

# Alkylation of Toluene with 1,3-Pentadiene over [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> Ionic Liquid Catalyst\*

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**Abstract** The alkylation of toluene with 1,3-pentadiene to produce pentyltoluene was carried out to obtain 2,6-dimethylnaphthalene, which is an important intermediate during the production of 2,6-naphthalene dicarboxylic acid. Based on our previous work using anhydrous AlCl<sub>3</sub> as catalyst, [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids were employed to catalyze the reaction of 1,3-pentadiene with toluene. The experimental results show that [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids are suitable for the reaction especially when the molar ratio of AlCl<sub>3</sub> to [bupy]BF<sub>4</sub> is 1.75 : 1, and the reaction could proceed at the temperature as low as 0°C. It could be as active as pure AlCl<sub>3</sub>, but much more environmentally friendly.

**Keywords** [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids, toluene, 1,3-pentadiene, pentenyltoluene

## 1 INTRODUCTION

2,6-dimethylnaphthalene (2,6-DMN) is the intermediate of 2,6-naphthalene dicarboxylic acid, a building block and raw material of the advanced polymer such as polyethylene naphthalate, polybutylene naphthalate and liquid crystalline polymers. Hence it is attracting more and more attention these days. As a raw material, it directly determines the cost of 2,6-naphthalene dicarboxylic acid and the expense of the above polymers. It is essential and desirable to produce 2,6-DMN using a cheaper and cleaner process. Generally 2,6-DMN is obtained through two routes. One is to extract a distilled fraction from coal tar or refinery streams, another is via a multistep synthesis. In this research, our interest in synthesizing 2,6-DMN is focused on the alkylation of toluene with 1,3-pentadiene, which is a side-product of the C5 diolefin in oil cracking for ethylene production[1]. With the development of the ethylene industry, the yield of C5 diolefin is also increased. Unfortunately, the C5 diolefin is mainly used as fuel, which leads to less than 20% utilization. Our technology, which can not only decrease the cost of 2,6-DMN but also make efficient use of C5 diolefin, is extraordinarily vendible.

This process is divided into two steps: the first is alkylation of toluene with 1,3-pentadiene, which is crucial for the whole process, and the second is pentenyltoluene cyclized, dehydrogenized and then isomerized to 2,6-DMN. The first step is a typical Friedel-Crafts alkylation reaction, which is always catalyzed over Lewis acids. However, the most useful catalyst is AlCl<sub>3</sub> which causes serious environmental problems. To avoid pollution a more environmentally friendly catalyst is desired.

Ionic liquids as “designer-solvents” have received great attention in the past decades[2—4]. The unique, highly solvating, non-coordinating environment of ionic liquids is an attractive medium for various types of chemical processes especially in Friedel-Crafts reaction[5—7]. To date, there is no re-

port on using ionic liquids to catalyze alkylation reaction with diolefin. Based on our previous work using AlCl<sub>3</sub> as catalyst for toluene and 1,3-pentadiene reaction to produce pentenyltoluene, herein, we report the application of butylpyridinium tetrafluoroborate ([bupy]BF<sub>4</sub>)-AlCl<sub>3</sub> ionic liquids as catalyst in the alkylation reaction of toluene with 1,3-pentadiene.

## 2 EXPERIMENTAL

### 2.1 Materials

Bromobutane (CP), pyridine (AR), sodium tetrafluoroborate (CP), toluene (AR) are from local market. 1,3-Pentadiene is supplied by Shanghai Petrochemical Co., which is a side-product of the C5 diolefin in oil cracking for ethylene production.

### 2.2 Synthesis of ionic liquids[8,9]

0.31mol pyridine was slowly added to 0.45mol bromobutane at room temperature. The mixture was heated to 65°C under agitation until it became cloudy and formed two phases. Under reduced pressure, the excess reactant was removed. The production was washed with tetrahydrofuran (THF), recrystallized from acetonitrile and THF and then dried in vacuum to obtain [bupy]Br.

0.30 mol of [bupy]Br and 0.32mol sodium tetrafluoroborate were dissolved in 250ml of acetonitrile, and the solution was stirred at room temperature, resulting in a milky-white mixture. Leftover NaBF<sub>4</sub> and byproduct NaBr were removed by filtration and the solvent was removed under reduced pressure. This yielded a clear, colorless liquid with some white solid at the bottom of the flask. The liquid was redissolved in dichloromethane, which gave more precipitation of the white solid. This mixture was filtered, and the solvent was removed from the cake under reduced pressure to yield 62.6 g of [bupy]BF<sub>4</sub> (95% purity).

A given amount of anhydrous AlCl<sub>3</sub> was slowly added to 1.2g of [bupy]BF<sub>4</sub>, and the mixture was stirred

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at 45°C until the catalyst was completely dissolved. [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids were thus obtained.

### 2.3 Alkylation of toluene with 1, 3-pentadiene

0.282mol of toluene and 0.069mol of 1,3-pentadiene were directly added to the [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids solution (15mmol). Two phases were formed and the reaction mixture was stirred at the desired temperature. The upper layer was the organic layer, and the lower was ionic liquids. After the reaction was finished, the mixture was separated by decanting.

### 2.4 Analysis[10]

An Agilent6890 (Agilent Co., USA) gas chromatograph equipped with a flame ionization detector (FID) was employed for the analysis. The detector temperature was maintained at 240°C. The column was programmed with an initial temperature of 60°C, and was increased thereafter to 220°C at the rate of 15°C·min<sup>-1</sup>. The column used for this purpose was HP-1, with dimension of 50m×0.25mm×0.50μm.

## 3 RESULTS AND DISCUSSION

### 3.1 Effects of molar ratio of AlCl<sub>3</sub> and [bupy]BF<sub>4</sub>

As shown in Figs.1 and 2, the yield of pentenyltoluene relied on [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> composition. It was noted that when the molar ratio of AlCl<sub>3</sub> to [bupy]BF<sub>4</sub> became 1.75 : 1, which is corresponding to the dosage of 1.2g of [bupy]BF<sub>4</sub> and 1.27g of anhydrous aluminum, respectively, the [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids showed the best performance in the alkylation reaction. At 4h, both the yield of pentenyltoluene and the conversion of the 1,3-pentadiene became the

maximum, although the selectivity of the target product is very low (about 10%).

However the reaction neither occurred in the ionic liquids without AlCl<sub>3</sub> nor in the ionic liquids in which the molar ratio of AlCl<sub>3</sub> to [bupy]BF<sub>4</sub> was 1 : 1. Two mechanisms accounted for the alkylation of toluene with 1,3-pentadiene, both involving electrophilic substitution of the aromatic ring, with the electrophile representing the alkyl cation (carbenium ion)[11]. The alkyl cation could be generated by a Lewis acid centre in AlCl<sub>3</sub>. Pure [bupy]BF<sub>4</sub>, as is known, appeared Lewis basic. Simple adjustments of the molar ratios of [bupy]BF<sub>4</sub> and AlCl<sub>3</sub> could produce ionic liquids with variable levels of acidity.

Carbenium ion was responsible for the side reactions accompanying alkylation, including isomerization, oligomerization, cracking, and hydrogen transfer, in addition to the disproportionation and alkylation of the alkyl aromatic. So far, further investigation into the relationship between acidity and the molar ratio of AlCl<sub>3</sub> and [bupy]BF<sub>4</sub> is underway.

### 3.2 Effects of temperature

Figures 3 and 4 showed the results of alkylation of toluene with 1,3-pentadiene at different temperatures. It is discovered that the highest yield of pentenyltoluene was seen at 0°C, but the highest conversion of 1,3-pentadiene was found at 60°C. It could be due to that the reaction was an exothermic reaction [12], while lower temperature might be in favor of the reaction. But 1,3-pentadiene was easily polymerized and gasified at higher temperature. These led to a higher yield at a lower temperature and a higher conversion at a higher temperature.

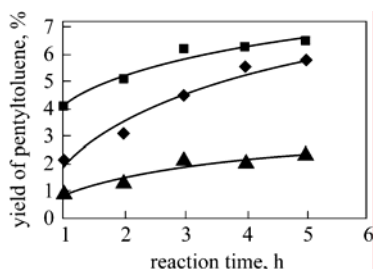


Figure 1 Effect of molar ratio of AlCl<sub>3</sub> and [bupy]BF<sub>4</sub> on the yield of pentyltoluene  
molar ratio of AlCl<sub>3</sub> to [bupy]BF<sub>4</sub>:  
♦ 2.0 : 1; ■ 1.75 : 1; ▲ 1.5 : 1

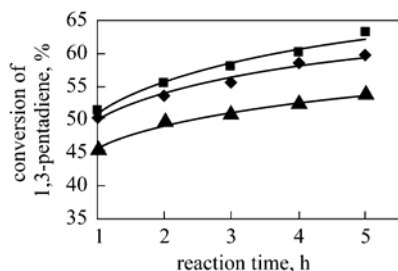


Figure 2 Effect of molar ratio of AlCl<sub>3</sub> and [bupy]BF<sub>4</sub> on the conversions of 1,3-pentadiene  
molar ratio of AlCl<sub>3</sub> to [bupy]BF<sub>4</sub>:  
♦ 2.0 : 1; ■ 1.75 : 1; ▲ 1.5 : 1

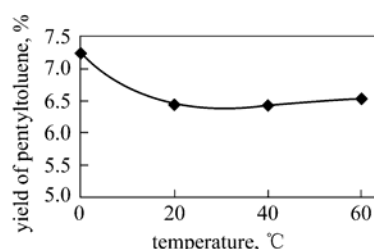


Figure 3 Effect of temperature on the yield of pentyltoluene

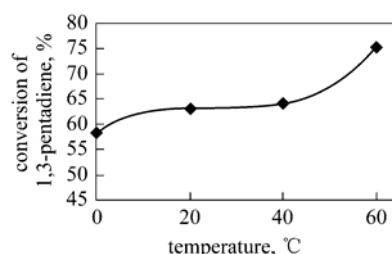


Figure 4 Effect of temperature on the conversions of 1,3-pentadiene

Our initial experimental results show that anhydrous AlCl<sub>3</sub> is an effective catalyst for the alkylation. Instead of using 15mmol [bupy]BF<sub>4</sub>-AlCl<sub>3</sub> ionic liquids

as alkylation catalyst, in which the molar ratio of  $\text{AlCl}_3$  to  $[\text{bupy}]\text{BF}_4$  is 1.75 : 1, when only 2.5g of anhydrous  $\text{AlCl}_3$  used as catalyst, the system demonstrated nearly the same catalytic activity as  $[\text{bupy}]\text{BF}_4\text{-AlCl}_3$  ionic liquid for alkylation of toluene with 1,3-pentadiene when the reaction temperature was above 45°C. Besides, anhydrous  $\text{AlCl}_3$  exhibited almost no catalytic activity when reaction temperature was below 40°C. However, the reuse times of  $[\text{bupy}]\text{BF}_4\text{-AlCl}_3$  ionic liquid should be taken into consideration in future study.

#### 4 CONCLUSIONS

$[\text{Bupy}]\text{BF}_4\text{-AlCl}_3$  ionic liquids were suitable for the Friedel-Crafts alkylation of toluene with 1,3-pentadiene. It could be as active as pure  $\text{AlCl}_3$ , but much more environmentally friendly and made it easy separation. The Friedel-Crafts alkylation was an exothermic reaction, and could occur even at 0°C over the catalyst of  $[\text{bupy}]\text{BF}_4\text{-AlCl}_3$ . The use of ionic liquids catalysts helped to increase the selectivity of the product and reduce the loss of 1,3-pentadiene. This reaction can proceed at ambient temperature, so it can also decrease the requirement of energy input. As a result, ionic liquid  $[\text{bupy}]\text{BF}_4\text{-AlCl}_3$  mixed medium seems appropriate for the Friedel-Crafts alkylation of toluene with 1,3-pentadiene, and it is a kind of green catalyst.

Synthesizing 2,6-DMN with toluene and 1,3-pentadiene can not only decrease the cost of 2,6-DMN but also make efficient use of the C5 diolefin.

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