Study on the Alkylation of Benzene and Long-Chain Olefin under Trifluoromethane Sulfonic Acid Catalyst

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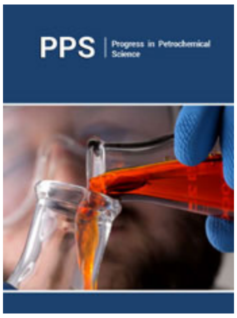

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Abstract

Using trifluoromethane sulfonic acid as catalyst for alkylation of benzene with long chain olefin process were studied. In the self-made alkylation unit, the effects of catalyst dosage, reaction time, reactant volume ratio and reaction temperature on the products were investigated. The results indicate that under the condition of 1v% catalyst dosage, 80 °C, 20min and the volume ratio of benzene and 1-decene is 8, the conversion of 1-Decene can reach 100%, and the selectivity of 2-LAB is 42.29%. Otherwise, the content of heavy alkylbenzene is small. Washing by water can separate the catalyst from reaction system easily.

Keywords: Alkylation; Trifluoromethane sulfonic acid; Alkylbenzene

Introduction

Linear Alkylbenzenes (LABs) with long chains(C_{10}-C_{14}) produced by the alkylation of benzene and α-olefin, is the important intermediate in the synthesis of industrial and household detergents. Linear Alkylbenzene Sulfonate (LAS) sulfonated by LAB is recognized as a high-quality surfactant with good biological activity and little harm to the environment [1,2]. LAB not only has strong deconstructing ability, high biological activity but low cost and is developed rapidly as early as the 1960s and 1970s, becoming the perfect substitute for early branched alkylbenzene (DDB). DDB is difficult to degrade, so the surface activity will exist for a long time after using, causing serious environment pollution. Compared with DDB, LAB has the great advantages. Nowadays, detergent as a necessity of people's life is gradually developing towards the direction of green, safety, health and fashion, which means that LAB has a huge market potentiality. LAB is mainly prepared by the alkylation of benzene and α-olefin and several isomers such as 2-, 3-, 4- and 5-alkylbenzene (2-, 3-, 4-, 5-LAB) are produced. Among them, 2-LAB is an ideal surfactant raw material because of good biodegradability and surface activity [3,4].

HF is used as catalyst in the traditional industrial preparation of LAB. However, HF is so corrosive that it is seriously damaging to the human body. At the same time, it will cause serious equipment corrosion in the production process and the industrial wastewater generated will seriously pollute the environment [5,6]. With the popularity of the concept of green chemistry, people's awareness of environmental protection has been gradually strengthened and a lot of researchers have begun to devote themselves to looking for a series of environmentally catalysts. 'Detel' method developed by UOP was the first successful way to produce LAB using solid acid catalyst. After that, many other kinds of solid acid catalyst were synthesized, including zeolites, heteropoly acids, supported heteropoly acids, solid super acids, clay catalysts and so on. In order to improve the activity of the catalyst, many scientists have ever tried to modify the catalyst by metal, acid activation and other treatments [2,7]. Although those solid acid catalysts solve the problem that the corrosion of equipment and the catalyst is difficult to separate from the products, it has high production cost. Otherwise, the solid catalysts are not only easy to deactivate because of olefin polymerization and but the regeneration is difficult and the reaction needs high temperature, which hinder the large-scale production of LAB [6,8-13]. In addition, since the 21st century, ionic liquid, as a new type of catalyst, has gradually attracted attention due to its high activity at low temperature, high selectivity of 2-LAB and excellent repeatability. However, the ionic liquid catalyst is expensive with complex synthesis method and difficult regeneration. As the research found, in the catalytic process of LAB, the activity of catalyst is greatly affected by the concentration of H+ in the ionic liquid. It is still the general trend to find new catalysts for the production of LAB efficiently and environment friendly [8,14-16].

Trifluoromethane sulfonic acid is the strongest known liquid organic acid. Because of its strong acidity, it is used as a catalyst for isomerization and alkylation. The reaction process catalyzed by trifluoromethane sulfonic acid is fast and the amount of catalyst needed is small and it is insoluble with the alkylation reaction system, so it can be easily separated. In previous studies, trifluoromethanesulfonic acid was used as a catalyst for the alkylation of isobutane and butene, showing good catalytic activity, high olefins conversion and C_8 selectivity. In order to improve its stability, a series of catalysts, such as trifluoromethane sulfonic acid supported zeolite and trifluoromethane sulfonic acid low eutectic solvent catalytic system, were synthesized for the alkylation process [17-20]. In this work, trifluoromethane sulfonic acid was used as catalyst to study the alkylation process of benzene and 1-decene, which is of great significance for the development of new catalytic system and technology.

Experimental

Chemicals and reagents

Benzene (AR, Sinopharm Chemical Reagent Co. Ltd, China), 1-Decene (AR, Aladdin Biochemical Technology Co., Ltd, China), Trifluoromethane sulfonic acid (AR, McLean Biochemical Technology Co., Ltd, China), Ethyl alcohol (AR, Sinopharm Chemical Reagent Co. Ltd, China), Victoria Pure Blue BO 6B (Sinopharm Chemical Reagent Co. Ltd, China), deionized water. Constant temperature magnetic stirrer, 85-2, Jintan Xinrui Instrument Factory, Gas Chromatograph, GC-2001, Tenghai Technology Co., Ltd, GC-MS, GC-MS-QP2020 NX, Shimadzu Group Co. Ltd.

The synthesis of phenyldecane

Benzene and 1-decene were added in proportion to a conical flask. After that, an appropriate amount of trifluoromethane sulfonic acid was quickly injected into a conical flask by a disposable syringe. Then, the conical flask was placed into a self-made alkylation device as shown in Figure 1. The conical flask was placed in a constant temperature water bath and magnetically stirred in the conical flask. When the reaction temperature reached the set temperature, the reaction started timing. After the reaction, standing for 20 minutes, the upper liquid would be taken to be measured the acid value with 0.01N potassium hydroxide ethanol solution. Last, the product was washed with deionized water to neutral and analyzed qualitatively and quantitatively by Gas Chromatograph.

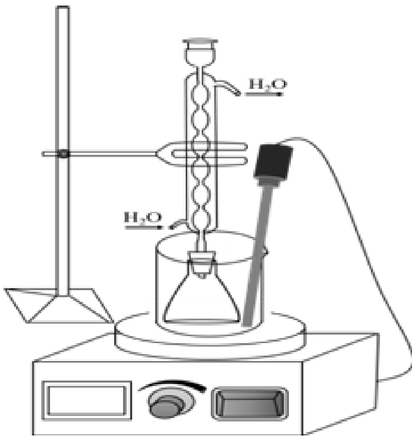

Figure 1: Schematic diagram of self-made simple alkylation device.

The analysis of products

The reaction products were qualitatively analyzed by QP2020 NX type GC-MS. Shunt injection was performed with a shunt ratio of 40:1. The inlet and detector temperature were 300 °C. And the programmed temperature rise started from 70 °C for 1 min and then increased to 300 °C for 10 min at a rate of 5 °C/min.

The reaction products were quantitatively analyzed by GC-2001 Gas Chromatograph. The inlet and detector temperature were 320 °C. And the programmed temperature rise started from 70 °C for 1 min and then increased to 320 °C for 10 min at a rate of 5 °C/min. The area normalization method was used to determine the relative content of each component in the reaction system. The acid value of the product was analyzed according to the standard of GB T510.

Results and Discussion

At the end of the reaction, the products were analyzed by gas chromatograph and it was confirmed that there were four isomers in the products, as shown in Figure 2. At the same time, it was found that there were a small number of by-products in the products. Due to the self-polymerization of olefin, two carbon chains were connected to the benzene ring in the alkylation process, resulting in the formation of heavy alkylbenzene (C_{26}). There were also four isomers, as shown in Figure 3.

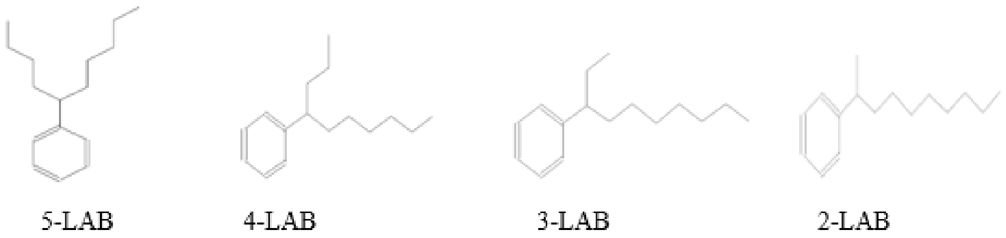

Figure 2: Structure diagram of alkylation products of benzene and 1-decene.

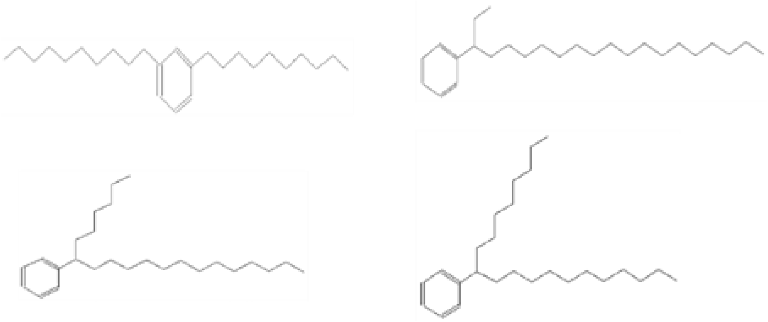

Figure 3: Structure diagram of C_{26}, by-product of alkylation of benzene and 1-decene.

Effects of catalyst dosage and reaction time

Due to the super acidity of trifluoromethanesulfonic acid, the effects of catalyst dosage and the reaction time were studied by using the methods of large amount of catalyst and short reaction time, small amount of catalyst and long reaction time. Under the conditions of reaction temperature of 80 °C and benzene/1-decene volume ratio of 4:1, the effects of different catalyst dosage and reaction time on alkylation results and acid value of products were investigated. The alkylation results were shown in Figure 4.

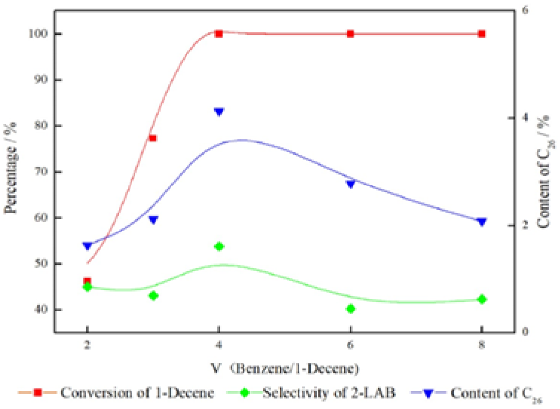

Figure 4: Effect of reaction time of 1v % catalyst dosage.

As can be seen from Figure 4, when the amount of trifluoromethane sulfonic acid is 1v%, with the increase of reaction time, the conversion of 1-decene gradually increases while the selectivity of 2-LAB decreases, and the content of C26 decreases to the bottom at 20 min, then increases slightly. It's obvious that when the reaction time is 20 min, the 1-decene conversion rate reaches 100%, the selectivity of product 2-LAB is also high and the content of alkylation by-product C_{26} is low. By measuring the acid value of the products at different reaction times, the acid value of the reaction system is also relatively small at 20 min, which was 0.44mgKOH/g. Therefore, when the amount of catalyst is 1V %, the reaction time of 20 min is the best condition. It can be seen from Figures 5 & 6 that the wanted results also can be obtained by increasing catalyst dosage and reducing the reaction time. When the trifluoromethanesulfonic acid dosage is 2v%, the conversion of 1-decene has little change with time. Although the maximum selectivity of 2-LAB is obtained at 10 min, the reaction time was 5 times longer than 2 min and the content of C_{26} is also slightly increased compared with that at 2 min. In summary, 2v% trifluoromethanesulfonic acid dosage, reaction time of 2 min, the conversion rate of 1-decene is close to 100%, which is the appropriate reaction conditions. When the amount of catalyst is increased to 3v%, the selectivity of 2-LAB decreases slightly while the content of C_{26} rises gently. At the same time, the acid value of the reaction system with different reaction time measured is generally above 4mgKOH/g, which means that the catalyst is seriously taken out with the reaction products causing the waste of the catalyst. Therefore, it is assumed that the catalyst dosage has a great impact on the acid value of the reaction system. To verify this guess, combining short reaction time with 5v%, 7v%, 10v% catalyst dosage was selected to investigate the effect on the alkylation results. The results are shown in Table 1.

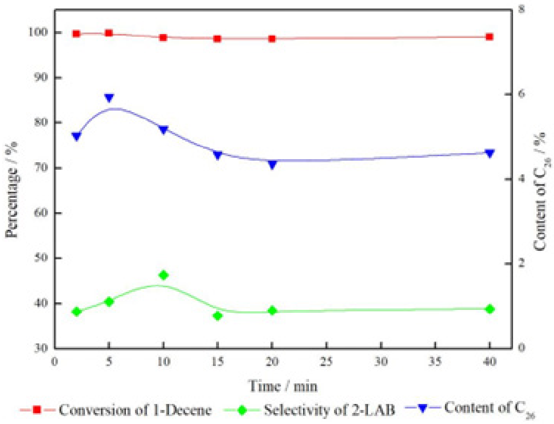

Figure 5: Effect of reaction time of 2v % catalyst dosage.

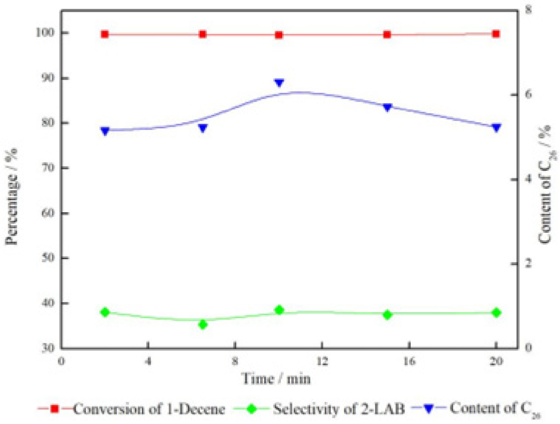

Figure 6: Effect of reaction time of 3v % catalyst dosage.

Table 1: The effect of different catalyst dosage and reaction time on the alkylation.

Catalyst Dosage (v%)	Time (min)	1-decene conversion (%)	Selectivity of 2-LAB (%)	Content of C26 (%)	Acid Value (mgKOH/g)
5	5	99.42	38.98	5.73	7.8
5	10	99.42	44.19	8.48	7.03
7	5	98.62	42.85	5.49	12.37
10	2	95.46	36.84	3.47	16.73

As can be seen from Table 1, at the high catalyst dosage, the olefin conversion rate and 2-LAB selectivity change slightly while the content of by-product C_{26} reduces. But the acid value of the product increases significantly meaning the catalyst is seriously taken out with the reaction products and the catalyst wastes a lot. In general, the high catalyst dosage is not considered.

Effect of volume ratio of benzene and 1-decene

The effects of different volume ratios of benzene and 1-decene on the alkylation results with trifluoromethanesulfonic acid as catalyst were investigated under two conditions:

A. 1v% catalyst dosage and reaction time of 20 min,

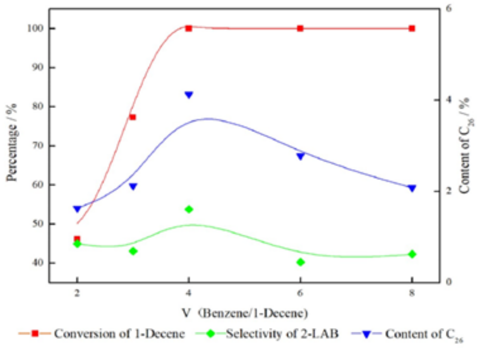

Figure 7: Effect of volume ratios of benzene and 1-decene of 1v% catalyst dosage and reaction time of 20 min.

B. 2v% catalyst dosage and reaction time of 2 min while other conditions were unchanged. The results are shown in Figures 7 & 8.

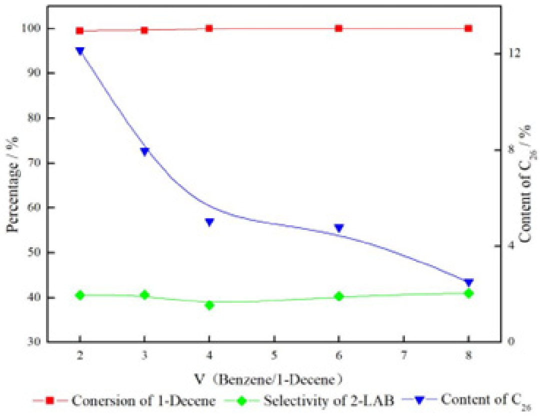

Figure 8: Effect of volume ratios of benzene and 1-decene of 2v% catalyst dosage and reaction time of 2 min.

As can be seen from Figure 7, in the case of the amount of trifluoromethanesulfonic acid is 1v% and the reaction time is 20 min, when the volume ratio of benzene and 1-decene is less than 4, the olefin conversion rate is small and the content of C_{26} is also low. Compared with Figure 8, when the volume ratio of benzene and 1-decene is 2, the olefin conversion rate can also reach more than 95%, but the content of C_{26} increases significantly. It can be seen that the content of by-products in the alkylation products is greatly affected by the volume ratio of benzene and 1-decene. As the olefin content increases, so does the content of C_{26} during alkylation. Compared with Figures 7 & 8, the selectivity of 2-LAB at 1V% catalyst dosage and reaction time 20 min is higher than that at 2V% and 2 min under the same volume ratio of benzene and 1-decene. Taking the conversion rate of 1-decene, the selectivity of 2-LAB and the content of by-product C_{26} into consideration, the optimum volume ratio of benzene and 1-decene is 8 when the amount of catalyst is 1v% and the reaction time is 20 min.

Effect of reaction temperature

The effect of reaction temperature on alkylation results was investigated under the conditions of trifluoromethanesulfonic acid dosage of 1v%, reaction time of 20 min and volume ratio of benzene and 1-decene of 8:1. The results are shown in Figure 9.

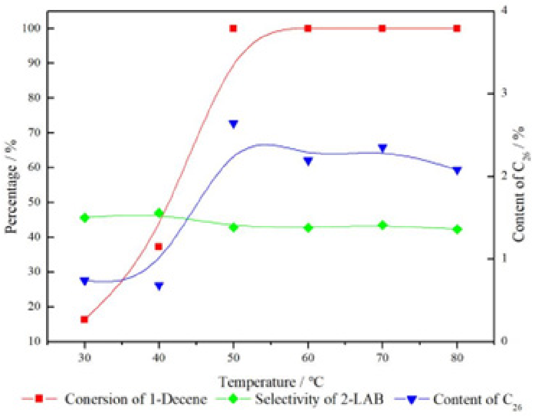

Figure 9: Effect of reaction temperature..

As Figure 9 shown, when the temperature is lower than 50, the olefin conversion rate is low, but the selectivity of 2-LAB is high and the content of C_{26} is low. When the temperature increases, the conversion of 1-decene increases, but the selectivity of 2-LAB and content of C_{26} decrease. When the temperature exceeds 50 °C, the selectivity of 2-LAB and the content of C_{26} change lightly. However, the acid value varies greatly. The acid value at 60 °C is 5.51mgKOH/g while at 80 °C is only 0.59mgKOH/g. Therefore, considering the selectivity of 2-LAB, the content of C_{26} and the acid value of reaction products, 80 °C is the most suitable reaction temperature.

The investigation of alkylation results of trifluoromethane sulfonic acid and traditional HF method and HY zeolite

As can be seen from Table 2, when trifluoromethane sulfonic acid is used as catalyst, the selectivity of 2-LAB can reach 42.29% under the optimal conditions and the content of heavy alkylbenzene is less than HF method whose selectivity of 2-LAB is only 15% [21,22]. Cheng Y et al. [23] tried to apply HF loaded USY zeolite to the alkylation reaction of benzene and hexadecane under the conditions of 130, 2.5MPa, mole ratio of benzene and hexadecane of 10:1 and the conversion of olefin reached 99.19%. Similarly, Wen QW et al. [24] applied HF on USY zeolite for the alkylation process of benzene and dodecane. The reaction temperature was 180 °C. The conversion of olefin was only 94.3%, and the selectivity of alkylbenzene in the product was 92.76%.

Table 2: Comparison of alkylation results between HF method and trifluoromethane sulfonic acid.

Composition of Alkylation Products	HF	Trifluoromethane Sulfonic Acid
Content of LAB (m), %	93	94.28
Selectivity of 2-LAB, %	15	42.29
Content of heavy alkylbenzene (m), %	7	5.72

In addition to HF, HY zeolite is a kind of solid acids used industrially to produce linear alkylbenzene. Although using HY zeolite as catalyst has no corrosion, HY zeolite is easy deactivate and has poor selectivity. Hornacek M et al. [25]. used three kinds of HY zeolite to catalyze the liquid phase alkylation of benzene with 1-alkene. The results are shown in Table 3.

Table 3: Composition of products catalyzed by HY zeolite DB-Fresh, deep-bed dealuminated HY; EF-Fresh, EFAL-extracted HY.

Catalyst	Conversion of 1-alkene (%)	Selectivity of 2-LAB (%)	Alkylbenzenes (%)
HY-Fresh	96.41	22.21	99.92
DB-Fresh	80.65	29.43	99.23
EF-Fresh	98.04	32.18	99.64

We can see from Table 3 that the content of alkylbenzene is higher than the process catalyzed by trifluoromethane sulfonic acid. But the conversion of olefin doesn't rach 100% and selectivity of 2-LAB is much lower than that of the catalytic products of trifluoromethane sulfonic acid. The results in this work are basically consist with Wen LY et al. [26] used HY zeolite to catalyze the alkylation of benzene with 1-dodecene. In his work, when the olefin is completely converted, the selectivity of 2-ALB is only 25%. The catalytic performance in these works is slightly worse than trifluoromethane sulfonic acid.

Conclusion

Trifluoromethane sulfonic acid has excellent catalytic performance for the alkylation of benzene with 1-decene. A small amount of catalyst can make the reaction complete in a short time. The conversion of 1-decene is close to 100% and selectivity of 2-LAB in the product is also relatively high. In addition, compared with HF method, the catalytic performance of trifluoromethane sulfonic acid is better and can replace HF as benzene alkylation catalyst, realizing industrial production. This work studied the effect of trifluoromethane sulfonic acid dosage, reaction time, volume ratio of benzene and 1-decene and reaction temperature on the alkylation reaction process. The results shows that when trifluoromethane sulfonic acid is used as catalyst, conversion of 1-decene can reach 100% and selectivity of 2-LAB is 42.29% under conditions of 80 °C, 1v% catalyst dosage, 20 min and volume ratio of 8:1.

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