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Kinetics Study of the Ketalization Reaction of Cyclohexanone with Glycol Using Brønsted Acidic Ionic Liquids as Catalysts

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Supporting Information

ABSTRACT: It is remarkable that Brønsted acidic ionic liquids (BAILs) have several unique advantages in the acid-catalysis reaction, which avoids the technical issues raised from mineral acids. The kinetics for the ketalization of cyclohexanone with glycol using BAILs as catalysts was therefore studied for the first time. The effects of various parameters such as kind of BAILs, temperature, catalyst loading, and molar ratio of the reactants on the conversion of cyclohexanone were examined in detail, and a pseudohomogeneous (PH) kinetic model was used successfully to correlate the experimental data in the temperature range from 313.15 to 343.15 K. The kinetic parameters such as reaction rate constant, activation energy, and chemical equilibrium constant then were proposed and utilized to interpret the catalytic activities of the BAILs catalysts. It was also validated from the comparison of catalytic performance among the BAILs, H_2SO_4, and solid resin that the BAILs were considered to be environmentally friendly and high efficient catalysts, and were suggested to replace mineral and solid acids in the synthesis of ketal.

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INTRODUCTION

Ketals are important intermediates and end products in the chemical industry, and they have been widely employed as steroids, pharmaceuticals, flavors, and perfumes, due to their distinctive fragrance.[1] Also, ketalization of carbonyl compounds with alcohols to form ketals is one of the most useful methods for protecting carbonyl compounds in organic synthesis.[2−4] The production of ketal therefore has been growing fast in the past two decades due to those continual demands.

Conventionally, ketal is mainly synthesized through the ketalization of alcohol with ketone. This reaction was carried out in the presence of a protonic acid catalyst such as H_2SO_4, HCl, or H_3PO_4. Although these homogeneous acids showed satisfactory catalytic performance for the ketalization reaction, they caused the problems of tedious purification process of the product, large amount of acidic wastes, corrosion of equipments, and severe environmental pollution. All of these disadvantages made ketalization inefficient and uneconomical. Therefore, there was an urgent need to develop environmentally friendly and high efficient catalysts for ketalization.

In recent years, ionic liquids (ILs) as being environmental-friendly reaction media had attracted significant attention for their unique properties, such as excellent thermal stability, negligible vapor pressure, tunable acidity, remarkable solubility, and effortless reusability.[5−7] Acidic ILs including the Lewis and the Brøsted ones had proved to be efficient catalysts for esterification, alkylation, acetalization, and ketalization.[8−13] In 2002, Deng et al. reported their early work on the acetalization and ketalization using acidic chloroaluminate ILs as catalyst with high conversion and selectivity.[11] After that, Cole et al. had first synthesized functionalized Brønsted acidic ionic liquids (BAILs) beared with an alkyl sulfonic acid and used these BAILs for the esterification of acetic acid with ethanol.[12] On the basis of Cole's work, Dai et al. had further illustrated the merits of using SO_3H-functionalized BAILs for acetalization and ketalization.[13] Sugimura et al. investigated the copolymerization of acidic 1-vinylimidazolium ILs with styrene and its use as an effective and reusable catalyst for acetal formation under mild reaction condition.[14] Qi et al. had explored the ketalization in the presence of the novel ILs with both Lewis and Brønsted acid sites and found that the catalyst isoquinoline ILs realized a considerable yield of produced ketals.[15] Although these works showed satisfactory conversion and selectivity for ketalization, several drawbacks of ILs were still restricted their widespread practical applications. For example, the chloroaluminate ILs being of water-sensitivity may be unstable in aqueous conditions.[11] A large amount of ILs and long reaction time for ketalization were required to achieve considerable conversion.[13] The complex preparation of SO_3H-functional BAILs led to the high cost.[15] Many BAILs containing halogens could cause serious equipment corrosion.[16] Thus, it is still desirable to explore efficient halogen-free BAILs catalysts for ketalization, which is synthesized through the cheap raw material and simple method. In addition, the above-mentioned studies are mainly focused on the catalytic performance of BAILs. The kinetic information of ketalization reaction catalyzed by BAILs has not been reported in the literature so far. Herein, we believe that further investigation is needed to study the intrinsic kinetics of ketalization using BAILs as catalysts, and this kinetics information can be applicable to provide optimal parameters for the synthesis of ketals.

Therefore, several BAILs were prepared via simple and atomeconomic reactions in this present work. The kinetics for

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the ketalization reaction of cyclohexanone with glycol catalyzed in the presence of BAILs was also investigated. The effects of various parameters such as kind of BAILs, temperature, catalyst loading, and initial molar ratio of reactants were explored in detail. The chemical equilibrium of this reaction was then studied, and a pseudohomogeneous (PH) kinetic model based on the activities was utilized for the correlation of experimental data.

EXPERIMENTAL METHODS

Materials. 1-Methylimidazole (purity ≥99%), 2-methylpyridine (purity ≥98%), and 1,4-butyl sultone (purity ≥99%) were purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). The ion-exchange resin Amberlyst 15 was obtained from Rohm and Haas. 1-Methylimidazole and 2-methylpyridine were redistilled in a vacuum before being used. Other reagents such as cyclohexanone, glycol, sulfuric acid, triethylamine, *n*-butyl bromide (C_4H_9Br), silver oxide, and pyridine were of analytical grade and used without any further purification.

Preparation and Characterization of BAILs. Six BAILs composed of $[HSO_4]$ anion and different cations were prepared via simple and atomeconomic reactions (Figure 1), and their preparation methods were similar to the procedure described in our previous work.[17] Thus, the thermal stability (Netzsch STA 449C) and ^1H NMR (Bruker DPX-300) spectrum of these BAILs were recorded, and the detailed preparation procedure and characterization results were found in the Supporting Information. In addition, the pH values of the BAILs solution (0.1 mol/L BAIL) were measured with a PHS-3C pH-meter equipped with a recorder (Shanghai Leici instrument Inc., China). All of the measurements were carried out in vessels externally thermostatted at 25 °C with a water jacket, and then the experimental results were summarized in Table 1.

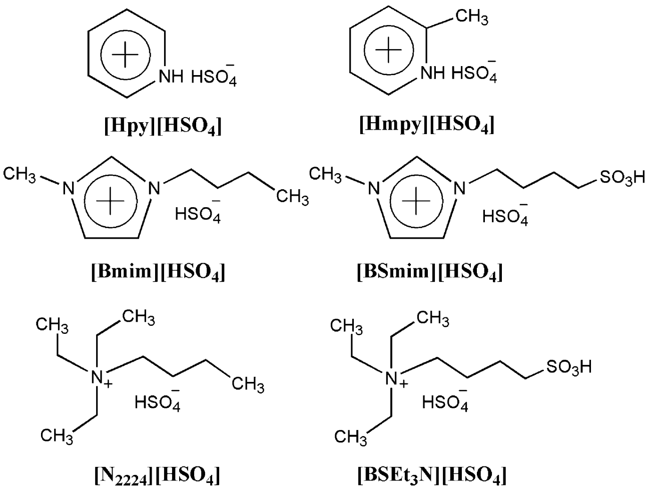

Figure 1. Structure of six Brønsted acidic ionic liquids.

General Procedure for the Ketalization Reaction. The ketalization reactions were performed in a 25 mL round-bottom flask with a magnetic stirrer. The temperature of the reaction mixture was controlled using a temperature controller with an accuracy of ±0.01 K. Weighed amounts of cyclohexanone, glycol, and catalyst (BAILs or H_2SO_4 or Amberlyst 15) were mixed and typically allowed to proceed for 0.5−2 h with vigorous stirring and heating at the designed temperature. After the reaction, the system became biphasic, the upper organic layer contained the expected ketal was separated by decantation, and then the product was detected by gas chromatography.

Table 1. pH Values of the Aqueous Solution of BAILs and H_2SO_4[a]

catalyst	pH value
H_2SO_4	0.63
$[BSEt_3N][HSO_4]$	0.67
$[BSmim][HSO_4]$	0.68
$[Hpy][HSO_4]$	1.16
$[Hmpy][HSO_4]$	1.17
$[N_{2224}][HSO_4]$	2.66
$[Bmim][HSO_4]$	3.35

[a] Solution in water at 25 °C.

Kinetic Runs. For a typical kinetic experiment, cyclohexanone and glycol were charged into the reactor fitted with a reflux condenser. When the temperature was raised to the desired value, the BAIL catalyst ($[Hpy][HSO_4]$ or $[Hmpy][HSO_4]$) was then added into the reactor, and this was taken as zero time for a run. About 0.2 mL of liquid sample was withdrawn from the reactor at regular intervals and was extracted with diethyl ether (3 mL × 2). The organic phase was combined and analyzed using gas chromatographic analysis. The residue BAILs phase could be easily recovered and reused in the next run after heat treatment under vacuum at 363.15 K for 12 h.

Equilibrium Runs. The equilibrium runs were carried out by the same procedure for kinetic runs. Equimolar amounts (around 0.1 mol each) of cyclohexanone and glycol with a catalyst loading of 0.5% w/w (based on the mass of cyclohexanone) were allowed to react until equilibrium was reached (as evidenced by the absence of any change in the conversion of cyclohexanone present in 0.2 mL of the withdrawn sample). The reaction temperatures were 313.15, 333.15, 353.15, and 373.15 K, respectively. Samples were taken 12, 24, and 48 h from the start of the reaction. Equilibrium mole fractions of cyclohexanone, glycol, cyclohexanone glycol ketal, and water were calculated to determine the overall equilibrium constant.

Analysis. The samples were analyzed using HP 6890 GC analyzer (Agilent) equipped with a hydrogen flame ionization detector (FID). A capillary column HP-1 (methyl polysiloxane, 30 m × 0.32 mm × 1 μm) was used to determine the composition of the samples with nitrogen as the carrier gas at a flow rate of about 3 mL/min. The temperatures of the column, the inlet, and the detector were kept at 453.15, 473.15, and 523.15 K, respectively.

RESULTS AND DISCUSSION

Catalyst Selection. The ketalization reaction of cyclohexanone with glycol in the presence of six BAILs composed of various cations was conducted to assess their catalytic activities at the temperature of 333.15 K, with a cyclohexanone to glycol molar ratio of 1, and catalyst loading of 0.5% w/w (based on the mass of cyclohexanone). As seen from Table 2, combined with the pH values from Table 1, it was obvious that the BAILs catalysts played various catalytic performances, and the catalytic performance of BAIL approximately depended on its acidity. The stronger acidity the BAILs had, the higher were the catalytic activities. For example, in the presence of 0.5% w/w $[BSEt_3N][HSO_4]$ and $[BSmim][HSO_4]$, the conversions of

Table 2. Ketalization of Cyclohexanone with Glycol Using Different Catalysts[a]

entry	catalyst	time (h)	conversion of cyclohexanone
1	[BSmim][HSO_4]	0.5	69.7
		2	71.6
2	[$BSEt_3N$][HSO_4]	0.5	69.9
		2	71.9
3	[Hpy][HSO_4]	0.5	67.9
		2	71.0
4	[Hmpy][HSO_4]	0.5	61.2
		2	68.3
5	[N_{2224}][HSO_4]	0.5	38.2
		2	44.7
6	[Bmim][HSO_4]	0.5	18.7
		2	27.5
7	H_2SO_4	0.5	72.0
		2	72.4
8	Amberlyst 15	0.5	51.3
		2	62.2

[a] Equimolar reactions of cyclohexanone with glycol with a catalyst dosage of 0.5% w/w at 333.15 K. No byproducts were found by GC.

cyclohexanone were 71.9% and 71.6% at 2 h, whereas [N_{2224}][HSO_4] and [Bmim][HSO_4] catalyzed the ketalization reaction to have conversions of only 44.7% and 27.5%, respectively. [$BSEt_3N$][HSO_4] and [BSmim][HSO_4] beared with an alkyl sulfonic acid group exhibited extremely strong acidities, and so they played more efficiently catalytic performances than [N_{2224}][HSO_4] and [Bmim][HSO_4] under identical conditions. In addition, it was also indicated that the conversions of cyclohexanone at 2 h in the presence of [Hpy][HSO_4] and [Hmpy][HSO_4] reached 71% and 68.3%, respectively, which were almost near the cases of [$BSEt_3N$]-[HSO_4] and [BSmim][HSO_4]. This meant that [Hpy][HSO_4] and [Hmpy][HSO_4] could induce the considerable conversions of cyclohexanone, even though their acidities were obviously inferior to those of [$BSEt_3N$][HSO_4] and [BSmim][HSO_4]. Furthermore, the SO_3H-functional BAILs [$BSEt_3N$][HSO_4] and [BSmim][HSO_4] were found to be extremely corrosive, contaminative, and cause serious equipment corrosion. Their preparation procedure was also too complicated and led to a high cost.[17] Instead, [Hpy][HSO_4] and [Hmpy][HSO_4] were derived from cheap pyridine and had been prepared via simple and atomeconomic acid−base neutralization reactions. Therefore, it is suggested that the strong acidity of BAIL is not necessary for the ketalization reaction. [Hpy][HSO_4] and [Hmpy][HSO_4] are considered to be suitable catalysts because of their reasonable acidities.

For comparison, the ketalization reaction in the presence of the resin Amberlyst 15 and H_2SO_4 was investigated. As seen from Table 2, H_2SO_4 was found to have the best catalytic activity among all of the catalysts investigated. The strongest acidity enabled H_2SO_4 to induce remarkable conversions, and this was in accordance with the general phenomena of acid catalysis for the ketalization reaction.[13] In addition, it was also indicated that the conversion of cyclohexanone in the presence of Amberlyst 15 resin was lower than that in the cases of [Hpy][HSO_4] and [Hmpy][HSO_4]. In comparison to the homogeneous catalysis of BAILs, the heterogeneous catalysis of Amberlyst 15 resin existed high transfer resistance and resulted in a relatively low conversion of reactants. Thus, it is demonstrated that [Hpy][HSO_4] and [Hmpy][HSO_4] are promising substitutes for corrosive mineral acids and solid resins in the production process of ketals, to overcome the technical difficulties such as serious equipment corrosion and high mass transfer resistance. The BAILs [Hpy][HSO_4] and [Hmpy][HSO_4] are therefore chosen as catalysts for further kinetics studies.

Optimization of Reaction Conditions. The investigation on the effect of temperature is very important because this information is useful in performing the kinetic study and calculating the activation energy. Thus, the experiments were carried out using [Hpy][HSO_4] and [Hmpy][HSO_4] as catalysts at temperatures of 313.15, 323.15, 333.15, and 343.15 K, molar ratio of cyclohexanone to glycol of 1, and catalyst loading of 0.1% w/w. As seen from Figure 2, the conversion of cyclohexanone increased rapidly with the increase in the reaction temperature. A similar trend had been observed for other BAILs-catalyzed acetalization and ketalization reactions.[18,19] Higher temperature yielded greater conversion of cyclohexanone under identical conditions. Therefore, increasing the temperature is apparently favorable for the acceleration of the forward reaction, and it indeed changes the time requirement for reaching the equilibrium.[20]

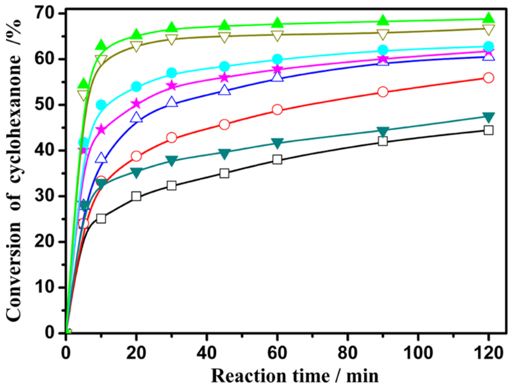

Figure 2. Effect of temperature on the conversion of cyclohexanone with time using [Hpy][HSO_4] (solid symbols) and [Hmpy][HSO_4] (open symbols) as catalysts at (green ▼, □) 313.15 K; (pink ★, ○) 323.15 K; (blue ●, △) 333.15 K; and (green ▲, ▽) 343.15 K, cyclohexanone to glycol molar ratio of 1:1, and catalyst loading of 0.1% w/w.

The effect of different catalyst loadings on the conversion of cyclohexanone was studied by setting the catalyst loading at 0.1%, 0.25%, and 0.5% w/w, respectively. The results as shown in Figure 3 indicated that, with an increase in the relative amount of BAILs, the rate of ketalization reaction was enhanced, resulting in a higher reaction rate for the conversion of cyclohexanone. For example, when the dosage of [Hpy]-[HSO_4] was increased from 0.1% to 0.25% w/w, the conversion of cyclohexanone obviously increased from 62% to 69% in 2 h, showing that the amount of catalyst had an obvious influence on the catalytic performance. This was attributed to the increase in acidity in the reaction system. However, a slight increase in the conversion of cyclohexanone was observed when the amount of [Hpy][HSO_4] catalyst was increased 2-fold from 0.25% to 0.5% w/w. Beyond a certain catalyst loading, the conversion of cyclohexanone was improved slightly with increasing of catalyst loading and could not exceed the equilibrium conversion of cyclohexanone because of the limitation of chemical reaction equilibrium. Thus, it suggests that the further increase in the amount of catalyst is not very

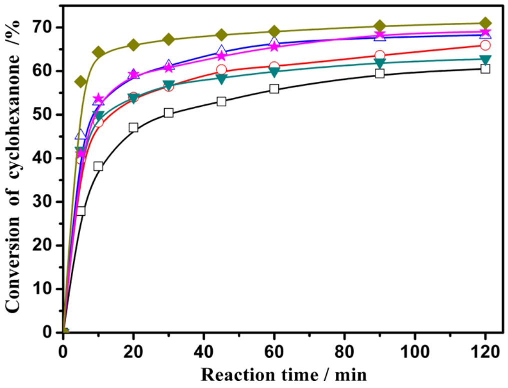

Figure 3. Effect of catalyst loading on the conversion of cyclohexanone with time using [Hpy][HSO_4] (solid symbols) and [Hmpy][HSO_4] (open symbols) as catalysts at 333.15 K, cyclohexanone to glycol molar ratio of 1:1, and catalyst loading of (green ▼, □) 0.1% w/w; (pink ★, ○) 0.25% w/w; and (brown ◆, △) 0.5% w/w.

necessary for the conversion of reactants. Considering the reaction rate and the cost of BAILs, 0.25% w/w is taken as the optimum catalyst loading and used in most of the ketalization experiments.

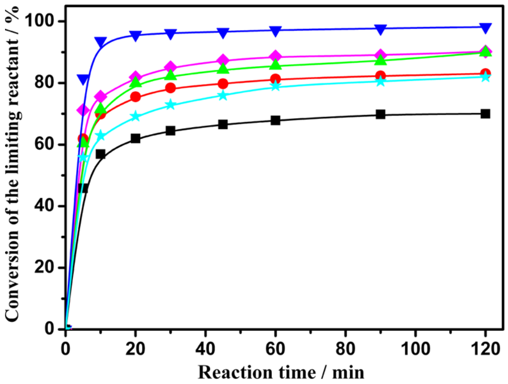

Figure 4. The conversion of the limiting reactant with time using [Hpy][HSO_4] as catalyst at 323.15 K, catalyst loading of 0.5% w/w, and initial molar ratio of (blue ▼) 3:1; (green ▲) 2:1; (aqua ★) 1.5:1; (■) 1:1; (red ●) 1:2; and (pink ◆) 1:3.

Figure 4 shows the effect of the molar ratio of cyclohexanone to glycol on the ketalization reaction (ranging from 1:3 to 3:1) in the presence of [Hpy][HSO_4] as catalyst. It should be noted that the limiting reactant is cyclohexanone for the runs at initial cyclohexanone to glycol ratios of 1:2 and 1:3, whereas the limiting reactant is glycol for the runs at initial cyclohexanone to glycol ratios of 3:1, 2:1, and 1.5:1. At an equimolar feed ratio of 1:1, either the cyclohexanone or the glycol can be considered to be the limiting reactant. As seen from Figure 4, it was indicated that as the amount of cyclohexanone or glycol increased, the conversion of the limiting reactant was rapidly increased. For example, the conversion was obviously increased from 70% to 90% in 2 h, while the initial molar ratio of cyclohexanone to glycol increased from 1:1 to 2:1. Higher conversions were also obtained with the molar ratio of 1:2 and 1:3 in comparison to the case of 1:1. Thus, it is demonstrated that increasing the amount of both cyclohexanone and glycol is beneficial to the forward reaction because the ketalization of cyclohexanone with glycol is a reversible reaction. In addition, it was also found that the initial molar ratio of 2:1 resulted in higher conversions in compassion to the initial molar ratio of 1:2. The reaction profile in the initial molar ratio of 1:2 was just comparable to the case of 1.5:1. Similarly, the conversions in the initial molar ratio of 3:1 were much more than those in the case of 1:3. This implies that an initial excess of cyclohexanone rather than glycol exhibits more efficiency and appears to be more preferable. In summary, the optimal molar ratio of cyclohexanone to glycol is suggested to be 1.5:1.

Equilibrium Constants. The experimental runs were carried out at four different temperatures to obtain the chemical equilibrium constant under the condition (molar ratio of cyclohexanone to glycol of 1, and catalyst loading of 0.5% w/w). It was concluded that the mixture was at equilibrium when the composition of the mixture remained unchanged. Thus, the chemical equilibrium constants can be obtained from the equilibrium concentrations of cyclohexanone, glycol, cyclohexanone glycol ketal, and water. Taking into account the nonideal behavior of the liquid phase, the activities were employed to substitute concentrations because the interaction force between different components of the real mixtures cannot be negligible. Next, the chemical equilibrium constants were calculated experimentally according to the following formula:

$$K_e = \frac{a_{\text{Ketal}}a_{H_2O}}{a_{\text{Ketone}}a_{\text{Glycol}}} = \frac{x_{\text{Ketal}}x_{H_2O}}{x_{\text{Ketone}}x_{\text{Glycol}}}\frac{\gamma_{\text{Ketal}}\gamma_{H_2O}}{\gamma_{\text{Ketone}}\gamma_{\text{Glycol}}} \quad (1)$$

where K_e is the equilibrium constant of the reaction, a_i is the activity of the component, x_i is the mole fraction of the component, and γ_i is the activity coefficient of the component. The activity coefficients can be estimated with the UNIFAC group contribution method, and the values of the volume and area parameters of the groups are obtained from DECHEMA.[21]

The equilibrium constants were found to decrease with the increase in the reaction temperature. The temperature dependency of the equilibrium constants was determined from the plot of ln K_e versus $1/T$, as given in Figure 5. The equilibrium constants obtained can be described by

$$K_e = \exp(-5.1075 + 2241.83/T) \quad (2)$$

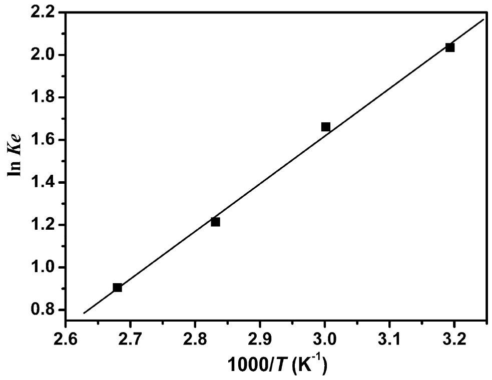

Figure 5. Variation of chemical equilibrium constant with temperature.

Assuming the enthalpy of reaction is constant within the operating temperature range, the enthalpy ($\Delta_r H^\circ$) and entropy ($\Delta_r S^\circ$) of reaction can be estimated from

$$\ln K_e = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \quad (3)$$

The reaction enthalpy $\Delta_r H^\circ$ and entropy $\Delta_r S^\circ$ were found to be −18.64 kJ/mol and −42.46 J/(mol·K) in this work, respectively.

Kinetics Study. The reaction equation for the ketalization of cyclohexanone with glycol was written as

$$\text{ketone} + \text{glycol} \overset{k_1}{\underset{k_2}{\leftrightarrow}} \text{ketal} + \mathrm{H_2O} \tag{4}$$

A pseudohomogeneous (PH) model was usually applied for the liquid-phase reaction system where one of the reactants or solvents was of high polarity, and it was used to interpret the experimental kinetic data for many reactions.[22−25] In this work, the ketalization kinetic equation of cyclohexanone with glycol in the presence of [Hpy][HSO_4] and [Hmpy][HSO_4] as catalysts can be established on the basis of the PH model. For the nonideal mixing behavior of the bulk liquid phase, the activities of the components are employed to describe the kinetic model. For a homogeneously catalyzed system, the reaction rate equation for the PH model in terms of equilibrium constant is as follows:

$$\begin{aligned} r = n_0 \frac{\mathrm{d}x_i}{\mathrm{d}t} &= M_{\mathrm{cat}}(k_1 a_{\mathrm{Ketone}} a_{\mathrm{Glycol}} - k_2 a_{\mathrm{Ketal}} a_{\mathrm{H_2O}}) \\ &= M_{\mathrm{cat}} k_1 \left(a_{\mathrm{Ketone}} a_{\mathrm{Glycol}} - \frac{1}{K_{\mathrm{e}}} a_{\mathrm{Ketal}} a_{\mathrm{H_2O}} \right) \end{aligned} \tag{5}$$

where $K_e = k_1/k_2$, and M_{cat} is the catalyst loading per unit mass of cyclohexanone. k_1 and k_2 are the kinetic constants for the forward and reverse reactions, respectively. The kinetic equations were integrated numerically using a fourth-order Runge−Kutta method. The parameters for the kinetics model were estimated from the minimization of the sum of residual squares (SRS) between the experimental and calculated conversions of cyclohexanone, which was

$$\mathrm{SRS} = \sum_{\mathrm{samples}} (X_{\mathrm{expt}} - X_{\mathrm{calc}})^2 \tag{6}$$

where SRS is the minimum sum of residual squares, and X is the conversion of cyclohexanone. The subscripts "expt" and "calc" denote experimental and calculated values, respectively. The nonlinear least-squares method was used as the optimization method for the parameter estimation.

A comparison was drawn (shown in Figures 6 and 7) between the experimental data and the PH model values at different reaction conditions. It was found that the calculated values were in a good agreement with the measured results with an averaged relative deviation (ARD) of less than 5%. The value of ARD was though to be well within the acceptable limit for engineering purpose. The PH kinetic model could give a good description of the ketalization kinetic behavior.

Further, the temperature dependency of the rate constant k can be expressed by Arrhenius law:

$$k_i = k_i^0 \, \mathrm{e}^{-E_{\mathrm{A},i}/RT} \tag{7}$$

Equation 7 can be rewritten into

$$\ln k_i = \ln k_i^0 - \frac{E_{\mathrm{A},i}}{RT} \tag{8}$$

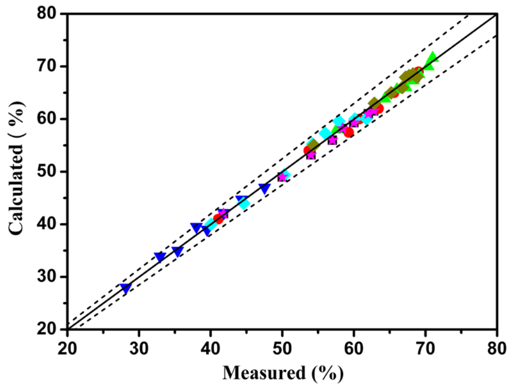

Figure 6. Comparison between measured and calculated conversions of cyclohexanone in the presence of [Hpy][HSO_4] under conditions as follows: reaction temperature of (blue ▼) 313.15 K, (aqua ◆) 323.15 K, (pink ★) 333.15 K, and (brown ◆) 343.15 K; catalyst loading of (■) 0.1% w/w, (red ●) 0.25% w/w, and (green ▲) 0.5% w/w. The dashed lines represent the deviation limits of ±5%.

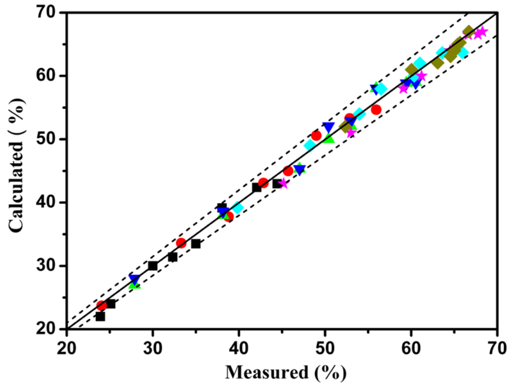

Figure 7. Comparison between measured and calculated conversions of cyclohexanone in the presence of [Hmpy][HSO_4] under conditions as follows: reaction temperature of (■) 313.15 K, (red ●) 323.15 K, (green ▲) 333.15 K, and (brown ◆) 343.15 K; catalyst loading of (blue ▼) 0.1% w/w, (aqua ◆) 0.25% w/w, and (pink ★) 0.5% w/w. The dashed lines represent the deviation limits of ±5%.

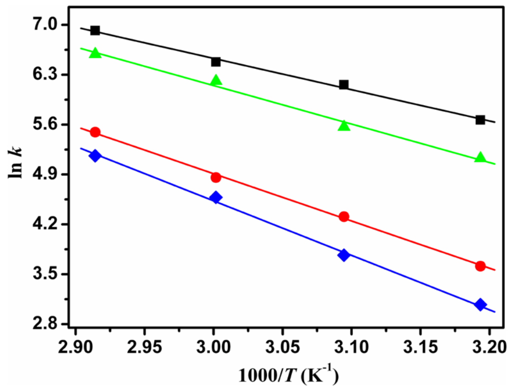

Figure 8. Arrhenius plot for the ketalization of cyclohexanone with glycol using [Hpy][HSO_4] and [Hmpy][HSO_4] as catalysts. (■) k_1^0 of forward reaction and (red ●) k_2^0 of reverse reaction for [Hpy][HSO_4]; (green ▲) k_1^0 of forward reaction and (blue ◆) k_2^0 of reverse reaction for [Hmpy][HSO_4]. The solid lines represent the regression of ln k versus 1000/T.

Plotting ln k_i versus $1/T$, straight lines with the slope of $(-E_{A,I}/R)$ can be obtained from eq 8 and are shown in Figure 8. The values of preexponential factor (k_1^0,k_2^0) and activation energy ($E_{A,1}$,$E_{A,2}$) are listed in Table 3. It was found that the activation energies for [Hpy][HSO_4] and [Hmpy][HSO_4] catalytic systems were near each other, but the preexponential

Table 3. Kinetic Parameters for the Pseudohomogeneous Model

	k_j^0 (kmol/s)		$E_{A,j}$ (kJ/mol)	
catalyst	$j = 1$	$j = 2$	$j = 1$	$j = 2$
[Hpy][HSO_4]	9.85	1627.72	36.50	55.14
[Hmpy][HSO_4]	141.25	23 350.35	44.94	63.58

factors of reverse reaction for these two catalysts were quite different. Meanwhile, the kinetic data as investigated in the previous section indicated that [Hpy][HSO_4] gave high performance and showed more efficiently than [Hmpy][HSO_4]. Thus, it suggests that the catalytic activity is mainly affected by the preexponential factors, when the reaction energy barriers (activation energy) are relatively similar. The [Hpy][HSO4] catalytic system is of low reverse reaction rate and results in high conversion of reactants, due to its relatively smaller value of the preexponential factor of reverse reaction. All of the kinetic information therefore can be applicable to design the ketalization process, and to provide an optimal setup of various operating parameters.

Recycling of Catalyst. The catalyst [Hpy][HSO_4] was recycled five times to test its activity as well as stability. In each cycle, the catalyst was separated from the reaction mixture by simple decantation and then washed with diethyl ether, followed by drying before the next run. The conversions of cyclohexanone from five consecutive runs thus were as shown in Figure 9 (temperatures of 323.15 K, molar ratio of cyclohexanone to glycol of 1, catalyst loading of 0.5% w/w, and reaction time of 0.5 and 2 h). The experimental results indicated that the catalyst [Hpy][HSO_4] for the ketalization was stable enough to be recycled. Five cycles had been successively completed, and no sign of deactivation was observed for the reused catalyst. The slight decrease in the conversion of cyclohexanone should be ascribed to the slight loss of [Hpy][HSO_4] due to the transferring of samples during the regeneration.

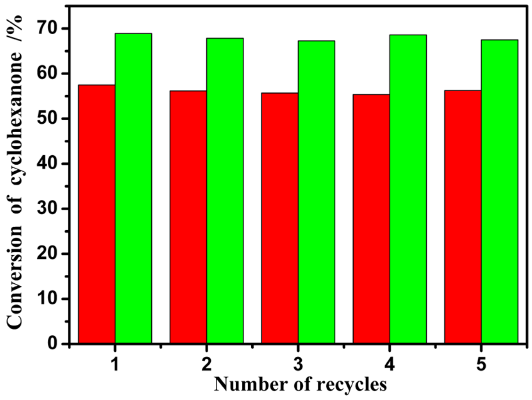

Figure 9. The recycle test of [Hpy][HSO_4] catalyst (red column for 0.5 h and green column for 2 h).

CONCLUSIONS

The BAILs [Hpy][HSO_4] and [Hmpy][HSO_4] had been synthesized via simple and atomeconomic acid−base neutralization reactions, and these two catalysts were chosen as catalysts for the first time to study the kinetics of the ketalization reaction of cyclohexanone with glycol. The kinetic experimental data indicated that [Hpy][HSO_4] displayed comparable catalytic performances with H_2SO_4 and Amberlyst 15 resin in the ketalization reaction, and could be easily recovered and used repetitively without significant losses of activity and quantity. The conversion of cyclohexanone was also found to be improved effectively with the increase of reaction temperature and catalyst loading in the presence of [Hpy][HSO_4] and [Hmpy][HSO_4]. An appropriate initial excess of cyclohexanone rather than glycol appeared to be more beneficial. The PH model was applied to correlate the kinetic data and gave a good representation of the kinetic behavior for this ketalization system containing BAILs. Therefore, the BAILs [Hpy][HSO_4] and [Hmpy][HSO_4] catalysts are considered to be talented and prospective substitutes for the production of ketals, and this kinetic information can be also applicable to provide an optimal setup for the ketalization process.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

[Hpy][HSO_4] = pyridinium hydrogensulfate
[Hmpy][HSO_4] = 2-methylpyridinium hydrogensulfate
[Bmim][HSO_4] = 1-butyl-3-methylimidazole hydrogensulfate
[N_{2224}][HSO_4] = butyltriethylammonium hydrogensulfate
[$BSEt_3N$][HSO_4] = *N*-(4-sulfonic acid) butyl triethylammonium hydrogensulfate
[BSmim][HSO_4] = 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogensulfate

Nomenclature

α_i = activity of the *i*th component in the liquid phase
γ_i = the activity coefficient of the component
x_i = mole fraction of the *i*th component in the liquid phase
n_0 = initial mole number of cyclohexanone
$E_{a,1}$ = activation energy for the forward reaction, kJ/mol
$E_{a,2}$ = activation energy for the reverse reaction, kJ/mol
k = reaction rate constant, kmol/min
k_1^0 = pre-exponential factor for the forward reaction, kmol/s
k_2^0 = pre-exponential factor for the reverse reaction, kmol/s
k_1 = forward reaction rate constant, kmol/s
k_2 = reverse reaction rate constant, kmol/s
K_e = equilibrium constant of ketalization
X_{calc} = calculated conversion
X_{expt} = experimental conversion

T = temperature, K
R = gas constant, J/(mol·K)
M_{cat} = the catalyst mass based on the mass of cyclohexanone, kg/kg
w/w = weight of catalyst/weight of cyclohexanone, kg/kg
SRS = the sum of residual squares

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