Effects of Chloroaluminate Ionic Liquid on Alkylation of Benzene with Mixture of Alkenes and Alkanes

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Abstract

Linear alkyl benzene was produced by alkylation of benzene with mixture of C_{10}~C_{13} alkenes and alkanes from Fushun Detergent Chemical Factory in the presence of chloroaluminate ionic liquid. Results indicated that ionic liquid catalyst showed better reaction activity than that of HF and high conversion of alkenes and good selectivity of 2-LAB at 30^{o} C and mole ratio of catalyst to alkenes 1.The reaction system can be separated into two phases , which were easy to separate ionic liquid catalyst from product. Results of ionic liquid recycling were not ideal, but the catalyst activity had an improvement after modified with HCl.Product quality conformed to the high-class grade of industrial standard.

Keywords: Ionic liquids; Alkylation; Benzene; mixture of C_{10}~C_{13} alkenes and alkanes; Linear alkyl benzene

1. Introduction

Linear alkyl benzenes (LAB) are manufactured by alkylation of benzene with alkenes C_{10}~C_{13}, in the presence of HF in Fushun Detergent Chemical Factory. However, the process has met with some problems, such as equipment corrosion, HF purification and separation, high operating costs and safety aspects .Today many efforts have been made to improve this process with environmentally safer and alternative high conversion and selectivity catalysts. Room temperature ionic liquids is more and more recognized and accepted as a kind of novel green solvents and catalyst [1, 2].

Ionic liquids are generally defined as salts that melt at or below 100^{o}C to afford liquids composed solely of cations and anions [3]. Remarkable properties of ionic liquids are follows: Firstly, they exhibit very low vapor pressures under ambient conditions and possess wider liquid range as well as good reusability, which are very important when environment problem is more and more cared by people, Secondly, they can be designed to achieve desirable physical and chemical performance by adjusting proportion of cation to anion, such as chloro-aluminate ionic liquids, their acidity can be varied through a wide range depending on the proportions of organic base to anhydrous $AlCl_3$, Lewis activity chloro-aluminate ionic liquids showed better reaction activity and selectivity of 2-LAB when they are used to catalyze alkylation of benzene with 1-dodecene [4-7].

Chloro-aluminate ionic liquid ([BMIM] Cl-$AlCl_3$) was used to catalyze the alkylation reaction in laboratory. The effect of reaction temperature, molar ratio of benzene to alkenes, amount, acidity and reusability of ionic liquid on the reaction were investigated and compared to HF system of Fushun Detergent Chemical Factory.

2. Experiment

2.1.Experimental material

Experimental material is the mixture of C_{10}~C_{13} alkenes and alkanes from Fushun Detergent Chemical Factory, and its physical properties are listed in Table 1

Table 1 Physical properties of raw material

Item	Index
Density ,g/cm^3 at 15.6^{o}C	0.751
Average molecular weight	160.7
Olefin content, wt%	10.1
Bromine value ,g/100g	10.7
Total non-n-hydrocarbon, wt%	5.4
Total n-paraffin, wt%	84.5
Total n-olefin ,wt%	10.1

2.2 Synthesis of ionic liquid

2.2.1.Synthesis of BMIC (chloro-1-butyl -3 - methylimidazole)

BMIC was prepared as follows: Acetonitrile and 1-chloro-n-butane were placed into a dry three-neck flask equipped with a reflux condenser, a magnetic stirrer and a glass thermometer to measure the temperature of the mixture in the flask. The mixture was heated under nitrogen. When reaction temperature reached to 70, N-methylimidazole was added into the flask .the temperature was maintained between 70~80^{o}C.After 48h, the mixture was cooled. Then, the product was washed by solvents. The washed product was dried in a vacuum dryer to remove the residual solvents and water.

2.2.2 Synthesis of [BMIM]Cl-$AlCl_3$

[BMIM]Cl-$AlCl_3$ was prepared by addition of the desired amount of anhydrous aluminium chloride in batches to the BMIC. The mixture was stirred for 1h at room temperature .The whole process was kept under a dry nitrogen atmosphere to avoid the hydrolysis of aluminium chloride. [BMIM]Cl-$AlCl_3$ is yellow and transparent and sticky.

2.3 Synthesis of Linear alkyl benzenes (LAB)

A certain amount of chloroaluminte ionic liquid as catalyst and excess benzene were added to a dry three-neck flask equipped with a reflux condenser, a magnetic stirrer and a glass thermometer to measure the temperature of the reactants in the flask. The mixture of alkenes and alkanes was placed into the flask in batches when temperature reached to the desired reaction temperature. After the completion of alkylation reaction, the upper solvent layer containing the alkylated products and unreacted reactants was separated from the ionic liquid catalyst layer at the bottom of the flask simply by decantation .The whole reaction was kept under a dry nitrogen atmosphere because chloroaluminate ionic liquid is very sensitive to moisture.

2.4 Analysis

Quantitative analysis were carried out with a gas chromatograph SP-6800A equipped with FID detector and an OV-101 capillary column .The temperature program used was a beginning at 70^{o}C, going to 200^{o}C at 2^o C/min. Analytical data were directly given by the system of GC chemstation according to the area of each chromatograph peak. The conversion of alkenes and selectivity of 2-LAB were used as the evaluation standards of technology.

We used the applied standard of Fushun Detergent Chemical Factory as a reference to assess the grade of product.

3. Results and Discussion

3.1 Effect of reaction temperature on alkylation reaction

Operating temperature of alkylation plant in the factory is 54°C, and per pass conversion of alkenes and selectivity of 2-LAB are 94% and 31% respectively. The effect of reaction temperature on conversion and selectivity catalyzed by chloroaluminte ionic liquid was investigated in our experiments. The results were shown in Table2.The results indicated that a dramatic effect on conversion and a slight effect on selectivity for 2-LAB were observed. It can be seen a 97% conversion was realized at 50°C.The reason is that, raising the temperature would accelerate the molecular thermal motion and the molecular collision probability between carbonium ion and aromatic ring would increase .Further, the catalytic ability of ionic liquid was still great when the temperature is 20°C.Using ionic liquids as catalysts had decreased the temperature compared with the traditional HF system of the factory.

Table2 Effect of reaction temperature on alkylation reaction

Number	Temperature °C	Conversion of alkenes%	Products distribution (%)				
			2-LAB	3-LAB	4-LAB	5-LAB	6-LAB
1	20	85	25.73	18.63	19.95	20.71	14.98
2	30	92	28.56	19.71	17.36	18.63	15.74
3	40	95	32.23	19.05	19.85	17.69	11.18
4	50	97	30.97	20.12	18.36	19.81	10.74

Reaction conditions: mole ratio benzene/alkenes=8; mole ratio ionic liquid/alkenes=1; t=60min; X_{AlCl_3}=0.64.

3.2 Effect of mole ratio of benzene to alkenes on alkylation reaction

Whether mole ratio of benzene to alkenes is rational or not, has a direct effect on quality of product. The effect of mole ratio of benzene to alkenes on conversion and selectivity catalyzed by chloroaluminte ionic liquid was investigated in our experiments. The results were shown in Table3.The results indicated that, there was a slight change in conversion of alkenes, and the selectivity of 2-LAB became better with the increasing of mole ratio of benzene to alkenes. Therefore, we can increase the yield of desired product by adjusting mole ratio benzene to alkenes. Taking production cost into account, the mole ratio of 8 was preferable

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Table 3 Effect of mole ratio of benzene/alkenes on alkylation reaction

No	mole ratio of benzene/alkenes	Conversion of alkenes (%)	Products distribution (%)				
			2-LAB	3-LAB	4-LAB	5-LAB	6-LAB
1	6	93	23.92	18.72	24.52	18.91	13.93
2	8	97	30.97	20.12	18.36	19.81	10.74
3	10	97	31.36	21.62	19.02	16.98	11.02

Reaction conditions: mole ratio ionic liquid/alkenes=1; t=60min; T=323K; XAlCl3=0.64.

3.3 Effect of dosages of catalyst on alkylation reaction

In order to keep the reaction carried out under enough catalyst condition, mole ratio of HF to the mixture of alkenes and alkanes in the factory is about 16.As a result ,loaf of HF regeneration tower and cost of HF purification have been increased. The effect of catalyst amount on conversion and selectivity catalyzed by chloroaluminte ionic liquid was investigated in our experiments. The results were shown in Table 4.The results indicated that ,dosage of ionic liquid was not only obviously less than HF, but also ionic liquid had better reaction activity .As dosage increased, alkylation reaction was hastened .Meanwhile, a series of side reactions would also take place, which led to a decrease in the selectivity of 2-LAB.

Table 4 Effect of dosages of catalyst on alkylation reaction

No	Mole ratio of catalyst/alkene	Reaction time ,min	Conversion alkene,%	Products distribution,%				
				2-LAB	3-LAB	4-LAB	5-LAB	6-LAB
1	1	60	97	30.97	20.12	18.36	19.81	10.74
2	2	40	97	29.14	19.75	21.96	18.18	10.97
3	3	40	97	26.68	20.51	17.94	19.67	15.20

Reaction conditions: mole ratio benzene/alkenes=8; T=323K; X_{AlCl_3}=0.64.

3.4 Effect of acidity of catalyst on alkylation reaction

$AlCl_3$ mole fraction has a critical effect on the acidity of ionic liquid, which decides the catalytic activity .It was reported that ionic liquid was acidic as long as $AlCl_3$ mole fraction was more than 0.5. The effect of catalyst acidity on conversion and selectivity catalyzed by chloroaluminte ionic liquid was investigated in our experiments. The results were shown in Table 5.The results indicated that conversion had no obvious variety. Take all kinds of factors into account; the X_{AlCl_3} of 0.64 was preferable.

Table 5 Effect of acidity of catalyst on alkylation reaction

Number	X_{AlCl3}	Conversion Alkenes (%)	Products distribution□%				
			2-LAB	3-LAB	4-LAB	5-LAB	6-LAB
1	0.62	92	28.44	17.6	19.89	18.32	15.75
2	0.64	95	32.23	19.05	19.85	17.69	11.18
3	0.67	95	30.36	20.12	19.57	17.48	12.47

Reaction conditions: mole ratio benzene/alkenes=8; mole ratio ionic liquid/alkenes=1; t=60min; T=313K.

3.5 Effect of catalyst reusability on alkylation reaction

Ionic liquid can be separated from product by simply decantation, so purification operation was reduced compared to HF. The effect of catalyst reusability on alkylation reaction was investigated in our experiments. The results were shown in Table 6.The results indicated that the catalyst had nearly half activity as it was reused without modification. After Ionic liquid was modified with HCl, conversion of alkenes became better and reached to 88%.It was believed that water contained in the reactants was the principal reason for the deactivation of the catalyst .Much work had been done for the deactivation problem [8, 9]

Table 6 Effect of catalyst reusability on alkylation reaction

Number	Conversion alkenes,%	Products distribution,%				
		2-LAB	3-LAB	4-LAB	5-LAB	6-LAB
1	97	32.23	19.05	19.85	17.69	11.18
2	39	17.79	15.81	19.12	27.56	19.72
3	87	23.29	18.90	17.79	21.59	18.43

Reaction conditions: mole ratio benzene/alkenes=8; mole ratio ionic liquid/alkenes=1; t=60min; T=313K. X_{AlCl_3}=0.64.

1- Ionic liquid was used in the first reaction run
2- Ionic liquid was reused without modification
3- Ionic liquid was reused after modification

Chromatographic analysis of alkylation products was shown in Fig1 and Fig2 respectively. The four groups peak of a to e, f to j, k to o and p to s represented C_{13} to C_{10} alkylated products respectively, and every group represented 2-LAB to 6-LAB from right to left. We can get the products distribution from peak area. Grade of alkylation product was assessed according to the applied standard of Fushun Detergent Chemical Factory. Test results were listed in Table7 and analytical data met with demand of high-class grade.

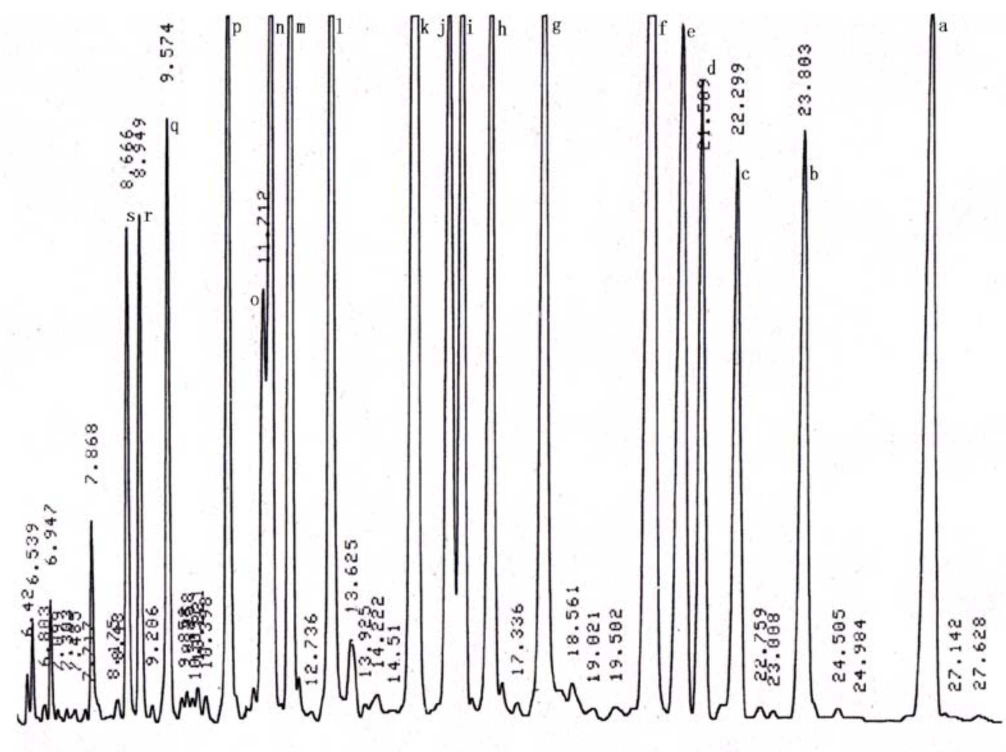

Fig 1 GC map of alkylation products distribution

Table 7 Analysis of product index

Item	Assay value		Analytical method
External appearance	Colorless and transparency		
Color HAZEN	10		GB5177.1
Refractive ,n	1.484		GB514
Density ,g/ml,20□	0.865		GB6115.2
Bromine value, g/100g	≤0.02		GB5177.4
Sulfonated bodies, %	≥98.5		GB5177.2
Average relative molecular weight	248		GB5177.3
Moisture content ,wt ppm	□100		GB6283
Distillation range,□	5%	□280	GB255
	95%	□310	

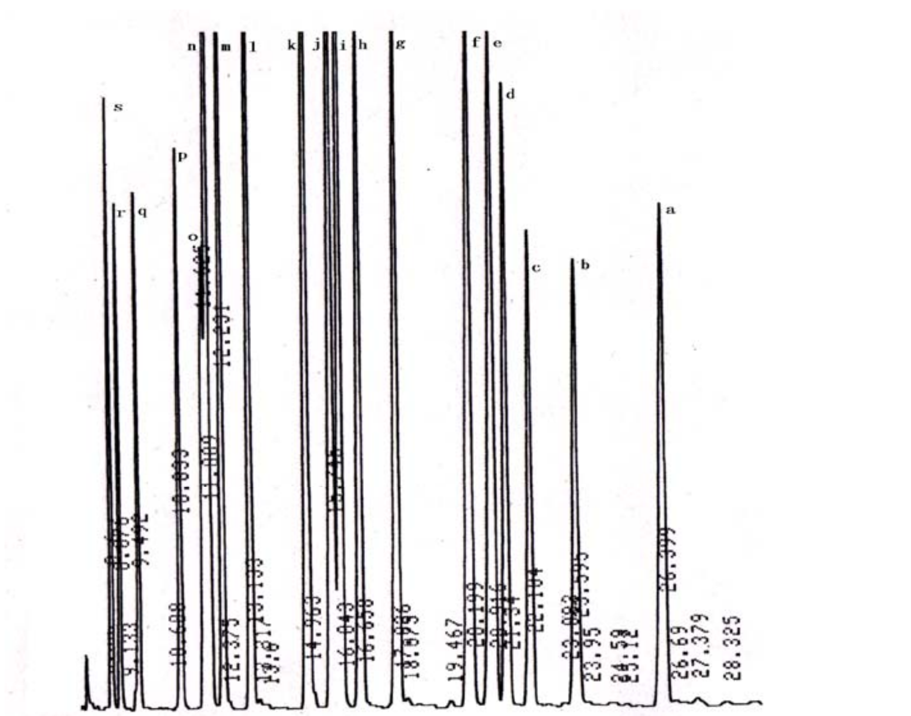

Fig 2 GC map of alkylation products distribution under catalyst modified

4. Summary

1.Using chloroaluminate ionic liquid as catalyst has decreased the reaction temperature and catalyst amount .Ionic liquid showed better reaction activity than that of HF .A 92% conversion of alkenes was achieved under the conditions of temperature of 30 □, catalyst / alkenes mole ratio of 1 and benzene / alkenes mole ratio of 8.

2.Catalytic activity of ionic liquid was associated with its acidity .The results indicated

That the X_{AlCl_3}=0.64 is the optimal condition.

3.Because the reaction system can be

automatically separated into two phase ,ionic liquid was easy to be separated from product. Catalyst purification operation was reduced compared with the conventional F-system.

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