Construction of Fixed Bed Reactor and Catalytic Performance of the PS-ILs Enabled by Immobilized Ionic Liquids for Esterification

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Abstract. Polystyrene (PS) microspheres, prepared by suspension polymerization, were applied to synthesize chloromethylated polystyrene microspheres (PS-CH₂Cl) by chloromethylation. PS-CH₂Cl was then used for the immobilization of acidic ionic liquid to prepare immobilized ionic liquid polystyrene microspheres (PS-ILs) as catalyst, thus avoiding the difficulty of ionic liquid separation. The structure of PS-ILs was characterized by SEM and FT-IR. PS-ILs was loaded in a fixed-bed reactor to catalyze the esterification of acetic acid and n-butanol. The experimental results indicated that the catalyst had good catalytic performance. The conversion rate of acetic acid was about 81.58% after 4 h reaction in the fixed-bed reactor.

1. Introduction

N-butyl acetate is an important chemical product, which can be used in the production of artificial perfume, safety glass, medicine and dehydrating agent [1]. The catalysts for traditional esterification reaction were mainly liquid acids (such as H₂SO₄, HF). Although these traditional catalysts had high catalytic activity, there was a series of issues such as corrosion of production equipment, pollution of the environment, complicated operating procedures, and high costs in the process of industrialization [2]. In order to overcome these shortcomings, it was particularly important to develop a green and friendly high efficiency catalyst instead of the traditional catalyst.

Ionic liquid was a "green solvent", but there were difficulties in separation and purification, high prices and other problems in use of it. To solve the problems, the acid ionic liquid was immobilized on the polymer carrier, and the supported ionic liquid with high activity and repeatably continuous use was developed. Barghi et al. added ionic liquids to the alumina membrane and applied to study the permeability, diffusivity and selectivity of CO₂ and CH₄ [3]. Amarasekara et al. prepared a catalyst for cellulose hydrolysis by immobilized sulfonic acid functionalized acidic ionic liquid on silicon dioxide by chemical bonding [4].

In this study, we mainly investigated the immobilized ionic liquid polystyrene microsphere catalyst, which was loaded to the designed fixed bed reactor and used for esterification. The structure of PS-ILs catalyst was characterized by SEM and FT-IR.

2. Experimental

2.1. Materials and chemicals

N-butyl alcohol (AR) was purchased from Shanghai Macklin Biochemical Co., Ltd. Zinc chloride
anhydrous was purchased from China Sinopharm Chemical Reagent, China. Toluene, methylene dichloride and acetic acid (AR) were purchased from Beijing Tong Guang Fine Chemical Co., Ltd. Chloromethyl methyl ether was purchased from Kegonghua (Beijing) Chemical Technology Co., Ltd. Imidazole was purchased from Aladdin Chemical Company (Beijing, China). 1,4-butylyl sultone (AR) was purchased from Baishun chemical technology company. Sulfuric acid was purchased from Beijing Chemical Works.

2.2. Preparation of PS-ILs
Firstly, PS microspheres were prepared by suspension polymerization. Secondly, PS-CH2Cl was prepared by chloromethylation. Finally, PS-ILs was prepared by grafting ionic liquid. The specific reaction process was shown in the figure 1:

Figure 1. Schematic diagram of polystyrene microspheres chloromethylation and grafting ionic liquid.

2.3. Characterization
The structure of the prepared catalyst material was evaluated by a scanning electron microscopy (ZEISS SUPRA™ 55, German). The catalyst materials were analyzed with Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Nicolet RX/BX-IS10, USA) at scanning range of 4000–400 cm⁻¹.

2.4. Titration test
The content of acetic acid in the reaction system was determined by sodium hydroxide titration, with phenolphthalein as an indicator. The conversion rate of acetic acid was determined by calculating the concentration of acetic acid before and after the reaction. The acetic acid conversion (%) was calculated by the equation (1):

$$X_A(\%) = \frac{C_{A0} - C_{A_t}}{C_{A0}} \times 100\%$$  (1)

where $C_{A0}$ (mol/g) and $C_{A_t}$ (mol/g) were the initial concentration of acetic acid and the concentration of acetic acid at a time.

2.5. Fixed bed reactor
In order to make it easier and convenient to separate the catalyst and reactant, a fixed-bed reactor, as shown in figure 2, was designed. The raw material liquid was pre-loaded into the storage tank, then it was fed into the heating coil with peristaltic pump and heated to the temperature required for the esterification reaction. Devices inside the dashed box were submerged in an oil bath to heat the material and keep the temperature constant. It entered the fixed-bed reactor from the bottom and contact with catalyst PS-ILs. The thermometer could monitor the reaction temperature in the reactor at any time. After the reaction, the material liquid flowed out from the upper side of the fixed-bed reactor and flowed back to the storage tank through the cooling coil to complete a cycle. The design of the upper bend tube sampling in the storage tank avoided the backmixing of samples, which made the measurement result more accurate.
Figure 2. Flow chart of experimental devices of PS-ILs fixed bed catalytic reactor.

3. Results and discussion

3.1. Characterization of PS-ILs

3.1.1. SEM.
The microscopic morphology and particle size of PS-ILs spherical catalyst were observed by scanning electron microscopy (SEM). As shown in figure 3(a), the overall morphology of catalyst PS-ILs microsphere was a neat sphere with a diameter of about 1.5 mm. Therefore, in the design of fixed-bed reactor, the inlet and outlet sizes of reactor feedstock should be designed according to the size of catalyst particle size, so as to avoid the loss of catalyst caused by excessive inlet and outlet sizes. Figure 3(b) indicated that the PS-ILs spherical catalyst prepared by suspension polymerization had no internal pores and was a solid sphere.

Figure 3. Surface and cross-section SEM images of PS-ILs microspheres.

3.1.2. FT-IR.
The infrared characterization of the catalyst was shown in figure 4. According to figure 4(b), after chloromethylation reaction, a new peak appeared based on the characteristic absorption peak of PS: 660 cm$^{-1}$ was due to the stretching vibrations of C-Cl bond in
-CH₂Cl, and 1432 cm⁻¹ was due to the in-plane bending vibration of C-H bond in -CH₂Cl. Therefore, FT-IR analysis proved that chloromethylated polystyrene cross-linked microspheres had been prepared. Figure 4(c) indicated that 1219 cm⁻¹ was the asymmetric stretching vibration of S=O bond in -SO₃H, which proved that the ionic liquid was successfully grafted to PS-CH₂Cl [5].

3.2. Catalytic performance of PS-ILs in a fixed-bed reactor

In order to verify the catalytic performance of the spherical PS-ILs catalyst, PS-ILs was used to catalyze the esterification of acetic acid and n-butanol. With a certain flow rate, the optimal reaction conditions for the esterification reaction in a fixed-bed reactor were obtained by investigating the reaction temperature, reaction time, molar ratio of acid to alcohol and catalyst dosage. The reuse efficiency of the spherical catalyst was tested to verify the stability of the catalyst.

3.2.1. Effect of temperature and reaction time.

The effect of temperature on acetic acid conversion was shown in figure 5(a). The conversion rate of acetic acid increased with the increase of temperature, because the rising temperature could increase the kinetic energy of the reactant molecules, and increase the contact probability between reactant molecules and active sites of the catalyst [6]. When the temperature raised 100 °C, the reaction rate increased slowly and the conversion rate did not increase significantly. Thus 90 °C was determined as the experimental temperature.

As shown in figure 5(b), the conversion rate of acetic acid increased with the extension of reaction time. However, when the reaction time exceeded 4 h, the acetic acid conversion rate did not increase significantly, indicating that the reaction is balanced. So a reaction time of 4 h was recommended to carry out the subsequent experiments.

![Figure 5](image_url)

Figure 5. Effect of reaction temperature (a) and reaction time (b) on conversion ratio of acetic acid; Esterification conditions: n(n-butyl alcohol):n(acetic acid)=2, m(PS-ILs):m(reactants)=0.1, 4 h.

3.2.2. Effect of molar ratio of reactants and catalyst dosage.

The effect of molar ratio of acid to alcohol on conversion rate of acetic acid was shown in figure 6(a). The conversion rate of acetic acid increased with the increase of molar ratio. Because this esterification reaction was reversible, increasing the amount of one reactant was beneficial to the forward reaction [7]. However, when the amount of ethanol increased too much, it would dilute the reaction liquid and reduce the concentration of reactants. At the same time, more product water would slow down the forward reaction, which was not conducive to the formation of n-butyl acetate [6].

The effect of catalyst dosage on acetic acid conversion was shown in figure 6(b). The conversion rate of acetic acid increased with the increase of catalyst dosage. Mainly because the sufficient amount of catalyst provided more catalytic active sites, thus increasing the chance of contact between reactants and active sites, which was conducive to the forward reaction. However, when the ratio of catalyst to reactant mass reached 0.1, the acetic acid conversion rate did not increase significantly. Therefore, the
ratio of catalyst to reactant mass was determined as 0.1.

![Figure 6. Effect of molar ratio of reactants (a) and catalyst dosage (b) on conversion ratio of acetic acid. Esterification conditions: 90 ºC, 4 h.](image)

3.2.3. Reusability of PS-ILs membrane.

The reusability of the catalyst was shown in figure 7. The conversion rate of acetic acid gradually decreased with the increasing use PS-ILs microsphere catalyst, from the initial 85.14% to 76.49% after six uses. This might be on account of a little loss of anion $\text{HSO}_4^-$ during the reaction, resulting in less efficient esterification than before.

![Figure 7. Reusability of PS-ILs membrane. Esterification conditions: 90 ºC, n(n-butyl alcohol):n(acetic acid)=2, m(PS-ILs):m(reactants)=0.1, 4 h.](image)

4. Conclusions

In this study, PS microspheres were prepared by suspension polymerization, and then PS-ILs catalyst was synthesized by chemical bond grafting of acidic ionic liquid. Its catalytic performance for esterification of acetic acid and n-butanol was investigated in a fixed-bed reactor. The results revealed that the catalyst showed good catalytic activity in the esterification reaction. Furthermore, the experimental operation is convenient and the catalyst is easy to separate and recycle.

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