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A titania-supported highly dispersed palladium nano-catalyst generated via in situ reduction for efficient Heck coupling reaction

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ABSTRACT

Supported metal catalysts have been applied in many current industrial processes. The dispersion of metal particles on solid supports has been proven to affect the performance of catalysts greatly. In this study, a titania-supported palladium catalyst prepared by a simple pH-controlled adsorption method is efficient and recyclable for the Heck coupling reaction of aryl halides and alkenes. The pH-controlled adsorption method results in high dispersion of palladium species on titania surface. During the reaction, palladium nanoparticles are in situ generated via reduction on the surface of titania. TEM images indicate that the nanoparticles are nearly monodisperse in size. Recycling studies have shown that the catalyst can be readily recovered and reused several times without significant loss of catalytic activity.

1. Introduction

The cross-coupling reaction of aryl or vinyl halides with alkenes, that is, Heck reaction, is among the most commonly used methods for C–C bond formation and widely applied to organic and fine-chemical synthesis [1–4]. In the past few years, the development of ligands has provided highly active homogeneous palladium catalysts for Heck reactions under mild conditions and enabled using a wide range of aryl halides [1,4]. However, homogeneous processes suffer from the problems concerning separation from reaction mixture, reuse of expensive palladium catalysts. In addition, most of ligands for Heck reactions are undesirable in the industrial chemistry because of their toxicity, high price and air-sensitivity.

In principle, the use of supported palladium catalysts could address some of these problems mentioned above. Thus, the practical applications of Heck reactions have greatly driven the need for the development of recyclable and efficient heterogeneous palladium catalysts [5–10]. In this regard, supported palladium catalysts exhibit particularly promising performances for the Heck reaction. A variety of solid materials as supports have been investigated, for example, active carbon [11], mesoporous silica [12], metal oxides [13–16], zeolites [17,18], magnetic materials [19], hydrotalcites [20], hydroxyapatite [21], and organic–inorganic hybrid materials [22]. Traditionally, supported palladium catalysts are typically prepared by impregnation these solid supports with a palladium salt aqueous solution, followed by drying or calcination in air and reduction. The resultant palladium particles are usually randomly dispersed on the surface of support with broad size distribution, which may cause a decrease in catalytic performance. Therefore, preparation of supported palladium catalysts with high dispersion and narrow size distribution of palladium particles becomes particularly desirable for the improvement in catalytic performance.

Very recently, a highly dispersed palladium catalyst supported on ordered mesoporous silica–carbon composites was reported to be highly active and reusable in the Heck reaction [10] probably because the high dispersion of palladium species on the surface of support could prevent formation of catalytically deactivated palladium black and keep all active palladium species available for the reaction [9]. The increase in catalytic activity and reusability for highly dispersed catalyst would allow use of low palladium loading for achieving efficient turnover and thereby reduce the cost of products in large-scale processes. In addition, a simple and efficient absorption method has appeared as an attractive approach to highly dispersed palladium on γ-Al_2O_3 [23], in which palladium content can be tuned by varying pH value of aqueous solution and palladium(II) concentrations in the absorption stage.

As a typical metal oxide, TiO_2 usually shows pH-dependent surface charges when it is immersed in aqueous solution because of the existence of Ti–OH on the surface. The absorption property of TiO_2 greatly changes with environment of different pH value. In

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this paper, we report the high catalytic performance of the highly dispersed Pd on TiO_2 catalyst prepared by the adsorption method for the Heck cross-coupling reaction of aryl halides and alkenes. The method represents a simple and efficient approach to highly dispersed catalysts. Moreover, we demonstrate that this heterogeneous catalyst can be readily recovered and reused several times without significant loss of activity.

2. Experimental

2.1. General

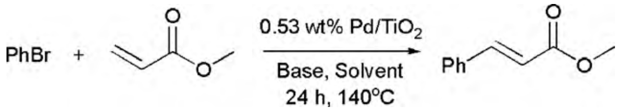
Commercially Titania P-25 (TiO_2, 80% anatase 20% rutile, BET surface area: $53\,m^2\,g^{-1}$) was provided by Degussa. $PdCl_2$ (AR) was obtained from Shanghai July Chemical Co. Ltd. and used as received. Solvents were obtained from Sinopharm Chemical Reagent Co. Ltd and purified prior to use. Other chemicals were purchased from Sigma–Aldrich or Alfa Aesar and used without further purification or drying. Water used in the experiments was deionized (DI) and doubly distilled prior to use. Unless otherwise stated, all experiments were performed in nitrogen atmosphere.

2.2. Catalyst preparation

Pd/TiO_2 catalysts prepared by an adsorption method (Pd/TiO_2-*ads*) were prepared by the following procedures: 2.0 g of TiO_2 was added to 60 mL aqueous solution of $PdCl_2$ (0.03 mol/L), of which different pH was adjusted by 2 M HCl aqueous solution. The suspension was then vigorously stirred for 2 h at room temperature. After the adsorption, the powdery solid was separated by filtration and washed for several times with a large amount of water until no Cl^- could be detected in the filtrate by $AgNO_3$ aqueous solution, followed by drying at 120 °C overnight and calcination in air at 500 °C for 3 h. The resulting light yellow solid powder was cooled to room temperature and stored in a vacuum desiccator. For comparison, the 0.26 wt% Pd/TiO_2 catalyst was prepared by a conventional wet impregnation method (Pd/TiO_2-*imp*). TiO_2 was added into a $PdCl_2$ aqueous solution without pH adjustment and the mixture was evaporated to dryness at 60 °C. The resultant powdery solid was further dried at 120 °C and finally calcined in air at 500 °C for 3 h. The resulting solid powder was cooled to room temperature and stored in a vacuum desiccator.

2.3. Characterization

Inductively coupled plasma (ICP) analyses of the content of Pd in each solid catalyst sample and the filtrate after the reaction were performed on an Ultima 2 analyzer (Jobin Yvon). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max RA diffractometer with Cu Kα radiation at 40 kV and 40 mA with a scan speed of $2^\circ\,min^{-1}$ and a range of 2θ from 10° to 80°. The morphology, structure and EDX spectra of catalyst were analyzed on a JEOL 2010 transmission electron microscope (TEM) with energy dispersive X-ray (EDX) spectrometer. The sample for TEM analysis was prepared by placing a drop of the suspension in ethanol onto a continuous carbon-coated copper TEM grid and dried at room temperature under atmospheric pressure. For the sample, more than 100 particles from different parts of the grid were used to determine the particle size distribution. X-ray photoelectron spectroscopy (XPS) measurements were analyzed on coated alumina with a physical Electronics PHI-Quantum 2000 Scanning ESCA Microprobe using Al Kα radiation (1846.6 eV) as X-ray source to investigate the oxidation state of Pd before and after reaction. Diffuse reflectance UV–Vis reflectance spectra of the samples in the wavelength range of 300–800 nm were measured by a Lambda-900 spectrophotometer with an integrating sphere, and $BaSO_4$ was used as a reference sample.



Scheme 1. Heck reaction between bromobenzene and methyl acrylate.

Unless otherwise stated, product yields from the Heck reaction were determined by column chromatography. GC analysis was measured by a Varian 430 Gas Chromatograph using a 3-m length column packed with DC-200 stationary phase. ^1H and ^{13}C NMR spectra were recorded using a Burker Avance 400 spectrometer using $CDCl_3$ as solvent.

2.4. Catalytic reactions

In a typical reaction, 0.26 wt% Pd/TiO_2-*ads* catalyst (0.10 g, 0.5 mol% Pd relative to bromobenzene), bromobenzene (0.5 mmol), methyl acrylate (0.6 mmol), and KOAc (0.6 mmol) were added to a pressure tube, followed by addition of DMA 2 mL under nitrogen atmosphere. The tube was sealed and the mixture was allowed to stir in a preheated oil bath at 140 °C for 24 h. After the reaction was completed, the solid catalyst was separated by centrifuge, washed with water to remove base and salt and finally with acetone to remove adsorbed organic substrate, followed by drying at 120 °C and activated at 250 °C under vacuum (2 Torr) for 2 h prior to being reused. The filtrate was diluted by water followed by extraction with ethyl acetate (3× 10 mL). The combined organic phase was washed with water (2× 10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed and the resultant residue was purified by column chromatography (SiO_2, ethyl acetate/hexane gradient). The product was dried under vacuum, weighted and characterized by ^1H and ^{13}C NMR spectroscopy. To study heterogeneity of the Heck reaction, a hot filtration test was also adopted. After 5 h of reaction time the 0.26 wt% Pd/TiO_2-*ads* solid catalyst was filtered by hot filtration under nitrogen atmosphere and the hot filtrate was further reacted with fresh KOAc (0.6 mmol) at 140 °C for additional 10 h. After the reaction, the samples of the reaction mixture were analyzed by GC and ICP.

3. Results and discussion

3.1. Heck reaction catalyzed by catalysts with different palladium content

Initially, Heck reaction of bromobenzene and methyl acrylate was chosen as a model reaction (Scheme 1) with 0.53 wt% Pd/TiO_2-*ads* catalyst that was prepared when the pH value of aqueous solution of $PdCl_2$ was 2. Bases, solvents, and loadings of the catalyst were screened to optimize reaction conditions (Table 1). The effect of bases in the reaction was observed. Alkali carbonates gave low or moderate yields (entries 1–3) and K_3PO_4 gave a lower yield (entry 4). When organic base Et_3N was used, the moderate product yield (39%) was obtained (entry 7). Gratifyingly, the use of KOAc dramatically improved the yield (79%) (entry 6). DMA was found to be more effective than other solvents such as DMF, DMSO and NMP (entry 6 and entries 11–13). Reducing the amount of the catalyst loading from 0.5 mol% to 0.25 mol% or 0.1 mol% led to decrease in yields (entries 8 and 9). The oxidative conditions seriously inhibited the desired reaction, as indicated by the reaction performed under air or oxygen atmosphere (entries 14 and 15). In addition, the time dependence of the yield under the optimized condition is shown in Fig. 1. It is clear that the reaction of bromobenzene