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Uniform acid poly ionic liquid-based large particle and its catalytic application in esterification reaction

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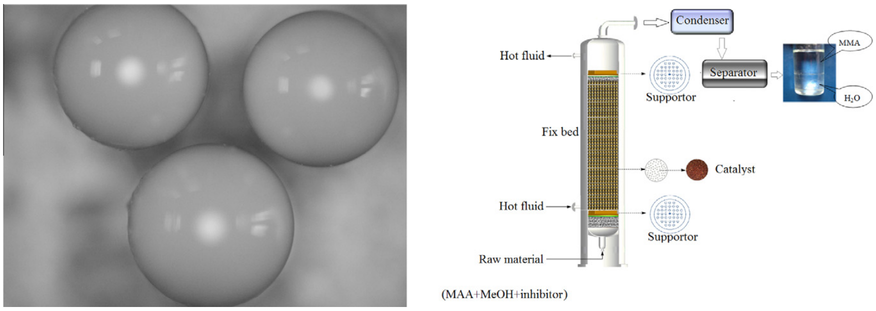
HIGHLIGHTS

- We prepared uniform large particle of acid poly ionic liquid (PIL-A) successfully.
- Thermostability and mechanical strength of PIL-A are much higher than that of commercial resin.
- PIL-A had a higher catalytic activity to different esterification.
- Continuous reaction to methyl methacrylate (MMA) with a fixed bed reactor proved its higher catalytic activity further.

GRAPHICAL ABSTRACT

Uniform large particle of acid poly ionic liquid-based and its application in esterification reaction with fix bed.



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ABSTRACT

Uniform large particles (millimeter class) of acid poly ionic liquid (PIL-A) were synthetized, and characterized by FT-IR, XRD, TGA/DCS, and SEM. Thermostability and mechanical strength of PIL-A are much higher than that of commercial resin. Its catalytic properties were investigated through the esterification of methacrylic acid and methanol as the objective reaction. Results showed that the catalytic activity of PIL-A was higher than that of commercial resin. The optimum reaction conditions were as follows: 5 wt% catalyst, 95 °C reaction temperature, 3 h reaction time, and methacrylic acid to methanol mole ratio of 1:1.2. The yield of methyl methacrylate is 100%, under optimum reaction conditions. The catalytic activities of PIL-A with different esterifications were also investigated. PIL-A had a higher catalytic activity to different esterification. The catalytic activity of PIL-A did not decrease after it was reused for five times. Continuous reaction to methyl methacrylate (MMA) with a fixed bed reactor was further investigated. The percentage of MMA in the product was >96%.

1. Introduction

The esterification reaction of carboxylic acid with alcohol is one of the most important and commonly used reactions in organic and bioorganic synthesis. Esters were generally used as plasticizers, solvents, perfumes and also as precursors for pharmaceuticals, agrochemicals and fine chemicals. However, esterification reactions usually use inorganic acids, such as H_2SO_4, HF and H_3PO_4 [1], solid acids [2,3], solid base [4–6], or bioenzymes as catalysts. These catalysts have some disadvantages. For example, inorganic acids could cause the problems such as equipment corrosion and

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severe environmental pollution. Solid acids require high molecular weight/active-site ratios and high mass transfer resistance, extended reaction time, low thermal stability and rapid deactivation from coking [7,8]. Solid base catalyst was used usually in transesterification. Bio-enzymes were generally expensive for commercial use and difficult to recycle without any catalytic activity loss. Therefore, the development of environmentally friendly catalysts with high catalytic activity become of great important and research focus.

In recent years, ionic liquids (ILs) have been attracting significant attention as alternative solvents and catalysts for chemical reactions because of their negligible volatility, remarkable solubility, and potential recyclability [9–11].

Though ILs have so many promising advantages, several drawbacks still hampered their widespread practical application: (1) high viscosity, which results to the participation of only a minor part of ILs in the catalytic reaction, (2) homogeneous reaction, which is difficult for product separation and catalyst recovery, and (3) consequently, the high cost for the use of relatively large amounts of ILs [12–14].

Therefore, an effective method was to support ILs onto the surface of support materials [15–18], such as silica gel [19], mesoporous silica [20,21], magnetic nanoparticles [22] and polymers [23] to solve the problems mentioned above. In 2004, Kim and Chi [24] developed polystyrene (PS)-supported IL catalysts for a series of nucleophilic substitution reactions. Afterwards, many researcher investigated PS-supported ILs and examined their catalytic activities in different reactions [25–28]. All the reported PS-supported ILs catalysts mentioned above could catalyze the organic reactions efficiently, and give high yield, high selectivity and good reusability. However, all preparation of PS-supported ILs includes two major steps: first, synthetizing PS by polymerization of styrene, divinylbenzene and vinyl benzyl chloride; second, IL grafted with PS by covalent bond. Vinyl benzyl chloride is necessary to link PS to imidazole (IL cation), however, vinyl benzyl chloride is also very expensive. Recently, poly (ionic liquid)s, the polymers made from ionic liquid monomers, have received much research interest for their potential applications such as gas separation materials [29]. Tang et al. found poly[p-vinylbenzyltrimethyl ammonium tetrafluoroborate] (P[VBTMA] [BF_4]) and poly [2-(methacryloyloxy)ethyltrimethylamnonium tetrafluoroborate] (P[MATMA][BF_4]) have absorption capacities 7.6 and 6.0 times of those of room temperature ILs, e.g. [bmim][BF_4], respectively, with reversible and fast sorption and desorption; polymer electrolytes [30]. Ricks-Laskoski et al. reported synthesis and electrowetting of a new IL monomer and polymer system. The uniqueness of the oxyethylene amine in the formation of the ammonium cationic species contributes to both the ionic and liquid nature of the monomer and polymer. Even more remarkable is the ability of this polymer to maintain its liquid nature as a macromolecule and to wet a substrate, showing preference for one polarity based upon the makeup of the ionic backbone of the polymer formed; Ogihara et al. found PIL having piperidinium cation, which is electrochemically more stable than that of imidazolium cation, showed higher lithium ion transference number. There are many researches on the use of PIL as ionic conductive materials [31–34].

By contrast, the papers on the use of PIL as catalysts are few. Xie et al. [27] copolymerized 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) with the cross-linker divinylbenzene (DVB) to prepare a highly cross-linked polymer-supported IL (PSIL). The catalytic performance of the PSIL for the cycloaddition of CO_2 to epoxides was investigated, and was demonstrated that the catalyst was very active, selective, and stable, and could be easily separated from the products and reused. Li et al. [35] prepared acidic ionic liquid-functionalized mesoporous copolymer P(VB-VMS)PW by anion-exchange of 1,3-propanesulfonate poly(N-vinylimidazole-co-divinylbenzene) with Keggin 12-phosphotungstic acid. P(VB-VMS)PW showed a relatively high yield of benzylating products (96.7%), and be facilely recovered and reused, in the Friedel–Crafts benzylation reaction.

Poly(ionic liquid)s in reported paper were usual prepared to nanoparticles for obtaining large specific surface [36,37] However, the expensive and toxic reagents used for immobilization further add to the catalyst costs. Furthermore, the catalytic activities were found to drop quickly upon recycling. The stability of these supported ILs should be investigated. The acid sites on the support surface were easily removed from the surface and reduced the activities [38]. Moreover, nanoparticle catalysts are studied only in laboratories, and using an industry reactor is not appropriated if the catalyst particle size is too small, because of the large pressure drop.

In this study, we prepared a larger sized acid poly IL particle (millimetre, even bigger size) by copolymerized acid IL monomer (vinylpyddine cation), styrene and ethyleneglycol dimethacrylate (EGDMA). The catalytic performance of the poly IL for the esterification reaction was investigated in detail.

2. Experimental

2.1. Materials

Vinylpyddine (VPy, analytical reagent), styrene (St, analytical reagent), ethyleneglycol dimethacrylate (EGDMA, analytical reagent), 1,4-butane sultone (analytical reagent), trifluoromethanesulfonic acid (analytical reagent), 2,2′-azobis(2-methylpropionitrile) (AIBN), sulfuric acid (98%, chemical reagent), and polyvinyl alcohol (PVA) were purchased from Sinopharm Chemical Reagent Co., Ltd. All solvents were purified by standard procedures before being used. VPy, St and EGDMA were removed polymerization inhibitor before being used.

2.2. Synthesis of ionic liquid monomers

Vinylpyddine and 1,4-butane sultone were added in a flask, with magnetic stirring, at 70 °C for 24 h. The mixture of vinylpyddine (g, 0.1 mol), 1,4-butane sultone (12.2 g, 0.1 mol) and 20 ml tetrahydrofuran was stirred magnetically for 24 h at 70 °C. Then, the white solid was formed. The white solid was filtrated and washed repeatedly with ether. The white solid was obtained in good yield (95%) after it was dried in vacuum. Equimolar amount of trifluoromethanesulfonic acid (sulfuric acid) was added to the obtained solid and the mixture was stirred for 8 h at 60 °C to form the IL monomer (yellow, thick liquid yellowish-brown). It was defined as IL-A.

2.3. Polymerization of ionic liquid monomers

The mixture of IL monomer, styrene, EGDMA and AIBN (0.5 mol%) were stirred magnetically for 1 h at room temperature, then the mixture was poured into aqueous solution (5% PVA) in a three-necked flask. The mixture was stirred mechanically at 65 °C for 2 h, then at 75 °C for 2 h, and finally at 85 °C for 2 h. The mixture was cooled to room temperature, and filtered. The ball particles were obtained. Obtained polymer ball particles were washed with dehydrated ethanol two times and then dried at 90 °C in the drying oven. It was defined as PIL-A. The product copolymerized vinylpyddine with styrene and EGDMA was defined as PVBS-E.

The preparation of the PIL-A was outlined in Scheme 1.