Efficient and Easily Recyclable Catalyst for the Alkylation Reaction of Phenol and tert-Butyl Alcohol

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ABSTRACT: tert-Butylphenol is widely used as an intermediate in organic synthesis, and the catalyst for the alkylation reaction of phenol and tert-butyl alcohol is the key to synthesizing tert-butylphenol. In our work, a catalyst, 1H-imidazole-1-acetic acid tosilate ([HIMA]OTs), was synthesized and characterized, and an efficient and easily recyclable catalytic system of an ionic liquid was established. In addition, the kinetic and thermodynamic parameters were calculated; the positive value of \( \Delta H^* \) indicated the endothermic nature of the alkylation reaction, and the positive value of \( \Delta S^* \) and negative value of \( \Delta G^* \) implied that the process of alkylation of phenol and tert-butyl alcohol was spontaneous in the current reaction system. The recovery experiments of [HIMA]OTs were performed, and an excellent recycling performance was obtained. This method provides a potential way for the industrial synthesis of tert-butylphenol.

1. INTRODUCTION

As one of the most important organic chemicals, tert-butylphenol is widely used as an antioxidant, stabilizer, fungicide, and so on.\(^1^\)-\(^5\) Although many methods were used to synthesize tert-butylphenol, alkylation of phenol and tert-butyl alcohol is the most effective way, and the key to the preparation of tert-butylphenol by the alkylation reaction is the catalytic system. A series of mesoporous molecular sieves (A1MCM-41) were synthesized by Selvam et al., and a silicon-to-aluminum ratio of around 60 exhibited the highest conversion and good selectivity for vapor-phase tertiary butylation of phenol.\(^6\) Dumitru et al. reported the effects of channel structures and acid properties of large pore zeolites in the liquid-phase tert-butylation of phenol, and the three-dimensional interconnecting pore system of \( \beta \) and USY zeolites showed a higher catalytic activity than the mono-dimensional system of pores of the MOR zeolites.\(^7\) In addition, homogeneous catalysts were also reported. For example, perchloric acid was used for the alkylation of phenol with tert-butyl alcohol.\(^8\) However, the problems such as corrosivity of the catalyst, difficulty in separating it from the reaction system, and unfriendliness to the environment still remain challenging.\(^9^\)-\(^11^\)

In recent years, ionic liquids have attracted much attention due to their specific properties, such as undetectable vapor pressure, easy to separate from the reaction system, and environmentally friendly.\(^12^\)-\(^18^\) Hence, ionic liquids have been used in many fields, especially in catalysis; it was proved that a large number of reactions could be catalyzed by ionic liquids, such as esterification,\(^19^\)-\(^22^\) carboxylation,\(^23^\)-\(^25^\) cycloaddition,\(^26^\)-\(^28^\) and alkylation reaction.\(^29^\)-\(^32^\)

As one of the most important Friedel–Crafts reactions in the chemical industry, alkylation of phenol and tert-butyl alcohol was also investigated using an ionic liquid as a catalyst. A heteropolyanion-based ionic liquid catalyst was synthesized and characterized, and the maximum phenol conversion of 93% was achieved.\(^33^\) In addition, N-methyl imidazole-, pyridine-, and triethylamine-based Bronsted acidic ionic liquids with sulfonic acid functionalities were obtained, and a maximum phenol conversion of 86 with 57.6% selectivity to 4-tert-butylphenol was achieved at a temperature of 70 °C.\(^34^\) Particularly, a series of deep eutectic solvents were synthesized by Zhang et al., only 30 °C was needed by alkylation of phenol and tert-butyl alcohol, and 99.5% conversion of tert-butyl alcohol was obtained; however, it is regrettable that the reaction time was as long as 7 h.\(^3\) Here, a new and easily recyclable catalytic system of an ionic liquid was established, which may provide a potential way for the industrial synthesis of tert-butylphenol.
2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Imidazole-1-yl-acetic acid was purchased from Shanghai Adamas Reagent Co., Ltd.; p-toluenesulfonic acid was obtained from Macklin Biochemical Technology Co., Ltd.; and phenol and tert-butyl alcohol were purchased from Nanjing Wanqing Reagent Co., Ltd. All of the reagents were used without further purification.

2.2. Preparation of 1H-imidazole-1-acetic Acid Tosilate ([HIMA]OTs). Briefly, 12.6 g of imidazole-1-yl-acetic acid and 17.2 g of p-toluenesulfonic acid were mixed in a 100 mL flask, 50 mL of deionized water was employed as a solvent, and the mixture was stirred at 50 °C for 8 h. Then, the solvent was removed by evaporation under vacuum, and [HIMA]OTs were obtained after drying for 24 h.

2.3. Characterization of [HIMA]OTs. 1H and 13C NMR characterization of [HIMA]OTs are shown in Figures 1 and 2, and the details are listed as follows:

![Figure 1. 1H NMR of [HIMA]OTs.](image)

![Figure 2. 13C NMR of [HIMA]OTs.](image)

2.4. Procedure for the Alkylation Reaction. Briefly, 10 mmol of tert-butyl alcohol, 100 mmol of PhOH, and a certain amount of [HIMA]OTs were mixed in a closed flask, equipped with a condensation pipe, the reaction system was purged with N2 three times to remove air, and then the flask was stirred with 500 rpm at the set reaction temperature for 2 h. After the reaction, ethyl acetate was used to separate the catalyst, and the conversion of tert-butyl alcohol and selectivity of tert-butylphenol were determined by gas chromatography. The reaction equation is listed as follows:

\[
\text{OH} + \text{OH} \rightarrow \text{[HIMA]OTs} \rightarrow \text{OH} + \text{OH} + \text{OH}
\]

2.5. Determination of Conversion and Selectivity. The conversion of tert-butyl alcohol and the selectivity of 2-tert-butylphenol (2-TBP), 4-tert-butylphenol (4-TBP), and 2,4-di-tert-butylphenol (2,4-DTBP) were determined using a Shimadzu GC 2014C subsequently, equipped with an RTX-5 capillary column (30 m × 0.32 mm × 0.25 μm) and an FID detector; n-octane was employed as the internal standard. The temperatures of the detector and gasification chamber were 300 °C, the initial temperature of the column was 50 °C and held for 3 min, and then it was programmed to heat up at a rate of 40 °C/min and held at 300 °C for 5 min. The conversion of tert-butyl alcohol is calculated as follows

\[
\text{conversion (%) } = \frac{\text{mole}_{2\text{-TBP}} + \text{mole}_{4\text{-TBP}} + (2)\text{mole}_{2,4\text{-DTBP}}}{\text{total moles TBA}}
\]

2.6. Kinetic and Thermodynamic Studies. The kinetic and thermodynamic parameters are very important to the application of the alkylation reaction for tert-butyl alcohol and PhOH catalyzed by [HIMA]OTs. The kinetic and thermodynamic studies were carried out at different temperatures from 323 to 343 K under standard reaction conditions.

3. RESULTS AND DISCUSSION

3.1. Characterization of [HIMA]OTs. 1H and 13C NMR characterization of [HIMA]OTs are shown in Figures 1 and 2, and the details are listed as follows:
$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm): 9.09 (s, 1H), 7.72 (d, 2H), 7.51 (d, 2H), 7.13 (d, 2H), 5.14 (s, 2H), 2.28 (s, 3H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm): 168.84, 145.84, 138.43, 137.17, 128.70, 126.00, 123.89, 120.05, 49.92, 21.32.

FTIR spectra are also performed in Figure 3. The broad absorption bands at 3070 cm$^{-1}$ were assigned to the stretching vibration of $-\text{COOH}$, and the peak at 1729 cm$^{-1}$ was the stretching vibration of $\text{C}==\text{N}$ in the imidazole ring; in addition, the characteristic skeleton vibration peaks for the benzene ring were at 1585, 1552, and 1421 cm$^{-1}$. Thermogravimetric analysis was also performed for [HIMA]OTs in Figure 4, and the mass loss of the catalyst was only 4.2% before 270 °C, which indicated the excellent thermostability of [HIMA]OTs.

Figure 3. FTIR spectra of [HIMA]OTs.

Figure 4. TG curve of [HIMA]OTs.

3.2. Optimization of Reaction Conditions for the Alkylation Reaction. 3.2.1. Effect of Dosage of Catalyst on Conversion of tert-Butyl Alcohol. The optimization of reaction conditions for alkylation of tert-butyl alcohol and PhOH was performed. The effect of dosage of [HIMA]OTs on conversion of tert-butyl alcohol was investigated; a reaction temperature of 70 °C and a reaction time of 120 min were used in our experiments, and the results are shown in Figure 5. The results indicated that the dosage of catalyst has a significant influence on the conversion of tert-butyl alcohol, and there was no tert-butyl alcohol existed when the dosage of catalyst increased to 10 mol % (based on tert-butyl alcohol) in the current reaction system. The result indicated that 10 mol % [HIMA]OTs was necessary for our experiments.

3.2.2. Effect of Reaction Time on Conversion of tert-Butyl Alcohol. The effect of reaction time on conversion of tert-butyl alcohol was investigated; a reaction temperature of 70 °C and [HIMA]OTs (10 mol %) were used in our experiments, and the results are shown in Figure 6. The conversion of tert-butyl alcohol increased with the increase of reaction time, and 100% of conversion was obtained when the reaction time was 120 min. The result implied that a reaction time of 120 min was needed for alkylation of tert-butyl alcohol and PhOH.

3.2.3. Effect of Reaction Temperature on Conversion of tert-Butyl Alcohol. The effect of reaction temperature on conversion of tert-butyl alcohol was investigated; a reaction time of 120 min and [HIMA]OTs (10 mol %) were used in our experiments, and the results are shown in Figure 7. Although the alkylation reaction could be conducted at 50 °C,
a much longer reaction time was needed; hence, a reaction temperature of 70 °C was used in our experiments.

![Figure 7. Effect of temperature on conversion of tert-butyl alcohol.](image)

3.3. Kinetic Study. Kinetic parameters are of great importance to the application of the alkylation reaction for tert-butyl alcohol and PhOH catalyzed by [HIMA]OTs; hence, the kinetic studies were carried out at different temperatures from 323 to 343 K under standard reaction conditions. The excessive PhOH (tert-butyl alcohol: PhOH = 1:10) was used in our experiments; thus, the reaction rate can consider irrelevant to the concentration of PhOH. Consequently, the kinetic model of the alkylation reaction catalyzed by [HIMA]OTs can be expressed as follows

\[
\ln k = \ln k_0 - \frac{E_1}{R} \left( \frac{1}{T} \right)
\]

(5)

where \(E_1\) (kJ/mol) is the activation energy, \(k_0\) is the frequency factor, \(R\) (J/(mol·K)) is the universal gas constant, and \(T\) (K) is the reaction temperature.

The activation energy was estimated by plotting \(\ln k\) versus \(1/T\) in Figure 8. The results exhibited a good fitting (\(R^2 = 0.84394\)), and an activation energy \(E_1\) of 97.46 kJ/mol and a pre-exponential factor \(k_0\) of 2.7598 × 10^{13} were obtained. The calculated value of activation energy is similar to the literature values. For example, an activation energy of 30 kJ/mol was obtained by Ojha et al.\(^{35}\) for the alkylation of PhOH and tert-butyl alcohol catalyzed by HZOP-31; however, a much higher reaction temperature of 453 K was needed; an activation energy of 34.8 kJ/mol was obtained by Patra et al.,\(^{36}\) and a SO_3·H functionalized Bronsted acidic ionic liquid was employed to catalyze the alkylation reaction; however, the mole ratio of an ionic liquid to phenol was as high as 1:1; in addition, a triethylammonium-based sulfonic acid-functionalized ionic liquid was used as a catalyst for the alkylation of PhOH and tert-butyl alcohol, and 11.13 kcal/mol was calculated in the temperature range of 50–90 °C.\(^{34}\)

3.4. Thermodynamic Study. The linearized Eyring equation based on transition state theory was employed to calculate the enthalpy of activation \(\Delta H^*\) and the entropy of activation \(\Delta S^*\), and the equation was expressed as\(^{37-41}\)

\[
\ln \frac{k}{T} = - \left( \frac{\Delta H^*}{RT} \right) + \ln \kappa + \ln \left( \frac{k_b}{h} \right) + \frac{\Delta S^*}{R}
\]

(6)

where \(\kappa\) is the transmission factor (we assumed that the value is 1), \(h\) is the Planck’s constant, which is equal to 6.626 × 10^{-34} J/s\(^{-1}\), and \(k_b\) is the Boltzmann’s constant, which is equal to 1.381 × 10^{-23} J/K.

![Figure 8. Arrhenius plot for the alkylation reaction catalyzed by [HIMA]OTs.](image)

| Table 1. Kinetic Parameters at Different Temperatures |
|--------------------------------|---------|---------|---------|---------|---------|
| kinetic parameters           | 323 K   | 328 K   | 333 K   | 338 K   | 343 K   |
| \(k\) (L/(mol·min))          | 0.00662 | 0.007   | 0.00965 | 0.02255 | 0.05282 |
| \(k^2\)                      | 0.9477  | 0.97277 | 0.97087 | 0.98757 | 0.97453 |
| standard error               | 0.00077 | 0.00058 | 0.00082 | 0.00145 | 0.00046 |
Therefore, the values of $\Delta H^*$ and $\Delta S^*$ were obtained by plotting $\ln k/T$ against $1/T$, and the results are shown in Figure 9 and Table 2. The positive value of $\Delta H^*$ indicated the endothermic nature of the alkylation reaction; hence, the higher reaction temperature is favorable to the alkylation of phenol and tert-buty-alcohol, and the result is compatible with Figure 7. In fact, many literature studies have been reported with a positive value of $\Delta H^*$ in the alkylation of phenol and tert-buty-alcohol.\(^{34}\) In addition, the Gibb’s free energy of activation $\Delta G^*$ can be calculated as

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T}$$  \hspace{1cm} (7)

The positive value of $\Delta S^*$ and negative value of $\Delta G^*$ implied that the process of alkylation of phenol and tert-buty-alcohol was spontaneous in the current reaction system.

### 3.5. Recycling Performance for [HIMA]OTs

The recovery experiments were carried out to investigate the recycling performance of [HIMA]OTs. At the beginning of the alkylation reaction, an obvious interface existed between the catalyst and solvent, and then the interface disappeared as the reaction went on; it was favorable for the alkylation reaction because of the much lower transfer resistance in the homogeneous system than the heterogeneous system. After the reaction, ethyl acetate was used to separate the catalyst from the reaction system, and the precipitation of [HIMA]OTs was obtained. The precipitation was used for the recovery experiments after drying at 60 °C for 8 h. The results of recovery experiments are shown in Figure 10, and the conversion of tert-buty-alcohol decreased a little, which may be due to the small amount of catalyst lost during the recovery process. The results indicated that the recovery performance of [HIMA]OTs was excellent.

### 4. CONCLUSIONS

An efficient and easily recyclable catalyst [HIMA]OTs was synthesized. \(^1\)H and \(^13\)C NMR, FTIR spectra, and thermogravimetric analysis were employed to characterize the catalyst. The alkylation reaction conditions were optimized, and [HIMA]OTs (10 mol %), a reaction time of 120 min, and a reaction temperature of 70 °C were obtained. The kinetic studies were carried out at different temperatures from 323 to 343 K under standard reaction conditions, and an activation energy $E_a$ of 97.46 kJ/mol and a pre-exponential factor $k_0$ of $2.7598 \times 10^{13}$ were obtained. In addition, the enthalpy of activation $\Delta H^*$, the entropy of activation $\Delta S^*$, and the Gibb’s free energy of activation $\Delta G^*$ were calculated, and the results indicated the endothermic nature and spontaneity of the alkylation reaction in the current reaction system. The new catalytic system provides a potential way for the synthesis of tert-buty-phenol in industry.
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Notes
The authors declare no competing financial interest.

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