



Short communication

Novel porous and hydrophobic POSS-ionic liquid polymeric hybrid as highly efficient solid acid catalyst for synthesis of oleate



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ABSTRACT

A novel porous and hydrophobic Brønsted acidic solid catalyst (POSS-[VMPS][H₂SO₄]) was successfully synthesized by copolymerization of polyhedral oligomeric vinylsilsequioxanes (POSSs) and sulfonic acid-functionalized imidazole ionic liquids. Catalytic tests for the esterification of oleic acid with methanol have shown that this newly obtained polymeric hybrid exhibits very high catalytic activity and selectivity, which was more active or comparable to those of the common solid acid Amberlite-732 and liquid acid H₂SO₄. Moreover, the catalyst has a good recyclability without significant loss in the activity.

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1. Introduction

Due to the growing concerns of the exhaustion of fossil fuel resources and degradation of the environment, the production of eco-friendly fuels from abundant and renewable biomass resources has attracted much attention [1,2]. Biodiesel, a mixture of C₁₂–C₂₂ fatty acid monoalkyl esters (FAMES), obtained from acid- or base-catalyzed transesterification of triglycerides (TGs) with short-chain alcohols or esterification of fatty acid with alcohols, is a sustainable, non-toxic, and biodegradable petrol fuel replacement [3–8]. However, the transesterification of TGs is often accompanied by the production of unavoidable side product glycerol. Esterification is an important class of organic reaction, and various mineral acids including H₂SO₄, HF, and H₃PO₄, have been employed as catalysts for biodiesel production [9]. Nevertheless, these acids are extremely corrosive, contaminative and need to be neutralized at the end of the reaction. Furthermore, it is very difficult to separate and reuse the mineral acid catalysts.

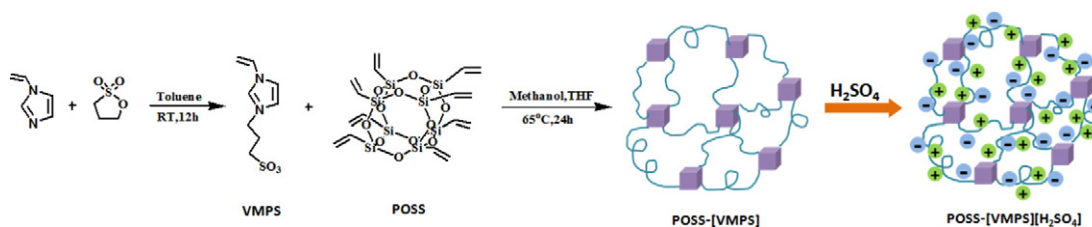
Ionic liquids (ILs) have been revealed as green reaction media owing to their negligible volatility, remarkable solubility, and the variety of structures available [10–12]. Many acid-catalyzed organic reactions based on acidic ILs have been reported, among which esterifications are a hot topic [13–15]. However, ILs usually cause homogeneous catalysis systems, which suffer from the high content of ILs (20–50 mol% with respect to substrate) needed in the reaction media. The replacement of homogeneous liquid catalysts by heterogeneous solid catalysts has received much attention because of the interest in green or

sustainable chemistry for catalyst recovery, operation and reuse. In particular, ILs supported on porous inorganic materials and organic polymers are efficient catalysts for the production of fine chemicals and have good recyclability [16–18]. Nevertheless, several factors such as low loading, tendency to deactivation, high mass transfer resistance, or hydrophilic frameworks retard the widespread implementations of many of these acidic catalysts. This has stimulated the development of strategies for preparation of novel IL-based solid catalysts with the high catalytic activity and steady reusability.

Poly(ionic liquids) (PILs) resulting from the combination of ionic liquid (IL) monomers or copolymerization of ILs with other monomers were shown to constitute an interesting system to develop IL-based solid catalysts [19,20]. A topic of interest in this context is the design of mesoporous PILs (MPILs), and many efforts have been devoted to controlling the pore structure, morphology, chemical composition, and surface functionality for various MPIL materials [21–23]. Previously, we designed and synthesized a family of porous polyhedral oligomeric silsesquioxanes (POSSs)-containing PILs by copolymerization of POSS and ILs, followed by ion exchange with polyoxometalates (POMs), revealing that the resulting POM-based PILs were highly efficient solid catalysts in epoxidations of alkenes [24–26]. Taking into account that the hydrophobicity of the inorganic core (Si₈O₁₂) in POSS can also be used to adjust hydrophobic features of the hybrid materials, which could separate out the produced water from the organic phase in time to shift the reaction to products side [27,28]. In this work, we have demonstrated a successful preparation of solid acid catalyst by copolymerization of octavinyl POSS with SO₃H-functionalized imidazole ionic liquids (Scheme 1). The obtained hybrid POSS-[VMPS][H₂SO₄] was proved to be porous material with excellent hydrophobicity and to

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Scheme 1. Synthesis of the POSS-ionic liquid polymeric hybrid POSS-[VMPS][H₂SO₄].

behave as highly efficient and recyclable heterogeneous catalyst for esterification of oleic acid with alcohols.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of octavinyl POSS and 1-vinyl-3-propylsulfonium imidazolium (VMPS)

Octavinyl POSS was prepared according to the previous literatures [29]. ²⁹Si NMR (400 MHz, CDCl₃, TMS) δ (ppm) = 80.19 (See Fig. S1 in Supplementary Material (SM)). VMPS was prepared according to the previous literature [30]. ¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm) = 2.25 (m, 2H, -CH₂), 2.85 (m, 2H, -CH₂), 4.43 (t, 2H, -CH₂), 5.32 (d, 1H, -CH), 5.68 (d, 1H, -CH), 7.04 (m, 1H, -CH), 7.60 (d, 2H, -CH₂), 9.05 (s, 1H, -CH) (Fig. S2, SM).

2.1.2. Preparation of POSS-[VMPS][H₂SO₄]

First, POSS-[VMPS] was synthesized through free radical copolymerization of octavinyl POSS with VMPS. 0.63 g of octavinyl POSS was added into 18 mL THF, followed by addition of 23 mL of methanol, then 1.73 g VMPS was introduced. After stirring at 60 °C for 1 h, 0.05 g of AIBN was added, the mixture was then reacted at 65 °C for 24 h. The formed solid product POSS-[VMPS] was filtered, washed with THF and methanol for three times, dried under vacuum at 60 °C for 10 h, which was further treated with sulfuric acid (H₂SO₄). 1.0 g POSS-[VMPS] was dispersed into 20 mL of ethanol, then 2 mL of 10 M H₂SO₄ was added with vigorous stirring. After stirring for 24 h at room temperature, the sample was treated by centrifugation and washed with ethanol until the supernatant was neutral. After drying at 60 °C for 12 h, POSS-[VMPS][H₂SO₄] was obtained. POSS-free sample Poly([VMPS][H₂SO₄]) was prepared in the same way without the adding of POSS units.

2.2. Procedure for catalytic performance

The esterification reactions were performed using oleic acid with different alcohols (methanol, ethanol, propanol and butanol) at different temperatures. Taking the esterification of oleic acid with methanol as an example, 0.01 mol oleic acid, 0.2 mol methanol, and 0.2 mmol catalyst were added into a 50 mL round-bottomed flask equipped with a reflux condenser. The mixture was reacted at 70 °C for 3 h without the addition of any solvents. Notably, the reactions performed at high temperatures (100 °C and 120 °C) were carried out in a 50 mL autoclave. After the reaction, the solid catalyst can be easily recovered by centrifugation, and the reaction product was determined by GC-MS.

3. Results and discussion

3.1. Preparation and characterization of catalysts

Fig. 1 shows the FT-IR spectra of POSS-[VMPS][H₂SO₄] and POSS-free sample Poly([VMPS][H₂SO₄]). Obviously, Poly([VMPS][H₂SO₄]) shows the featured peaks at 1553, 1187 and 1037 cm⁻¹ assigned to the stretching vibration of ν (C=N), ν (O=S=O), and ν (S-O) in [VMPS][H₂SO₄] IL, respectively. For POSS-[VMPS][H₂SO₄], these peaks

appeared distinctively with the appearance of a broad band at 1113 cm⁻¹, which is attributed to the asymmetric vibration of Si-O-Si in the POSS. Therefore, the FT-IR spectra confirm the successful combination of SO₃H functionalized IL with POSS through the copolymerization route. TG analysis in Fig. S3 in SM shows that the prepared POSS-[VMPS][H₂SO₄] has superior thermal stability with decomposition starting at about 250 °C. The significant weight loss in the range 250–400 °C is due to the decomposition of organic groups and the destruction of the polymer network.

The composition of POSS-[VMPS][H₂SO₄] was examined by CHNS elemental analysis. According to the CHNS elemental analysis results in Table 1, the actual molar ratio of [VMPS][H₂SO₄] to POSS is approximately 8.2, which is very near to the theoretical values of 8. Notably, the acid density of this type of polymeric solid acid catalysts solely depends on the charge ratio during the catalyst preparation, and the sulfur content of POSS-[VMPS][H₂SO₄] indicates a high acid concentration of 2.63 mmol/g, which is higher than those of the supported IL catalysts obtained by post modification method [31,32].

Fig. 2 shows the N₂ adsorption-desorption isotherms and the corresponding pore size distributions of the prepared polymeric hybrids, respectively. The sample POSS-[VMPS][H₂SO₄] displays a typical IV type isotherm, giving a steep increase at a relative pressure of 0.8 < P/P₀ < 1, indicating the presence of porous structures, including mesopores and macropores. Additionally, POSS-[VMPS][H₂SO₄] has a specific surface area of 43.56 m²/g and pore volume of 0.271 cm³/g (Table 1, entry 1). However, the surface area and pore volume of the POSS-free sample Poly([VMPS][H₂SO₄]) are significantly reduced to 7.55 m²/g and 0.039 cm³/g, respectively (curve b in Fig. 2A and B, Table 1, entry 2). Poly([VMPS][H₂SO₄]) shows artifact at about 4 nm which may be interpreted as partial blocking of the pores. These results demonstrate that the POSS plays important roles in the pore formation.

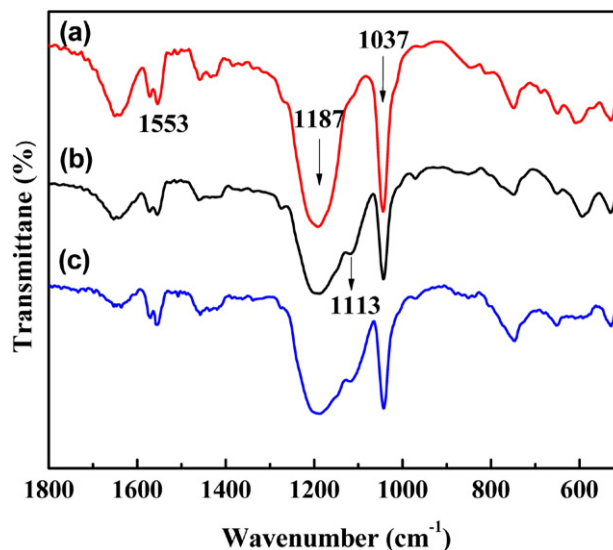


Fig. 1. FT-IR spectra of (a) Poly([VMPS][H₂SO₄]), (b) fresh POSS-[VMPS][H₂SO₄], and (c) reused POSS-[VMPS][H₂SO₄].

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