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Mesoporous silica-based nanotubes loaded Pd nanoparticles: Effect of framework compositions on the performance in heterogeneous catalysis

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ABSTRACT

Well-shaped mesoporous silica-based nanotubes with different framework compositions, such as organic groups (ethylene, phenylene), carbon/silica hybrids, could be controllably synthesized with the inner diameter of less than 10 nm and the surface areas of about 400–900 m^2 g^{-1}. Through an impregnation-reduction process, palladium (Pd) nanoparticles have been uniformly dispersed in the channels of these different nanotubes, which were confirmed by electron microscopy analysis. The catalytic performance of these silica-based nanotubes loaded Pd nanoparticles was evaluated by the aerobic oxidation of benzyl alcohol and enantioselective hydrogenation of α,β-unsaturated carboxylic acid, respectively. Due to one-dimensional nanotube structures and tunable hydrophilic/hydrophobic properties, the organosilica nanotubes supported Pd nanoparticles could afford >99% conversion of benzyl alcohol and 89% selectivity of benzaldehyde within 2 h. Importantly, carbon/silica hybrid nanotubes may have a positive effect on the reaction, which gave about 95% selectivity of benzaldehyde. The catalysts could be reused without an obvious decrease in both conversion and selectivity. Furthermore, the silica-based nanotubes supported Pd nanoparticles were also efficient for asymmetric hydrogenation of α,β-unsaturated carboxylic acids, which showed a highest conversion of 99% with 48% enantioselectivity.

1. Introduction

One-dimensional nanotubes perform an important role as the heterogeneous supports/catalysts owing to their unique physicochemical properties, such as high specific areas, mechanical stabilities and hollow structures facilitating easy diffusion of reactants and products [1–4]. Up to date, carbon, silica, metal oxide, or even metal with tubular morphology have been reported [5–8]. Organosilica nanotubes represent one of the most interesting materials for catalysis because they not only possess the ability for the adjustment of the hydrophobic/hydrophilic properties, but also can be further functionalized to derive new active sites easily. Moreover, organosilica nanotubes with bridging organic groups such as ethylene and phenylene could be facilely synthesized by using soft-template assembly method [9].

Recently, organosilica nanotubes have demonstrated their potential in catalysis. For example, Guo et al. reported that ethylene- or phenylene- organosilica nanotubes doped with sulfonic acids in the framework, which could efficiently catalyze the esterification of palmitic acid and transesterification of yellow horn seed oil with methanol [10]. Organosilica nanotubes containing bipyridine groups in their walls were found to act as efficient solid ligands to immobilize molecular catalyst for water oxidation reaction [11].

Palladium (Pd) nanoparticles dispersed on various supports have been extensively studied not only for the oxidation reactions of fine chemicals but also for the hydrogenation reactions of olefins [12–14]. Recently, carbon and pure silica nanotubes were used to encapsulate Pd nanoparticles for oxidation of benzyl alcohol and Suzuki-Miyaura coupling, respectively [15,16]. The heterogeneous Pd catalysts immobilized on nanotubes showed favorable activities due to the nano-confinement effects and higher accessibility of reactants. However, the effects of the nanotube framework compositions on the performance in the heterogeneous catalysis have been seldom systematically studied.

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Herein, by using silica-based nanotubes with the doping of ethylene, phenylene or carbon in the frameworks as the supports, we have constructed the heterogeneous catalysts containing Pd nanoparticles through the impregnation-reduction method. Pd nanoparticles are uniformly dispersed in the channels of the nanotubes with different framework compositions, which were applied in the oxidation of benzyl alcohol and enantioselective hydrogenation of α,β-unsaturated carboxylic acid, respectively (Scheme 1). The effects of the silica-based nanotubes with ethylene, phenylene, carbon or pure silicas in the frameworks on the catalytic performance were investigated.

2. Experimental section

2.1. Materials

1,2-bis(trimethoxysilyl)ethane (BTME), 1,4-bis(triethoxysilyl) benzene (BTEB), tetraethyl orthosilicate (TEOS) and potassium chloride were purchased from J&K Scientific Ltd. Hydrochloric acid (37%), ethanol, 1,4-dioxane, toluene and acetone were obtained from Real&Lead Chemical Co. LTD. $PdCl_2$ (>99.9%), Pluronic P123, α-phenylcinnamic acid (99%) and cinchonidine (CD) were received from Sigma–Aldrich and all reagents were used without further purification. Oxygen and hydrogen with purity of 99.999% were used in the oxidation and asymmetric hydrogenation, respectively.

2.2. Synthesis of silica-based nanotubes with different framework compositions

The organosilica nanotubes with ethylene or phenylene groups in the framework were synthesized according to the method we reported previously with minor modifications [9]. Typically, 0.55 g of P123 and 1.75 g of KCl were completely dissolved in 135 mL of HCl solution (2 mol L^{-1}) at 38 °C. After that, 3.50 mmol of 1,2-bis(trimethoxysilyl)ethane (BTME) was added into the solution under vigorous stirring. The mixture continually stirred for 6 min and remained quiescent for 24 h. Then the resultant mixture was transferred to a PTFE reactor and kept at 100 °C for an additional 24 h. Subsequently, the solid product was obtained by the filtration and air drying overnight at room temperature. Finally, 200 mL of ethanol containing 1.5 g of concentrated aqueous HCl solution was used to extract the surfactants from 1.0 g of synthesized material at 60 °C for 24 h and the surfactants-free samples were denoted as E-SNT. The synthetic process of organosilica nanotubes containing phenylene groups in the walls (named as B-SNT) was almost the same as that of E-SNT except for the replacement of the precursor with 1,4-bis(triethoxysilyl)benzene (BTEB).

To obtain the carbon-doped silica nanotubes E-CS-NT and B-CS-NT, the surfactants-free E-SNT and B-SNT were carbonized at 800 °C in nitrogen atmosphere for 2 h, respectively (CS refers to carbon/silica hybrid). Besides, the pure silica nanotubes (SNT) and SBA-15 were also synthesized as the references of the supports [17,18].

2.3. Preparation of immobilized Pd nanoparticles using nanotubes as the supports

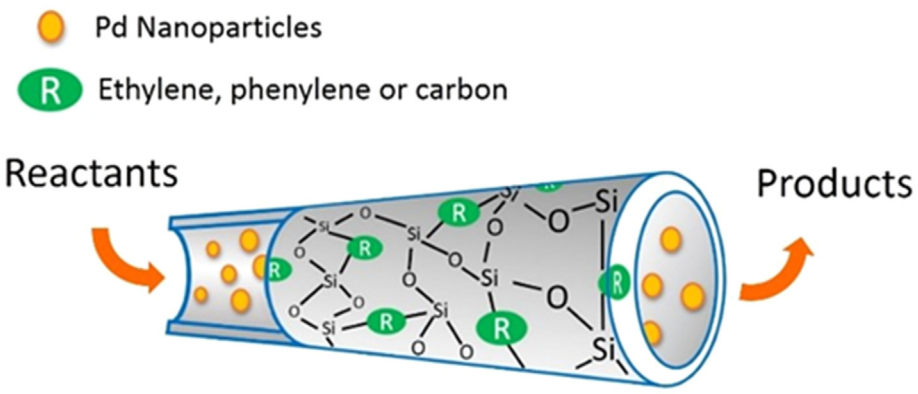
All of the catalysts supported Pd nanoparticles were prepared by using an impregnation-reduction process. For example, 150 mg of E-SNT were immersed into 10 mL ethanol solution containing 13 mg $PdCl_2$ while the content of Pd immobilized was 5 wt%. After ultrasonic treatment for 1 h, the suspension was stirred at an ambient temperature for 12 h. Then, the solvents were evaporated under a negative pressure slowly and the divalent Pd was reduced at 150 °C in H_2 for 5 h to obtain the heterogeneous catalysts with the immobilized Pd nanoparticles.

2.4. Oxidation of benzyl alcohol

The oxidation of benzyl alcohol was carried out in a 25 mL round-bottom three-necked flask with a magnetic stirring and a condenser. Since toluene may be a product of the oxidation reaction, we selected xylene as the solvent and undecane as an internal standard for the product analysis [19,20]. The powdery catalyst (typically 45 mg) was added into the flask charged with 0.6 g benzyl alcohol and 12.5 mL xylene as well as relevant amount of undecane. When the temperature raised to the set value, an O_2 flow was bubbled into the mixture to trigger the reaction under vigorous stirring. Samples of the reaction mixture were taken out at appropriate time intervals and analyzed by gas chromatograph (Bruker BR-GC-456) equipped with a flame ionization detector (FID) after solid removal.

2.5. Enantioselective hydrogenation of α,β-unsaturated carboxylic acid

Hydrogenation was carried out in a magnetically stirred autoclave under 0.1 MPa H_2 pressure at room temperature. The catalyst (20 mg) was pre-treated in a H_2 flow with modifier CD (0.02 mmol) in 4 mL 1,4-dioxane containing 2.5% (v/v) of water for 30 min. After that, 1 mmol of α-phenylcinnamic acid in 2 mL solvent was added to the mixture. The mixture was stirred immediately after adjusting the hydrogen pressure to 0.1 MPa. After 10 h, the mixture was neutralized with a diluted HCl solution, extracted with ethyl ether and analyzed by proton nuclear magnetic resonance (^{1}H NMR,



Scheme 1. Illustration of Pd supported ethylene, phenylene bridged or carbon doped organosilica nanotubes and common reaction process.