



Heteropolyanion-based ionic liquid-functionalized mesoporous copolymer catalyst for Friedel–Crafts benzylation of arenes with benzyl alcohol

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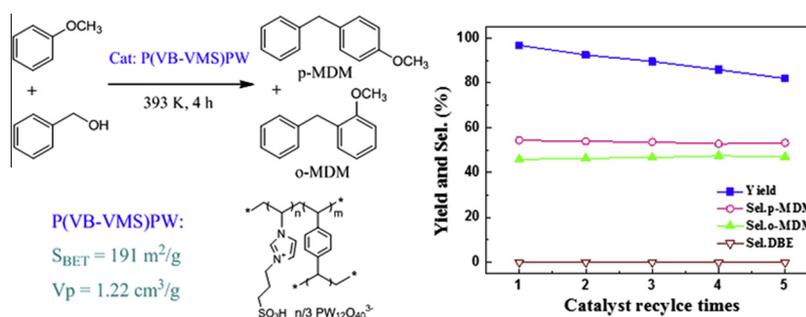
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HIGHLIGHTS

- Heteropolyanion-based mesoporous sulfonated copolymer catalyst is prepared.
- The catalyst is highly active in F–C reaction of arenes with benzyl alcohol.
- The catalyst is heterogeneous with high potential for reusability.
- Mesopores and heteropolyanion play key roles in catalytic performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A new heteropolyanion-based acidic ionic liquid-functionalized mesoporous copolymer P(VB-VMS)PW was prepared by anion-exchange of 1,3-propanesulfonate poly(N-vinylimidazole-co-divinylbenzene) with Keggin 12-phosphotungstic acid. The obtained hybrid material was characterized by fourier transform infrared spectroscopy, thermogravimetry, nuclear magnetic resonance, scanning electron microscope, X-ray diffractometer, nitrogen sorption isotherm, elemental analysis and Hammett indicator. Its catalytic performance was assessed and compared with analogues in the Friedel–Crafts benzylation reaction between single-ring aromatic compounds with benzyl alcohol under solvent-free condition. Owing to the suitable mesoporous copolymeric structure, P(VB-VMS)PW showed a relatively high yield of benzylation products (96.7%), and it could be facily recovered and reused. Besides, functionalization of the mesoporous ionic copolymer with heteropolyanion was able to enhance the structural stability and the acidity of the sulfonic group, favoring superior acid catalysis performance in benzylation reaction.

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1. Introduction

Friedel–Crafts (F–C) benzylation of arene is an important industrial reaction to produce numerous intermediates and fine chemicals [1–3]. Benzylation products are constituents of lubri-

cants, analgesics or anti-inflammatory agents [4,5]. The conventional synthetic methods for diarylmethane-derivatives are benzylation of arene with benzyl halide or benzyl alcohol using Lewis acids (e.g., AlCl₃, FeCl₃ and BF₃) or Brønsted acids (e.g., H₂SO₄, HF and H₃PO₄) as catalysts [6]. These homogeneous catalytic processes undesirably generate large amounts of environment harmful and equipment corrosive by-products, plus extreme difficulty in catalyst separation and recycling. Heterogeneous catalysis

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is known to be more environmental benign benefited from convenient catalyst isolation; among various heterogeneous catalysts [7–17], mesoporous silicas [7], supported metal triflates [8], H β zeolites [9,10], and mesoporous niobium oxide [11] are typical examples. However, there still exist drawbacks such as high molar ratio of anisole to benzyl alcohol, poor catalyst reusability, and/or selectivity, thus it is highly desirable to design efficient and reusable solid acid catalysts for F–C benzylation of arene with benzyl alcohol.

Ionic liquids (ILs) have attracted great attention because of their unique characteristics like negligible volatility and tunable structure. For many reactions, functional ILs can be task-specifically designed and used as catalysts/solvents [18,19]. It has been reported that benzylation reactions can be catalyzed by chloroaluminate Lewis acidic ILs [20] and Fe(III)-derived Lewis acidic ILs [21]; nonetheless, large amounts of ILs are needed in these processes and ILs separation and reuse are not as convenient as solid catalysts. Besides, heteropolyacids (HPAs), exemplified with Keggin-structured phosphotungstic acid (abbreviated as H $_3$ PW), are a group of classical acid catalysts with high activity towards benzylation reactions [22–26]. When HPA-anions are used as counter anions for ILs, a family of HPA-based organic-inorganic hybrid materials are achieved with enhanced thermal stability and modulated solubility [27–30], which have been used for heterogeneously catalyzing a number of organic transformations like esterification, Prins cyclization, and Beckmann rearrangement [31–35]. However, the previously reported HPA-IL hybrid catalysts usually encounter severe leaching problems in strong polar reaction media, especially with protic solvents. It is noticeable that ionic copolymers, mostly with highly stable poly(IL-cation) structures, have been used as heterogeneous solid catalysts [36–38], and in this area, mesoporous ionic copolymers have large surface areas, benefiting the diffusion of large guest molecules and improving mass transfer [39], but up to date, they have not been applied in F–C reactions.

In this work, we task-specifically design and prepare a new HPA-anion-paired ionic copolymer catalyst with strong acid sites and plenty of mesopores for F–C benzylation reactions. The mesoporous copolymer precursor is hydrothermally synthesized by copolymerization of the two monomers of divinylbenzene (VB) and N-vinylimidazole (vim), and the ionic copolymer catalyst is obtained through post-treatment of the copolymer precursor with 1,3-propanesulfonate, followed by the anion-exchanging with H $_3$ PW. The HPA-based ionic copolymer hybrid catalyst, as well as precursors, are systematically characterized and catalytically assessed in heterogeneous benzylation reaction of anisole with benzyl alcohol, demonstrating superior activity and selectivity with well recyclability.

2. Experimental

2.1. Characterization

All chemicals were analytical grade and used as received. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet iS10 FT-IR instrument (KBr discs) in the 4000–400 cm $^{-1}$ region. Thermogravimetry (TG) analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 K/min. Scanning electron microscope (SEM) images were performed on a Hitachi S-4800 field emission scanning electron microscope (accelerated voltage: 5 kV). X-ray diffraction (XRD) measurements were performed with a SmartLab diffractometer from Rigaku equipped with a 9 kW rotating anode Cu source at 40 kV and 200 mA, from 5° to 80° with a scan rate of 0.2 °/s. Brunauer–Emmett–Teller (BET) surface areas were measured at the temperature of liquid nitrogen (77 K) by using a BELSORP-MINI

analyzer, and the samples were degassed at 423 K for 3 h to a vacuum of 10 $^{-3}$ Torr before analysis. The CHN elemental analysis was performed on an elemental analyzer Vario EL cube. The acid strength (H $_0$) was measured from a series Hammett indicators, including methyl yellow (pKa = 3.3), crystal violet (pKa = 0.8), dicinnamalacetone (pKa = –3.0) and 2, 4-Dinitroaniline (pKa = –4.4). Nuclear magnetic resonance (NMR) experiments were carried out on a Bruker Avance III spectrometer in a magnetic field strength of 9.4 T, corresponding to the Larmor frequencies of 400.1 and 100.6 MHz for 1 H and 13 C nuclei, respectively. The 13 C cross-polarization (CP)/magic-angle-spinning (MAS) NMR were performed with a contact time of 1 ms, a recycle delay of 2 s, and a sample spinning rate of 14 kHz.

2.2. Catalyst preparation

The N-vinylimidazole functionalized copolymer P(VB-vim) was hydrothermally synthesized by copolymerization of vim with VB monomers consulting the previous literature [40]. 0.47 g vim and 1.69 g VB were added to 30 mL ethyl acetate solution containing 0.08 g AIBN. After stirring at room temperature for 3 h, the mixture was hydrothermally treated at 373 K for 24 h, followed by evaporation of the solvent at room temperature for 24 h. The white solid was washed with ethyl acetate and dried at room temperature to give the final P(VB-vim) sample. (Elemental analysis Found: C 86.19 wt.%; H 7.32 wt.%; N 6.44 wt.%)

The IL-functionalized copolymer was prepared as the followings. 1.0 g P(VB-vim) was added to 25 mL ethanol under stirring, followed by addition of 2.5 mL 1,3-propanesulfonate. After stirring for 24 h, the sample was filtrated and washed with a large amount of ethanol to remove 1,3-propanesulfonate. After drying for 12 h, the P(VB-VMS) sample was obtained. (Elemental analysis Found: C 76.10 wt.%; H 7.61 wt.%; N 5.22 wt.%; S 2.73 wt.%)

The sample P(VB-VMS)PW was prepared by the reaction of the above sulfonated ionic copolymer P(VB-VMS) and Keggin phosphotungstic acid, as shown in Scheme 1. 1.0 g P(VB-VMS) precursor was treated with a solution containing 25 mL of ethanol/H $_2$ O (3:1 v/v) and 0.82 g H $_3$ PW for 24 h at 353 K, followed by filtration, washed with ethanol and H $_2$ O and dried at 373 K for 12 h [27]. (Elemental analysis Found: C 47.78 wt.%; H 4.59 wt.%; N 3.27 wt.%; S 1.52 wt.%) P(VB-VMS)H $_2$ SO $_4$ was prepared by reacting P(VB-VMS) and H $_2$ SO $_4$ with the molar ratio of 1:1 at 273 K. (Elemental analysis Found: C 74.71 wt.%; H 7.31 wt.%; N 5.11 wt.%; S 4.75 wt.%) The synthesis of the control hybrids P(VMS)PW (VMS: 1-vinyl-3-propane sulfonate imidazolium) and (MimPS) $_3$ PW (MimPS: 1-methyl-3-propane sulfonate imidazolium) were prepared according to previous literatures [31,41]. Elemental analysis of P(VMS)PW Found: C 8.29 wt.%, H 1.43 wt.%, N 2.44 wt.%, S 2.76 wt.%. Calcd: C 8.15 wt.%, H 1.28 wt.%, N 2.38 wt.%, S 2.72 wt.%

2.3. Catalytic activity measurement

All F–C benzylation reactions were carried out in a 25 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer. In a typical run, 2.16 g (20 mmol) anisole and 0.43 g (4 mmol) benzyl alcohol (5:1 molar ratio) plus 0.1 g catalyst were taken in flask. The resultant mixture was heated at 393 K for 4 h. The reaction conditions were optimized by varying different parameters such as the molar ratio of anisole to benzyl alcohol, catalyst amount, and reaction temperature and time.

The reaction mixture was withdrawn at different intervals and analyzed by a gas chromatography (Shimadzu GC-2014) equipped with a SE-30 (50 m \times 0.25 mm \times 0.3 μ m) capillary column and flame ionization detector. The temperature of the GC column oven stayed at 403 K for 2 min, and then programmed to 513 K at the rate of 10 K/min, finally maintained at 513 K for 12 min. The

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