



Catalysis, Kinetics and Reaction Engineering

Reaction kinetics for synthesis of *sec*-butyl alcohol catalyzed by acid-functionalized ionic liquid[☆]

Ting Qiu^{*}, Wenli Tang, Chenggang Li, Chengming Wu, Ling Li

College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350108, China

ARTICLE INFO

Article history:

Received 13 November 2013

Received in revised form 7 January 2014

Accepted 17 January 2014

Available online 11 November 2014

Keywords:

Ionic liquids

sec-Butyl alcohol

Kinetic modeling

Transesterification

ABSTRACT

The acid-functionalized ionic liquid ([HSO₃Pmim]HSO₄) was synthesized by a two-step method. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR) show that the synthesis method is feasible and high purity of ionic liquid can be obtained. Using [HSO₃Pmim]HSO₄ as the catalyst, we studied the reaction kinetics of synthesizing *sec*-butyl alcohol from *sec*-butyl acetate and methanol by transesterification in a high-pressure batch reactor. The effects of temperature, initial molar ratio of methanol to ester, and catalyst concentration on the conversion of *sec*-butyl acetate were studied. Based on its possible reaction mechanism, a homogeneous kinetic model was established. The results show that the reaction heat ΔH is $10.94 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$, so the reaction is an endothermic reaction. The activation energies E_{a+} and E_{a-} are 60.38×10^3 and $49.44 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$, respectively.

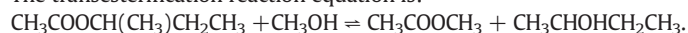
© 2014 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

sec-Butyl alcohol (SBA) is widely used in industry. It is used as a methanol co-solvent component for improving the octane number of gasoline and as an important chemical intermediate to produce methyl ethyl ketone [1,2]. Several synthetic routes for *sec*-butyl alcohol have been developed, such as direct hydration of butylene and indirect hydration. These routes suffer from several drawbacks such as high pressure and temperature conditions, high energy consumption, serious corrosion of equipment, low one-way conversion, and high requirement for raw materials [3]. The industrial synthesis of *sec*-butyl alcohol and methyl acetate (MeAc) from *sec*-butyl acetate (SBAC) and methanol (MeOH) by transesterification with the catalysis of sodium alkoxide can avoid these problems to some extent, but it involves some difficulties in catalyst separation [4].

The acid-functionalized ionic liquids, which are environmentally friendly solvents and liquid acid catalysts, present high catalytic activity of liquid acid and nonvolatility of solid acid, adjustable molecular structure and acidity, easy separation, high thermal stability, etc. [5–7]. Reactions with acid-functionalized ionic liquids as catalysts give desired results, such as nitration [8], transesterification [9,10], esterification [11, 12], and Beckmann rearrangement [13]. Because of their special properties and functionality, acid-functionalized ionic liquids will become truly designed green solvents and replace conventional catalysts [14–16].

Based on the concept “new and efficient green environmental protection, energy conservation and emissions reduction”, a new green process for the synthesis of *sec*-butyl alcohol via transesterification catalyzed by acid-functionalized ionic liquids has been proposed [17]. The transesterification reaction equation is:



In this work, the kinetic behavior of transesterification is investigated using 1-(3-sulfonic acid) propyl-3-methylimidazole hydrogen sulfate [HSO₃Pmim]HSO₄ as catalyst, and the effects of temperature, molar ratio of reactants and catalyst concentration are explored. A homogeneous kinetic model is established based on its possible reaction mechanism.

2. Experimental

2.1. Materials

The initial purities, purification methods, final purities, and sources of the materials are listed in Table 1. Deionized water was prepared in our laboratory. The purities of components were determined by gas chromatography.

2.2. Synthesis of acid-functionalized ionic liquid

The acid-functionalized ionic liquid ([HSO₃Pmim]HSO₄) (Fig. 1) was synthesized by the two-step method [18,19], with experimental procedures as follows. Under vigorous stirring, 1,3-propanesultone was dissolved in toluene and 1.2 equivalent (eq.) of 1-methyl imidazole was introduced dropwise in an ice bath. The mixture was heated to

[☆] Supported by the New Century Excellent Talents in Fujian Province (JA12014) and the Natural Science Foundation for Distinguished Young Scholars of Fujian (2014)06004).

^{*} Corresponding author.

E-mail address: tingqiu@fzu.edu.cn (T. Qiu).

Table 1
Purities of chemicals

Chemical	Source	Initial mass fraction	Purification method	Final mass fraction	Analysis method ^①
Methanol	SINOPHARM	0.997	None	–	GC
Methyl acetate	SINOPHARM	0.997	None	–	GC
sec-Butyl alcohol	Aladdin	0.997	None	–	GC
sec-Butyl acetate	Guangzhou Jinhua Chemistry	0.985	Distillation	0.997	GC
1,4-Dioxane	SINOPHARM	0.997	None	–	GC
Ether	SINOPHARM	0.995	None	–	GC
1,3-Propanesultone	Aladdin	0.990	None	–	–
1-Methyl Imidazole	Aladdin	0.990	None	–	–

^① GC is abbreviation of the gas chromatography.

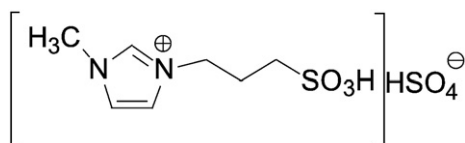


Fig. 1. Structure of $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$.

room temperature and stirred for 6 h. After filtration, zwitterion formed as white solid. It was washed by ether three times to remove residual material and dried in a vacuum at 353.15 K for 5 h. Then the zwitterion was dissolved in deionized water and equimolar sulfuric acid (98%, by mass) was added slowly at 273.15 K with vigorous stirring. The mixture was slowly heated to 363.15 K and stirred for 6 h. After the water was removed under vacuum, $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$ appeared as a light yellow transparent viscous liquid. It was dried in a vacuum at 353.15 K for 8 h. $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$ was obtained with a total yield of 86%.

2.3. Characterization of acid-functionalized ionic liquid

The structure of $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$ was analyzed by nuclear magnetic resonance (NMR) and fourier transform infrared spectroscopy (FT-IR). ¹H NMR and ¹³C NMR spectra in DMSO-d₆ were obtained using an AVANCE III 500 Bruker instrument, with tetramethylsilane (TMS) as internal standard. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer for KBr pellets.

¹H NMR (500 MHz, DMSO-d₆, TMS) δ (ppm): 9.11 (s, 1H, N-CH₂-N), 7.78 (m, 1H, N-CH₂-CH₂), 7.69 (m, 1H, CH₂-CH₂-N), 4.30 (t, 2H, N-CH₂-CH₂), 3.85 (s, 3H, -CH₃), 2.41 (t, 2H, CH₂-CH₂-S), and 2.09 (p, 2H, CH₂-CH₂-CH₂); ¹³C NMR (126 MHz, DMSO-d₆) δ (ppm): 137.24, 124.09, 122.79, 48.19, 47.82, 36.20, and 26.59.

FT-IR (KBr, cm⁻¹): 3400, 3116, 3158, 2875, 2961, 1510, 1172, 1068, and 850.

The NMR spectral and FT-IR spectral data of the $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$ agree with its designed structures (Fig. 1). No impurity peak appears in the ¹H NMR spectra. This demonstrates that the purity of the $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$ is more than 98%. Therefore, the synthesis and purification methods for the $[\text{HSO}_3\text{Pmim}]\text{HSO}_4$ are feasible.

2.4. Apparatus and procedure

In this study, the reaction system has a lower boiling point (about 338.15 K) at atmospheric pressure. In order to increase the reaction temperature to enhance the reaction rate, the reaction was carried out at pressure of 0.608 MPa. The reaction temperatures were 343.15–373.15 K.

The kinetic experiments were carried out in a stainless steel reactor (material: 0Cr18Ni9, reactor volume: 500 ml) equipped with an agitation and temperature control device (± 0.05 K). Its schematic diagram is shown in Fig. 2. In each run, the reactants were proportionately added to the reactor. The pressure was raised to 0.608 MPa by filling nitrogen, with some fluctuations and the maximum deviation of ± 0.1 kPa. In order to ensure uniform temperature in the reactor, a stirrer was set at

a desired level. Once the desired temperature was attained, the preheated catalyst (dissolved in methanol) was charged into the reactor by a tranquil flow pump and the time was regarded as the initial time. Samples were taken at a fixed time interval, cooled rapidly, and then analyzed by gas chromatography. The reaction was considered to reach chemical equilibrium when the composition of the reaction mixture was nearly constant. Then the mixture was removed from the reactor and kept for recycling catalyst.

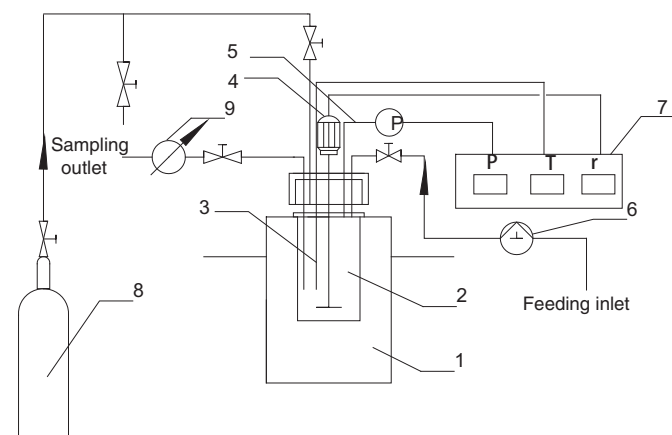


Fig. 2. Apparatus of kinetic experiment. 1 – heating mantle; 2 – stainless steel reactor; 3 – thermocouple; 4 – mechanical stirrer; 5 – pressure tap; 6 – tranquil flow pump; 7 – control cabinet; 8 – nitrogen cylinder; 9 – condenser.

2.5. Sample analysis

All samples were analyzed by gas chromatography (GC, Shanghai Branch Chong GC9800), with 1,4-dioxane as the internal standard and parameters as follows: flame ionization detector (FID); column: AT-FFTP, 50 m \times 0.32 mm \times 0.5 μm ; column temperature: started at 333.15 K for 2 min, increased to 341.15 K at 1.5 K \cdot min⁻¹ and held for 1 min, and then increased to 453.15 K at 15 K \cdot min⁻¹ and held for 1 min; injector temperature: 453.15 K; and detector temperature: 493.15 K. All samples were analyzed at least three times to eliminate the error. The mole fraction was within an uncertainty of ± 0.002 .

3. Results and Discussion

3.1. Effect of reaction temperature

Fig. 3 shows the effect of temperature (from 343.15 to 373.15 K) on the reaction rate and conversion of sec-butyl acetate. The reaction rate and the conversion increase with temperature, while the equilibrium conversion at different temperatures changes slightly. For a weakly endothermic reaction, the effect of temperature on the equilibrium conversion is slight, but is significant on the reaction rate. At 343.15 K, the

Download English Version:

<https://daneshyari.com/en/article/168140>

Download Persian Version:

<https://daneshyari.com/article/168140>

[Daneshyari.com](https://daneshyari.com)