

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

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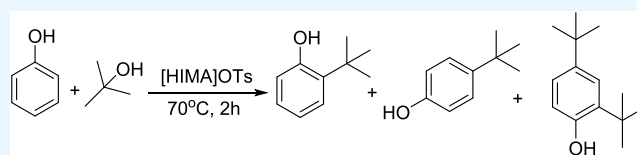
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ABSTRACT: *tert*-Butylphenol is widely used as an intermediate in organic synthesis, and the catalyst for the alkylation reaction of phenol and *tert*-butyl alcohol is the key to synthesizing *tert*-butylphenol. In our work, a catalyst, 1H-imidazole-1-acetic acid tosylate ([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 ΔH^* indicated the endothermic nature of the alkylation reaction, and the positive value of ΔS^* and negative value of ΔG^* 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 (AlMCM-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 Dumitriu 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 β 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} carbonylation,^{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.¹ 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.

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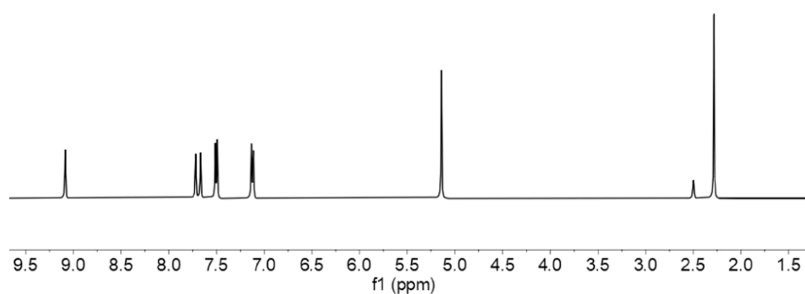


Figure 1. ^1H NMR of [HIMA]OTs.

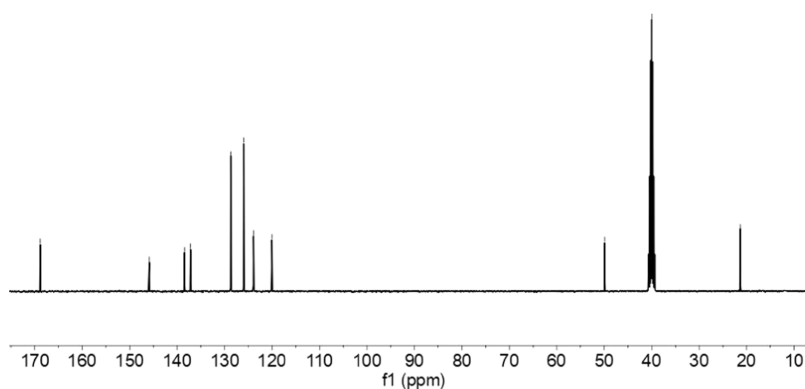


Figure 2. ^{13}C NMR of [HIMA]OTs.

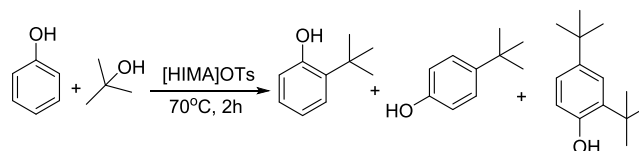
2. EXPERIMENTAL SECTION

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 1*H*-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 ^{13}C NMR spectra of [HIMA]OTs were recorded on a Bruker Avance 400 spectrometer, and DMSO- d_6 was employed as a solvent. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS 870 spectrometer; in addition, thermogravimetric analysis (TGA) was performed on a Pyris 1 DSC at a heating rate of 10 °C/min from 30 to 700 °C under a N_2 atmosphere.

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 N_2 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:



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 \times 0.32 mm \times 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

$$\text{conversion (\%)} = \frac{\text{mole}_{2\text{-TBP}} + \text{mole}_{4\text{-TBP}} + (2)\text{mole}_{2,4\text{-DTBP}}}{\text{total moles TBA}} \quad (1)$$

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 ^{13}C NMR characterization of [HIMA]OTs are shown in Figures 1 and 2, and the details are listed as follows:

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ (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, $\text{DMSO-}d_6$) δ (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

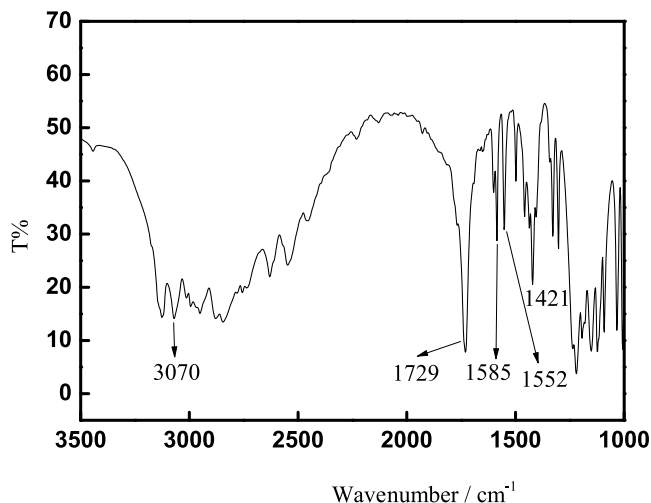


Figure 3. FTIR spectra of [HIMA]OTs.

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 $270\text{ }^\circ\text{C}$, which indicated the excellent thermostability of [HIMA]OTs.

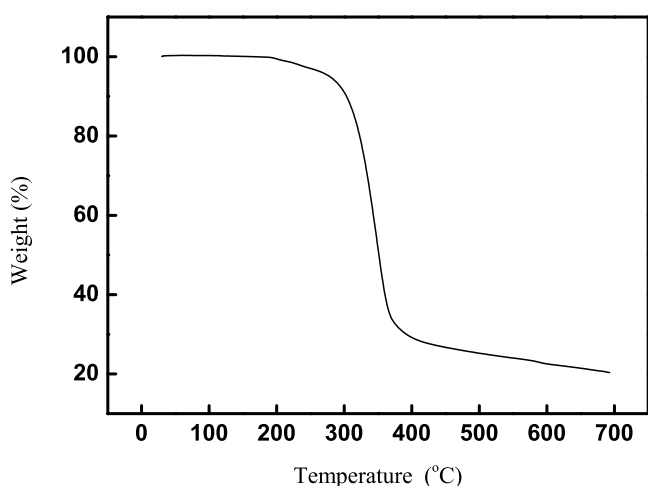


Figure 4. TG curve of [HIMA]OTs.

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 $70\text{ }^\circ\text{C}$ and a reaction time of 120 min were used in our experiments, and the results are shown in Figure 5.

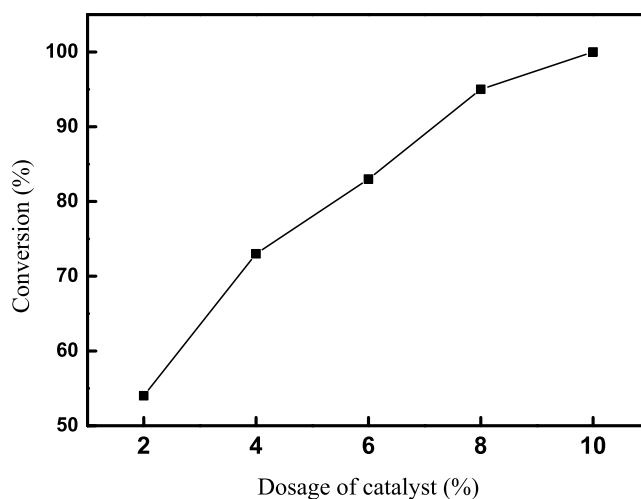


Figure 5. Effect of dosage of catalyst on conversion of *tert*-butyl alcohol.

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 $70\text{ }^\circ\text{C}$ and [HIMA]OTs (10 mol %) were used in our experiments, and the results are shown in Figure 6. The conversion of *tert*-butyl

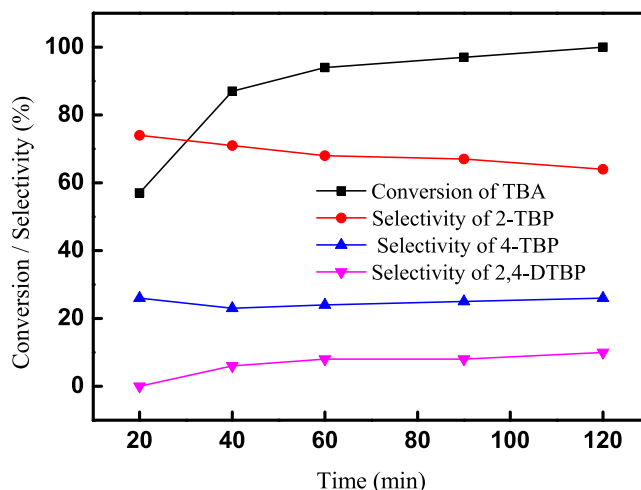


Figure 6. Effect of reaction time on conversion of *tert*-butyl alcohol.

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 $50\text{ }^\circ\text{C}$,

a much longer reaction time was needed; hence, a reaction temperature of 70 °C was used in our experiments.

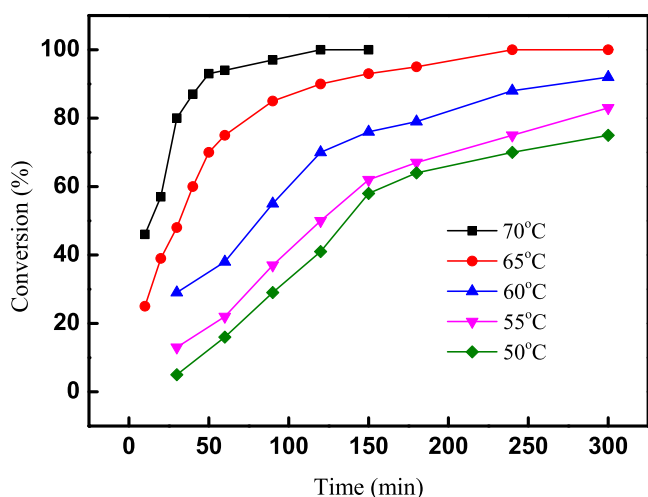


Figure 7. Effect of temperature on conversion of *tert*-butyl alcohol.

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

$$r = -\frac{dC_{\text{TBA}}}{dt} = kC_{\text{TBA}} \quad (2)$$

where k (L/(mol·min)) is the reaction rate constant, C_{TBA} (mol/L) is the concentration of *tert*-butyl alcohol in the reaction system, and t (min) is the reaction time.

Therefore, the following equation based on eq 2 can be obtained as

$$-\frac{dC_0(1-y)}{dt} = kC_0(1-y) \quad (3)$$

where C_0 (mol/L) is the initial concentration of *tert*-butyl alcohol and y (%) is the conversion of *tert*-butyl alcohol.

The equation can be rearranged to the linearized form as

$$-\ln(1-y) = kt \quad (4)$$

A plot of $-\ln(1-y)$ versus t allows the calculation of reaction rate constant k , and the calculated results of kinetic parameters at different temperatures are shown in Table 1. Additionally, the following equation can be expressed based on the Arrhenius equation

$$\ln k = \ln k_0 - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (5)$$

where E_a (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 T^{-1} in Figure 8. The results exhibited a good fitting ($R^2 =$

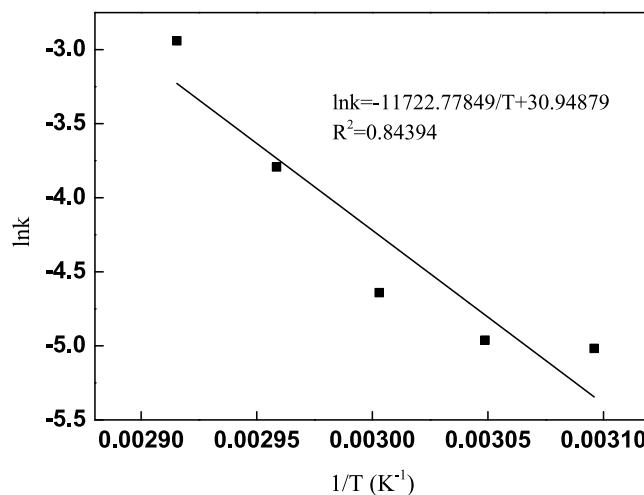


Figure 8. Arrhenius plot for the alkylation reaction catalyzed by [HIMA]OTs.

0.84394), and an activation energy E_a 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 $\text{SO}_3\text{-H}$ 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 ΔH^* and the entropy of activation ΔS^* , and the equation was expressed as^{37–41}

$$\ln \frac{k}{T} = -\left(\frac{\Delta H^*}{RT} \right) + \left[\ln \kappa + \ln \left(\frac{k_b}{h} \right) + \frac{\Delta S^*}{R} \right] \quad (6)$$

where κ 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.

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
R^2	0.9477	0.97277	0.97087	0.98375	0.97453
standard error	0.00077	0.00058	0.00082	0.00145	0.00426

Therefore, the values of ΔH^* and ΔS^* 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 ΔH^* indicated the

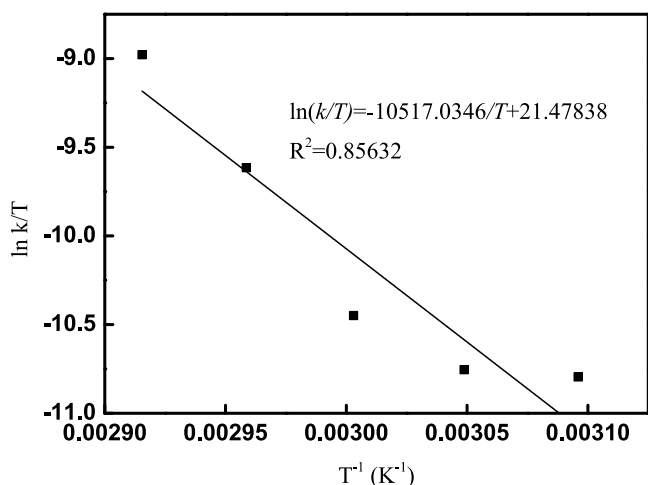


Figure 9. Fitting curve of $\ln(k/T)$ and T^{-1} .

Table 2. Parameters of Thermodynamics at Different Temperatures

entry	temperature (K)	ΔH^* (kJ/mol)	ΔS^* [J/(mol·K)]	ΔG^* (kJ/mol)
1	323	87.44	323.59	-17.08
2	328			-18.70
3	333			-20.32
4	338			-21.93
5	343			-23.55

endothermic nature of the alkylation reaction; hence, the higher reaction temperature is favorable to the alkylation of phenol and *tert*-butyl alcohol, and the result is compatible with Figure 7. In fact, many literature studies have been reported with a positive value of ΔH^* in the alkylation of phenol and *tert*-butyl alcohol.³⁴ In addition, the Gibb's free energy of activation ΔG^* can be calculated as

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

The positive value of ΔS^* and negative value of ΔG^* implied that the process of alkylation of phenol and *tert*-butyl 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*-butyl alcohol decreased a little, which may be due to the small amount of catalyst lost during the recovery

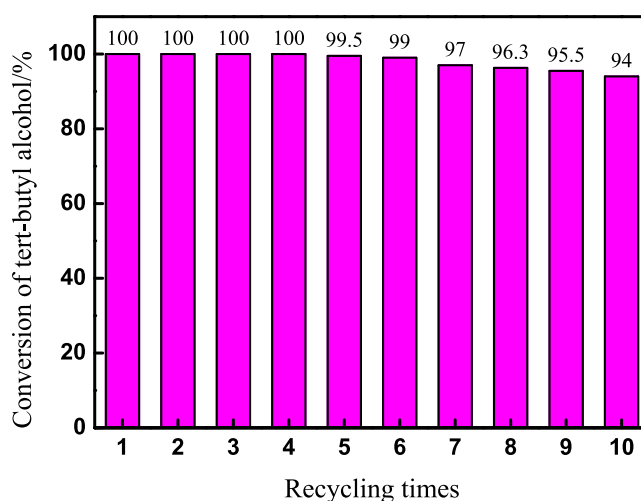


Figure 10. Results of recovery experiments.

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. ¹H and ¹³C 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 2.7598×10^{13} were obtained. In addition, the enthalpy of activation ΔH^* , the entropy of activation ΔS^* , and the Gibb's free energy of activation ΔG^* 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*-butylphenol in industry.

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Author Contributions

D.Z., S.S., Q.W., Y.X., and C.L.: Experimental investigation and writing original draft. C.W., K.Z., H.S.: Calculation of kinetic and thermodynamic results. X.Z., H.W.: Review and supervision.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Xiong, J.; Zhang, D.; Yang, G.; Zhang, Z. Alkylation of Phenol and tert-Butyl Alcohol Catalyzed by Deep Eutectic Solvents under Mild Conditions. *Ind. Eng. Chem. Res.* **2021**, *60*, 13204–13213.
- (2) Rueping, M.; Nachtsheim, B. J. A review of new developments in the Friedel–Crafts alkylation – From green chemistry to asymmetric catalysis. *Beilstein J. Org. Chem.* **2010**, *6*, No. 6.
- (3) Terekhov, A. V.; Zhanavskina, L. N.; Khadzhiyev, S. N. Selecting an optimum catalyst for producing para-tert-butylphenol by phenol alkylation with tert-butanol. *Pet. Chem.* **2017**, *57*, 714–717.
- (4) Kurian, M.; Sugunan, S. tert-Butylation of phenol catalyzed by metal exchanged iron pillared montmorillonites. *Catal. Commun.* **2006**, *7*, 417–421.
- (5) Ojha, K.; Pradhan, N. C.; Samanta, A. N. Kinetics of batch alkylation of phenol with tert-butyl alcohol over a catalyst synthesized from coal fly ash. *Chem. Eng. J.* **2005**, *112*, 109–115.
- (6) Sakthivel, A.; Dapurkar, S. E.; Gupta, N. M.; Kulshreshtha, S. K.; Selvam, P. The influence of aluminium sources on the acidic behaviour as well as on the catalytic activity of mesoporous H-AlMCM-41 molecular sieves. *Microporous Mesoporous Mater.* **2003**, *65*, 177–187.
- (7) Dumitriu, E.; Hulea, V. Effects of channel structures and acid properties of large-pore zeolites in the liquid-phase tert-butylation of phenol. *J. Catal.* **2003**, *218*, 249–257.
- (8) Sears, C. A. ALKYLATION OF PHENOL WITH t-BUTYL ALCOHOL IN THE PRESENCE OF PERCHLORIC ACID. *J. Org. Chem.* **1948**, *13*, 120–122.
- (9) Ghiaci, M.; Aghabarari, B. Vapor-Phase Alkylation of Phenol with Tert-butyl Alcohol Catalyzed by H₃PO₄/MCM-41. *Chin. J. Catal.* **2010**, *31*, 759–764.
- (10) Anand, R.; Maheswari, R.; Hanefeld, U. Catalytic properties of the novel mesoporous aluminosilicate AlTUD-1. *J. Catal.* **2006**, *242*, 82–91.
- (11) Nie, X.; Janik, M. J.; Guo, X.; Liu, X.; Song, C. Reaction mechanism of tert-butylation of phenol with tert-butyl alcohol over H-β zeolite: An ONIOM study. *Catal. Today* **2011**, *165*, 120–128.
- (12) Fang, D.; Zhou, X. L.; Ye, Z. W.; Liu, Z. L. Brønsted Acidic Ionic Liquids and Their Use as Dual Solvent–Catalysts for Fischer Esterifications. *Ind. Eng. Chem. Res.* **2006**, *45*, 7982–7984.
- (13) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.
- (14) Petrenko, V. I.; Fernandes, L. C.; Ivankov, O. I.; Tubio, C. R.; Tariq, M.; MSS Esperança, J.; Correia, D. M.; Lancers-Mendez, S. Structural organization of ionic liquids embedded in fluorinated polymers. *J. Mol. Liq.* **2022**, *360*, No. 119385.
- (15) Balchandani, S. C.; Mandal, B.; Dharaskar, S. Enrichment in CO₂ Absorption by 2-Methyl Piperazine-Activated Tertiary Amines, Physical Solvents, and Ionic Liquid Systems. *ACS Omega* **2022**, *7*, 23611–23623.
- (16) Hou, Y.; Zhang, Q.; Gao, M.; Ren, S.; Wu, W. Absorption and Conversion of SO₂ in Functional Ionic Liquids: Effect of Water on the Claus Reaction. *ACS Omega* **2022**, *7*, 10413–10419.
- (17) Li, C.; Zhao, T.; Yang, A.; Liu, F. Highly Efficient Absorption of CO₂ by Protic Ionic Liquids–Amine Blends at High Temperatures. *ACS Omega* **2021**, *6*, 34027–34034.
- (18) Singhal, S.; Agarwal, S.; Singh, M.; Rana, S.; Arora, S.; Singhal, N. Ionic liquids: Green catalysts for alkene-isoalkane alkylation. *J. Mol. Liq.* **2019**, *285*, 299–313.
- (19) Tran, A. T.; Lam, P. H.; Miller, Alexandra M.; Walczyk, D. J.; Tomlin, J.; Vaden, T. D.; Yu, L. Proton transfer and esterification reactions in EMIMOAc-based acidic ionic liquids. *RSC Adv.* **2017**, *7*, 18333–18339.
- (20) Gano, M.; Klebeko, J.; Pelech, R. Efficient esterification of curcumin in bis(trifluoromethylsulfonyl)imide-based ionic liquids. *J. Mol. Liq.* **2021**, *337*, No. 116420.
- (21) Mukesh, C.; Nikjoo, D.; Mikkola, J.-P. Production of C-14 Levulinic Ester from Glucose Fermentation Liquors Catalyzed by Acidic Ionic Liquids in a Solvent-Free Self-Biphasic System. *ACS Omega* **2020**, *5*, 4828–4835.
- (22) Lin, X.; Ling, X.; Chen, J.; Li, M.; Xu, T.; Qiu, T. Self-solidification ionic liquids as heterogeneous catalysts for biodiesel production. *Green Chem.* **2019**, *21*, 3182–3189.
- (23) Verma, K.; Sharma, A.; Singh, J.; Badru, R. Ionic liquid mediated carbonylation of amines: Selective carbamate synthesis. *Sustainable Chem. Pharm.* **2021**, *20*, No. 100377.
- (24) Urbán, B.; Szabó, P.; Srankó, D.; Sáfrán, G.; Kollár, L.; Skoda-Földes, R. Double carbonylation of iodoarenes in the presence of reusable palladium catalysts immobilised on supported phosphonium ionic liquid phases. *Mol. Catal.* **2018**, *445*, 195–205.
- (25) McNulty, J.; Nair, J. J.; Robertson, A. Efficient Carbonylation Reactions in Phosphonium Salt Ionic Liquids: Anionic Effects. *Org. Lett.* **2007**, *9*, 4575–4578.
- (26) Xing, D.; Lu, B.; Wang, H.; Zhao, J.; Cai, Q. An organic polymer-grafted ionic liquid as a catalyst for the cycloaddition of CO₂ to epoxides. *New J. Chem.* **2017**, *41*, 387–392.
- (27) Zheng, D.; Ning, P.; Jiang, J.; Liu, F.; Wang, L.; Zhang, J. Effect of ionic liquids clusters microenvironment on cycloaddition reaction of carbon dioxide. *J. Mol. Liq.* **2019**, *284*, 68–74.
- (28) Guglielmero, L.; Mezzetta, A.; Pomelli, C. S.; Chiappe, C.; Guazzelli, L. Evaluation of the effect of the dicationic ionic liquid structure on the cycloaddition of CO₂ to epoxides. *J. CO₂ Util.* **2019**, *34*, 437–445.
- (29) Wang, H.; Ma, S.; Zhou, Z.; Li, M.; Wang, H. Alkylation of isobutane with butene catalyzed by deep eutectic ionic liquids. *Fuel* **2020**, *269*, No. 117419.
- (30) Liu, Y.; Wu, G.; Pang, X.; Hu, R. Kinetics study on alkylation of isobutane with deuterated 2-butene in composite ionic liquids. *Chem. Eng. J.* **2020**, *387*, No. 123407.
- (31) Shen, H.-Y.; Judeh, Z. M. A.; Ching, C. B. Selective alkylation of phenol with tert-butyl alcohol catalyzed by [bmim]PF₆. *Tetrahedron Lett.* **2003**, *44*, 981–983.

- (32) Wang, Y.; Song, H.; Sun, X. Alkylation of toluene with tert-butyl alcohol over HPW-modified H β zeolite. *Chin. J. Catal.* **2016**, *37*, 2134–2141.
- (33) Amirfirouzkhouchi, H.; Kharat, A. N. Application of ionic liquids as recyclable green catalysts for selective alkylation of phenol. *Sep. Purif. Technol.* **2018**, *196*, 132–139.
- (34) Elavarasan, P.; Kondamudi, K.; Upadhyayula, S. Kinetics of phenol alkylation with tert-butyl alcohol using sulfonic acid functional ionic liquid catalysts. *Chem. Eng. J.* **2011**, *166*, 340–347.
- (35) Ojha, K.; Pradhan, N. C.; Samanta, A. N. Alkylation of phenol with tert-butyl alcohol over a catalyst synthesized from coal fly ash. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 659–666.
- (36) Patra, T.; Ahamad, S.; Upadhyayula, S. Highly efficient alkylation of phenol with tert-butyl alcohol using environmentally benign Bronsted acidic ionic liquids. *Appl. Catal., A* **2015**, *506*, 228–236.
- (37) Kurhade, A.; Dalai, A. K. Kinetic modeling, mechanistic, and thermodynamic studies of HPW-MAS-9 catalysed transesterification reaction for biodiesel synthesis. *Fuel Process. Technol.* **2019**, *196*, No. 106164.
- (38) Ong, L. K.; Kurniawan, A.; Suwandi, A. C.; Lin, C. X.; Zhao, X. S.; Ismadji, S. Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies. *J. Supercrit. Fluids* **2013**, *75*, 11–20.
- (39) Machado, T. F. G.; Gloster, T. M.; da Silva, R. G. Linear Eyring Plots Conceal a Change in the Rate-Limiting Step in an Enzyme Reaction. *Biochemistry* **2018**, *57*, 6757–6761.
- (40) Xiao, H.; Jiang, K.; Chen, Y.; Lei, Z.; Chen, K.; Cheng, X.; Qi, J.; Xie, J.; Huang, X.; Jiang, Y. Kinetics and Thermodynamic Analysis of Recent and Ancient Buried Phoebe zhennan Wood. *ACS Omega* **2020**, *5*, 20943–20952.
- (41) Doyle, P. J.; Savara, A.; Raiman, S. S. Extracting meaningful standard enthalpies and entropies of activation for surface reactions from kinetic rates. *React. Kinet., Mech. Catal.* **2020**, *129*, 551–581.