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Superoleophilic nanoporous polymeric ionic liquids loaded with palladium acetate: Reactants enrichment and efficient heterogeneous catalysts for Suzuki–Miyaura coupling reaction

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ABSTRACT

We report here successful synthesis of superoleophilic, nanoporous polymeric ionic liquids supported palladium acetate (PDVB-[C_3vim][SO_3CF_3]-Pd-*xs*, where *x* stands for the weight percentage of palladium acetate), which act as efficient heterogeneous catalysts in Suzuki–Miyaura cross-coupling reaction. PDVB-[C_3vim][SO_3CF_3] support was synthesized from solvothermal copolymerization of divinylbenzene with vinylimidazole without using any templates, followed by functionalized with ionic liquid groups. The resultant PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* possess large BET surface areas, good stability, homogeneous dispersion of Pd active species, and superwettability for various aromatic reactants, which result in their much improved reactants enrichment property. The above characters make PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* showed much improved catalytic activity and good recyclability in Suzuki–Miyaura reaction in comparison with those of palladium acetate supported onto activated carbon and ordered mesoporous silica of SBA-15. The superior activity found in PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* is attributed to synergistic effects between large surface areas and unique enrichment property for various aromatic reactants, which by themselves are capable of enhancing exposition degree of Pd active sites to reactants.

1. Introduction

Carbon–carbon bond forming reactions such as Suzuki–Miyaura cross-coupling reaction represent one of the most primary and essential transformations in organic synthesis, which are of great importance in the fields of agrochemicals, functional materials, and pharmaceuticals. With the fast development of Pd based catalysts, Suzuki–Miyaura reaction now could be carried out under rather mild conditions with great efficiency and selectivity [1–6]. However, from the point of view of environmental benign and sustainable chemistry, homogeneous Pd based catalysts such as Pd ligands usually suffer from the drawbacks such as high cost, complicated processes for catalyst regeneration, environmental concerns, and air or water sensitivity [7–12].

Loading Pd active species onto solid materials develops a cost-effective and green route for the wide applications of Pd based catalysts in the areas of cross-coupling reactions. The commonly used solid supports are silica, metal oxides, and resins *etc*. However, these supports usually show poor porosity, which results in the bad dispersion and partially embedding of catalytically active sites in these nonporous solid supports, further leading to their very low catalytic activities and limited catalytic lives [13–16].

Immobilization of Pd active species into nanoporous materials such as SBA-15, ordered mesoporous phenolic resins and activated carbons [17–26] develops completely new kinds of heterogeneous Pd based catalysts with good dispersion and high exposition degree of catalytically active sites, which showed much improved catalytic activities in the cross-coupling reactions [17–26]. However, the high cost of separation of reactants and products from reaction media at an industrial scale will demand new catalysts with extremely high effectiveness.

In principle, heterogeneous catalytic processes usually experience the steps of (i) reactants adsorption, (ii) reacting, and (iii) products desorption, among which the steps of (i) and (iii) play the key factors for the efficiency of various heterogeneous catalysts. Compared with homogeneous catalysts, heterogeneous catalysts usually gave lower exposition degree of catalytically active sites and obvious diffusion limitation, which largely decrease their catalytic activities [27]. Therefore, although the reported supports have abundant nanopores, the hydrophilic networks in nature lead to their bad wettability for various organic reactants, further

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resulting in the high adsorption activation energy and diffusion limitation. The above problem results in their lower catalytic activities than the correspondingly homogeneous systems.

Up to now, it is still challengeable to synthesize suitable nanoporous materials with controlled wettability and improved enrichment property for various organic reactants, which could act as effective supports for Pd active species. The resultant Pd based heterogeneous catalysts will show very good compatibility with reaction systems [28–32] and high exposition degree of Pd active species in various reactions such as Suzuki–Miyaura reaction. Recently, our group firstly reported ionic liquids grafted onto superhydrophobic, superoleophilic nanoporous polymers (*e.g.* PDVB-[C_3vim][SO_3CF_3]), which showed even better catalytic activity than homogeneous ionic liquids themselves. Their excellent catalytic activity was attributed to their much improved reactants enrichment property, further resulting in their homogeneous like exposition degree of catalytically active sites [27].

We report here that PDVB-[C_3vim][SO_3CF_3] act as an extraordinary support for palladium acetate, the resultant PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* catalysts showed large BET surface areas, abundant nanopores, and good dispersion of Pd active species. Notably, PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* exhibited superwettability and enhanced enrichment property for various aromatic compounds such as aryl (pseudo) halides and arylboronic acids, which should be attributed to the presence of strong $\prod\ldots\prod$ packing interactions between benzene rings in PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* and aromatic reactants, similar interactions between catalysts and reactants have also been reported in other type of catalytic reactions [32,33]. The strong interactions between catalysts and reactants largely increase the wettability and enrichment property of PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* for reactants, which result in their much improved catalytic activity in Suzuki–Miyaura reaction in comparison with those of palladium acetate supported on activated carbon and ordered mesoporous silica of SBA-15 supports, similar results have not been reported previously. The preparation of PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* will develop a green and cost effective approach to synthesize novel and efficient heterogeneous Pd based catalysts, which will be very important for their wide applications to catalyze synthesis of various organic compounds through Suzuki–Miyaura cross-coupling reaction.

2. Experimental sections

2.1. Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. Divinylbenzene (DVB), palladium acetate, nonionic block copolymer surfactant of poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) (Pluronic 123, molecular weight of about 5800) and 1-vinylimidazolate (vim) were purchased from Sigma–Aldrich Company. Azobisisobutyronitrile (AIBN), ethyl acetate, CH_3I, activated carbon, 1-bromobutane, 1,3-propanesultone, HSO_3CF_3, ethanol, toluene, CH_2Cl_2, dimethyl ether, tetrahydrofuran (THF), phenylboronic acid and various aryl halides were purchased from Beijing Chemical Agents Company.

2.2. Synthesis of samples

2.2.1. Synthesis of N-vinylimidazolate functionalized nanoporous polymers

N-vinylimidazolate (vim) functionalized nanoporous polymers (PDVB-vim) were synthesized from copolymerization of DVB with vim monomer in the starting mixture of DVB/vim/AIBN/ethyl acetate, methyl acetate or THF with the molar ratio at 1.0/0.5/0.027/20.8 under solvothermal conditions [29]. Typically, 2.0 g of DVB and 0.483 g of vim were added into a solution containing 0.07 g of AIBN and 30 mL of ethyl acetate. After vigorous stirring of the mixture for 3 h at room temperature, the mixture was transferred into an autoclave and solvothermally treated at 100 °C for 24 h. The superhydrophobic nanoporous polymers designated as PDVB-[vim] with monolithic morphology could be obtained from evaporation of solvent at room temperature, and drying at 60 °C under vacuum condition.

2.2.2. Synthesis of ionic liquids functionalized superhydrophobic nanoporous polymers

Ionic liquids functionalized, superhydrophobic nanoporous polymers were synthesized from quaternary ammoniation of PDVB-vim with (CH_3I: C_1), ($CH_2CH_2CH_2CH_2Br$: C_4) or (1, 3-propanesultone: C_3), and ion-exchanging with HSO_3CF_3 [27]. As a typical run for synthesis of PDVB-[C_1vim][SO_3CF_3], 1.0 g of PDVB-[vim] was dispersed into 25 mL of ethanol under vigorous stirring, followed by the addition of 2.5 mL of CH_3I, after stirring of the mixture for 12 h at 25 °C under dark condition, PDVB-[C_1vim] could be obtained from filtration, washing with large amount of ethanol and drying at 60 °C for 5 h. PDVB-[C_1vim][SO_3CF_3] could be synthesized from treating PDVB-[C_1vim] with a solution containing 25 mL of toluene and 3 mL HSO_3CF_3 for 24 h at room temperature, filtration, washing with large amount of CH_2Cl_2 and drying at 60 °C. Similarly, PDVB-[C_3vim][SO_3CF_3] and PDVB-[C_4vim][SO_3CF_3] could be also synthesized from treating PDVB-vim with 1,3-propanesultone and $CH_2CH_2CH_2CH_2Br$, followed by the similar ion-exchanging processes with HSO_3CF_3. For comparison, ordered mesoporous silica of SBA-15 was synthesized according to the literature [34].

2.2.3. Synthesis of palladium acetate functionalized nanoporous polymeric ionic liquids

Palladium acetate loaded nanoporous polymeric ionic liquids of PDVB-[C_3vim][SO_3CF_3]-Pd-*xs* could be synthesized from stirring of PDVB-[C_3vim][SO_3CF_3] into a solution containing THF and weight quantitative palladium acetate for 12 h, followed by evaporation of solvent under vacuum, washing with dimethyl ether and drying at 60 °C. As a typical run for synthesis of PDVB-[C_3vim][SO_3CF_3]-Pd-0.5: 1.0 g of PDVB-[C_3vim][SO_3CF_3] was added into a solution containing of 40 mL of THF and 0.005 g of palladium acetate, after stirring of the mixture for 12 h at room temperature ($\sim$25 °C), PDVB-[C_3vim][SO_3CF_3]-Pd-0.5 could be obtained from vacuum distillation for removing of THF solvent at 45 °C, washing with large amount of dimethyl ether and drying at 60 °C for 12 h. For comparison, Pd functionalized ordered mesoporous silica (SBA-15-Pd) and activated carbon (activated carbon–Pd) were synthesized as the similar procedures with that of PDVB-[C_3vim][SO_3CF_3]-Pd-*xs*.

2.3. Characterization methods

Nitrogen isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 4 h at 200 °C before the measurements. The pore-size distribution was calculated using Barrett–Joyner–Halenda (BJH) model. X-ray powder diffraction (XRD) patterns of samples were recorded on a Rigaku D/max2550 PC powder diffractometer using nickel-filtered Cu Kα radiation in the range of $10^\circ \leqslant 2\theta \leqslant 60^\circ$. Transmission electron microscopy (TEM) images were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα radiation at $y = 901$ for the X-ray sources, the binding energies were calibrated using the C1s peak at 284.9 eV.