady period of the reaction, the butene conversion was not impacted by methanol, indicating no obvious effect of methanol on the initial activity of the ionic liquid. The deactivation acceleration of ionic liquid may be the result of passivation of a part of the active $AlCl_3$ by methanol. Besides, no methanol was detected in the liquid products, indicating methanol remained in the ionic liquid through a certain kind of interaction with the ionic liquid.

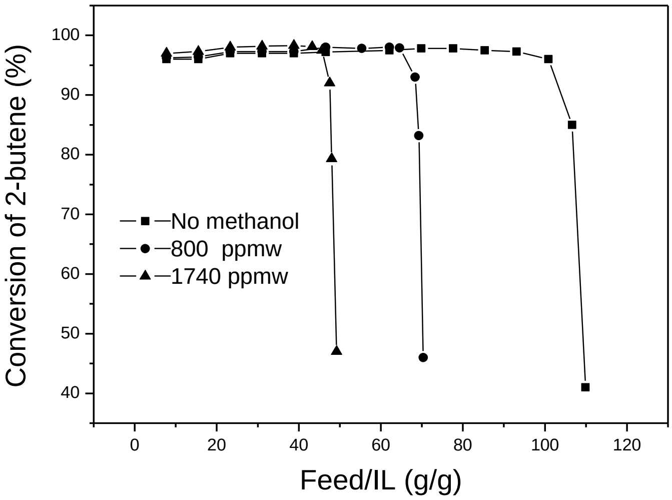

Figure 5. Effects of methanol content in the feedstocks on the mass of feedstock treated by 1 g ionic liquid, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in the feedstock was 375 ppmw.

The effects of methanol content in the feedstocks on the isooctane content in alkylates are shown in Figure 6. In the three curves, the isooctane content in alkylates increased at the onset period and then remained stable to a certain degree, finally decreasing until the deactivation of the ionic liquid. The length of the steady period decreased with the increase of the methanol content in the feedstocks. It also can be seen that the isooctane contents in the products with addition of methanol were generally higher than those without methanol. It was conjectured that addition of methanol was favorable for improvement of isooctane selectivity.

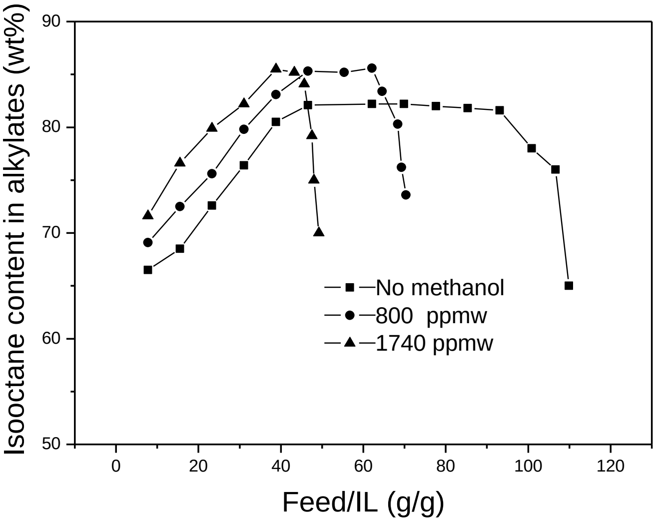

Figure 6. Effects of methanol content in the feedstocks on the isooctane content in alkylates. The reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in the feedstock was 375 ppmw.

In Figure 7, the effects of methanol content in feedstocks on TMP/DMH in alkylates were reported. As with the isooctane content in Figure 7, a similar trend of TMP/DMH in alkylates was observed. As the amount of the feedstocks treated increased, the ratio of TMP/DMH first increased and then remained stable. Finally, the ratio decreased with the deactivation of the ionic liquid. The ratios of TMP/DMH in the products with addition of methanol were also higher than those without methanol.

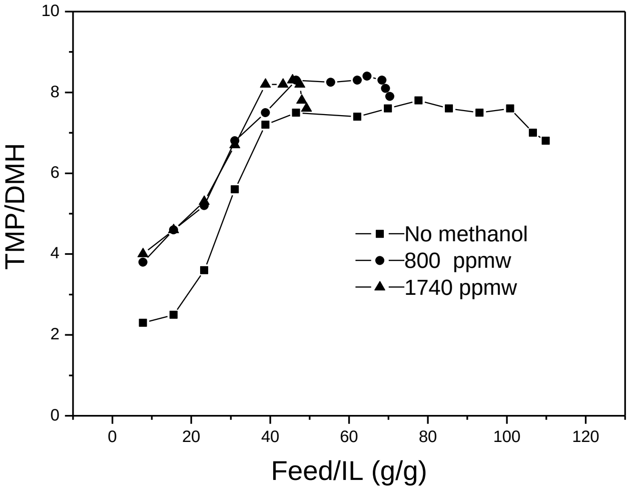

Figure 7. Effects of methanol content in the feedstocks on TMP/DMH, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in the feedstock was 375 ppmw.

The reason for the rapid deactivation of the ionic liquid by addition of methanol was studied by means of comparison of the amount of active $AlCl_3$ in the fresh ionic liquid and the amount of water and methanol accumulated. The results are listed in Table 2.

Table 2. The amount of accumulated methanol and water in the ionic liquid.

Methanol content in feedstock (ppmw)	1740	800
Mass of feedstock treated (g/g)	49	70
Molar quantity of accumulated water in 1 g ionic liquid (mmol)	1.021	1.458
Molar quantity of accumulated methanol in 1 g ionic liquid (mmol)	2.664	1.750
Difference of molar quantity of accumulated water and active $AlCl_3$ (mmol)	1.381	0.944

Water content in the feedstock was 375 ppmw, 1 g fresh ionic liquid contained 2.402 mmol active $AlCl_3$.

Table 2 shows the amount of accumulated methanol and water in 1 g ionic liquid when the ionic liquid was deactivated. As mentioned above, there was 2.402 mmol active aluminum chloride in 1 g of fresh ionic liquid used in this study. It can be clearly seen that, the molar quantities of the accumulated methanol were approximately twice as much as the molar quantities of active aluminum chloride except the aluminum chloride was deactivated by water. This result revealed that one mole of active aluminum chloride would be deactivated by two moles of methanol by a certain kind of chemical interaction. In a previous study on isobutane/butene alkylation catalyzed by solid aluminum chloride, the complex of $AlCl_3\bullet CH_3OH$ was a good catalyst and the catalytic performance was better than with $AlCl_3$ itself. However, the product of the complexation of aluminum chloride with two molecular proportions of methanol, i.e., $AlCl_3\bullet 2CH_3OH$, was not catalytically active for alkylation [21,22]. This conclusion was consistent with the result in this work. An improvement of catalytic performances such as isooctane selectivity and TMP/DMH was also observed in the continuous alkylation catalyzed by ionic liquids. Furthermore, it can be conjectured that the mechanism of alkylation catalyzed by the chloroaluminate ionic liquid would be analogous to that of alkylation catalyzed by solid aluminum chloride.

2.3. Effect of Diethyl Ether

Ether is another kind of impurity in the feedstock of the industrial alkylation process. A strong chemical interaction also occurred when ethers made contact with chloroaluminate ionic liquid. Therefore, the effect of ether on the catalytic performance of the ionic liquid was also investigated by means of a similar method as in Sections 2.2 and 2.3. Diethyl ether was used as a representative in this study. The water content in the feedstock was 375 ppmw. Diethyl ether was added into the feedstock tank by the same method as in Section 3.3. The diethyl ether contents in this study were 680 ppmw and 1525 ppmw, respectively.

Figure 8 shows the effect of diethyl ether on the amount of feedstock treated by 1 g ionic liquid. As with the effect of methanol, with the addition of diethyl ether into the catalytic system, the lifetime of the ionic liquids diminished. When the content of diethyl ether in the feedstock increased from 0 ppmw to 680 ppmw and 1525 ppmw, the mass of feedstock treated by 1 g ionic liquid decreased from 109 g to 77 g and 57 g before deactivation of the ionic liquid. The addition of diethyl ether also sped up the deactivation of the ionic liquid. Similarly, in the steady period of the reaction, the butene conversion was not impacted by diethyl ether and no diethyl ether was detected in the liquid products. It can be deduced that the deactivation acceleration of ionic liquid may also be the result of passivation of a part of the active $AlCl_3$ by diethyl ether through complexation, as methanol and diethyl ether with a pair of unshared electrons are both basic.

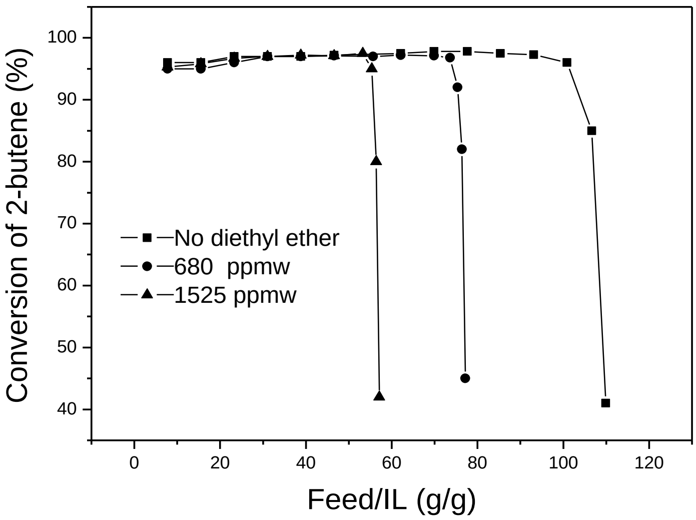

Figure 8. Effects of diethyl ether content in the feedstocks on the mass of feedstock treated by 1 g ionic liquid, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in the feedstock was 375 ppmw.

The effects of diethyl ether content in the feedstocks on the isooctane content in alkylates are shown in Figure 9. Under different conditions, the isooctane content in the alkylates exhibited a similar trend. No improvement of isooctane selectivity was observed.

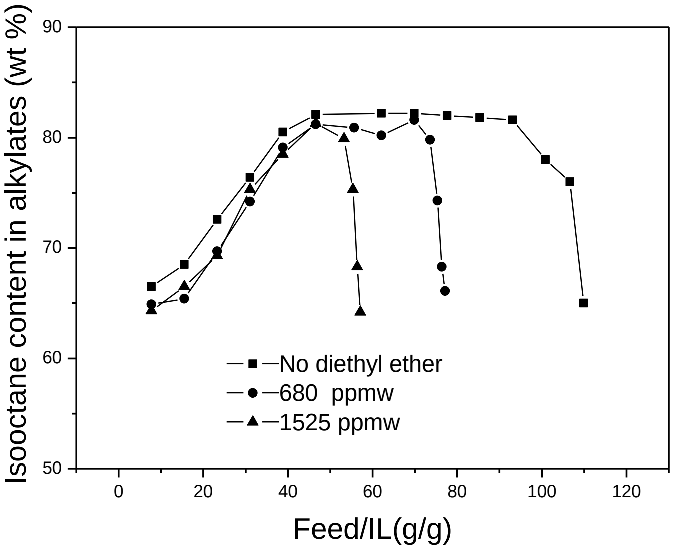

Figure 9. Effects of diethyl ether content in the feedstocks on the isooctane content in alkylates. The reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in the feedstock was 375 ppmw.

In Figure 10, the effects of diethyl ether content in feedstocks on TMP/DMH in alkylates are displayed. As with the isooctane content in Figure 9, a similar trend of TMP/DMH in alkylates was observed. Generally, the ratios of TMP to DMH were not impacted by addition of diethyl ether. No obvious increase or decrease of the ratio was seen with the change of diethyl ether content in the feedstock.

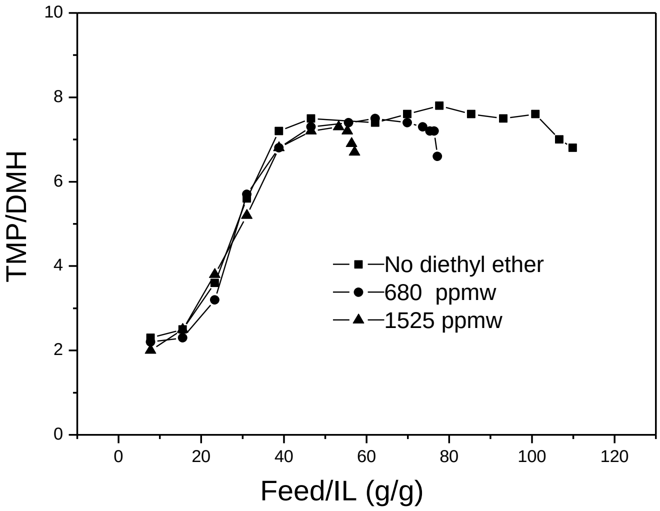

Figure 10. Effects of diethyl ether content in the feedstocks on TMP/DMH, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in the feedstock was 375 ppmw.

The amount of active $AlCl_3$ in the fresh ionic liquid and the amount of water and diethyl ether accumulated were also compared in order to study the deactivation of aluminum chloride resulting from addition of diethyl ether. The results are listed in Table 3.

Table 3. The amount of accumulated diethyl ether and water in the ionic liquid.

Methanol content in feedstock (ppmw)	1525	680
Mass of feedstock treated (g/g)	57	77
Molar quantity of accumulated water in 1 g ionic liquid (mmol)	1.188	1.604
Molar quantity of accumulated diethyl ether in 1 g ionic liquid (mmol)	1.175	0.708
Difference of molar quantity of accumulated water and active $AlCl_3$ (mmol)	1.214	0.798

Water content in feedstock was 375 ppmw, 1 g fresh ionic liquid contained 2.402 mmol active $AlCl_3$.

Table 3 shows the amount of accumulated diethyl ether and water in 1 g ionic liquid when the ionic liquid was deactivated. The molar quantity of active aluminum chloride in 1 g fresh ionic liquid used in this study was 2.402 mmol. It can be clearly seen that the molar quantities of the accumulated diethyl ether were approximately equal to the molar quantities of active aluminum chloride except the aluminum chloride was deactivated by water. This result revealed that the active aluminum chloride would be deactivated by diethyl ether with equimolar proportion through complexation described as $AlCl_3 \bullet C_2H_5OC_2H_5$. In a previous study, the researchers found that, although the equimolar complexes of aluminum chloride with dialkyl ethers had good solvency for the reactants, they were catalytically inactive for hydrocarbon alkylation. These complexes dissolved excess aluminum chloride to form an active alkylation catalyst [22–24]. This conclusion was consistent with the result in this work. The availability of the electron pair determined the extent of interaction of methanol or diethyl ether with aluminum chloride. The electron donating ability (i.e., the basicity) of diethyl ether seems stronger than that of methanol, thus it could inactivate aluminum chloride with an equimolar proportion, while the complexation of aluminum chloride with two molecular proportions of methanol was needed to inactivate the aluminum chloride.

2.4. Regeneration of Deactivated Ionic Liquids

In the above experiments, all the deactivated ionic liquids looked like slurries. The loss of aluminum chloride was the main reason for ionic liquid deactivation. Thus, the most effective method to regenerate the deactivated ionic liquids was replenishment of aluminum chloride. The added quantity of fresh aluminum chloride to the deactivated ionic liquid was equal to the amount of lost aluminum chloride, i.e., one half of the amount of aluminum chloride in the fresh ionic liquid. After regeneration, the slurry returned to a normal liquid. The result of the activity evaluation of the regenerated ionic liquid is reported in Figure 11. The catalytic activity of the spent ionic liquids was recovered substantially and the method of replenishment of aluminum chloride was effective.

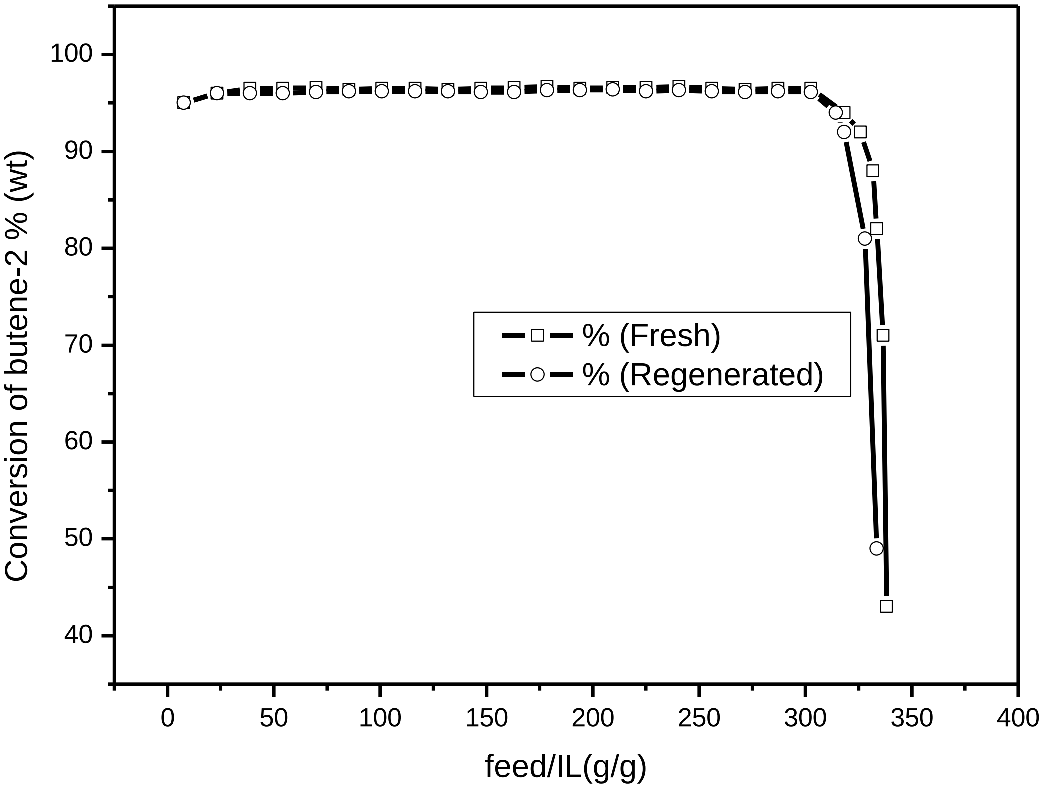

Figure 11. Comparison of the regenerated and the fresh ionic liquids, the reaction temperature was 30 °C, the molar ratio of isobutane/2-butene in feedstocks was 11:1, the water content in feedstock was 110 ppmw.

3. Experimental Section

3.1. Preparation of Ionic Liquid Catalyst

The room temperature chloroaluminate ionic liquid employed in this work was synthesized by mixing triethylamine hydrochloride and anhydrous aluminum chloride. Anhydrous aluminum chloride was carefully purified by sublimation in a sealed tube. Triethylamine hydrochloride was purified by recrystallization and the product was finally dried in vacuum (at 80 °C). The anhydrous aluminum chloride was slowly added to the purified triethylamine hydrochloride at 70 °C according to a molar ratio of 2:1. The whole process was carried out in a dry nitrogen atmosphere in a glove box in order to avoid hydrolysis of $AlCl_3$.

3.2. Purification of Isobutane and 2-Butene

Isobutane and 2-butene used in this work were analytical reagents and purchased from China Petrochemical Corporation (Beijing, China) with at least 99% purity. The main impurity in the isobutene was n-butane (internal standard not modified during the reaction). The main impurities in the 2-butene were 1-butene and isobutene. No alcohols or ethers were detected in these analytical reagents. Isobutane and 2-butene were mixed in a tank with a molar ratio of 11:1 and then treated by different dehydrating agents to reduce the water content to different degrees. Karl–Fischer analysis was used to measure the content of water in the feedstocks. The Karl–Fischer analyzer used was an SC-6 mini-amount water-detecting instrument (Hegong Scientific Instrument, Co., Ltd., Shanghai, China).

3.3. Alkylation of Isobutane and 2-Butene

In all experiments, the alkylation reactions were carried out in a 500 mL stirred pressure reactor (Jiayi Chemical Machinery Company, Weihai, China) shown as part of Figure 12 and 42.6 g (about 30 mL) modified ionic liquid was charged into the reactor and brought to the proper temperature before experimenting. The feed continuously passed through the stirred ionic liquid layer with a plunger pump according to a rate of 500 mL per hour until the deactivation of the ionic liquid. The counterbalance valve was kept at a certain pressure to ensure a liquid reaction. The effluent from the reactor was separated into gas and liquid products by a condenser of ice water. In all experiments, the molar ratio of isobutane to 2-butene was 11:1 and the rate of agitation was 800 rpm. The reaction temperature was controlled by a thermostatic water bath with temperature controller.

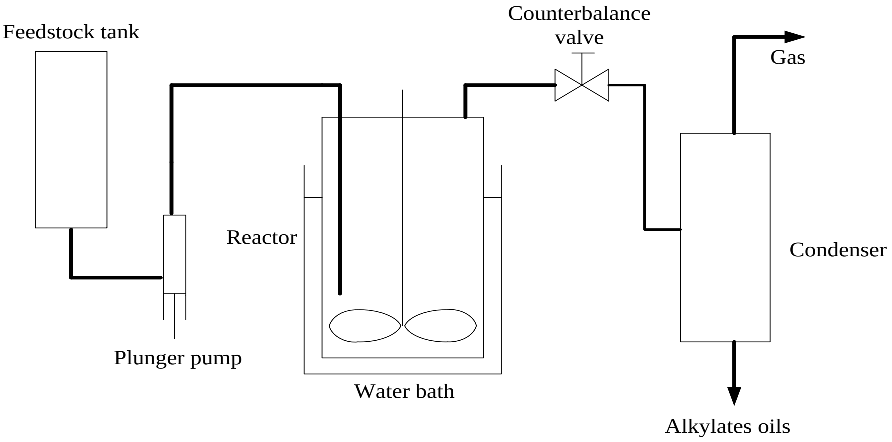

Figure 12. Schematic diagram of the apparatus used for the isobutane/2-butene alkylation.

3.4. Regeneration of the Spent Ionic Liquid

The regeneration of the deactivated ionic liquid was carried out in the reactor. A certain amount of fresh anhydrous aluminum chloride was added into the deactivated ionic liquid with stirring at 70 °C, which is the same temperature as that of the synthesis of the ionic liquid. The whole process was under the protection of dry nitrogen gas. After the fresh aluminum chloride was completely dissolved in the ionic liquid, stirring was stopped and then the reactor was closed up to start the alkylation reaction.

3.5. Analytical Procedures

The gaseous products were analyzed using a Varian CP3900 gas chromatograph (Varian, PaloAlto, CA, USA) with a OV-101 capillary column (Φ 0.53 mm × 50 m) and flame ionization detector. The alkylate mixtures were analyzed using a Shimadzu QP5000 mass spectrometer (Shimadzu, Tokyo, Japan) (with an ion source temperature of 180 °C, in the range of 40–400 amu, with scan rate of 1.4 s^{-1}) and a Varian CP3800 chromatograph with0.25 mm × 50 m PONA capillary column and flame ionization detector.

4. Conclusions

In summary, it was found that water, methanol and diethyl ether in the feedstock affected the catalytic performances of the ionic liquid such as lifetime, isooctane selectivity, and ratio of TMP/DMH. Low water content in the feedstocks led to a relatively high lifetime isooctane selectivity, ratio of TMP/DMH and low catalytic activity. Addition of methanol and diethyl ether decreased the lifetime of the ionic liquid. Besides, the addition of methanol improved the isooctane selectivity and ratio of TMP/DMH in the alkylates.

In the Et_3NHCl-$2AlCl_3$ ionic liquid, only one half of the aluminum chloride could act as active site. With a molar ratio of 1:1, the active aluminum chloride in the ionic liquid was deactivated by water by reaction or by diethyl ether through complexation, while the complexation of aluminum chloride with two molecular proportions of methanol inactivated the active aluminum chloride in the ionic liquid. The deactivation of chloroaluminate ionic liquid was observed when the active aluminum chloride, i.e., a half of the total aluminum chloride in the ionic liquid, was consumed completely. The catalytic activity of the deactivated ionic liquid could be recovered by means of replenishment with fresh aluminum chloride.

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