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Preparation and application of SBA-15-supported palladium catalyst for Heck reaction in supercritical carbon dioxide

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Abstract

A new method for the preparation of SBA-15-supported palladium catalyst for Heck reaction in supercritical carbon dioxide was presented. The newly formed SBA-15-supported palladium catalyst (Ph-SBA-15-PPh₃-Pd) exhibited high catalytic activity for the Heck reaction of 4-nitrobromobenzene with methyl acrylate. The catalyst can be reused several times without a loss of activity. \bigcirc 2011 Xiu Juan Feng. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: SBA-15-supported palladium catalyst; Heck reaction; Supercritical carbon dioxide

The Heck reaction is a powerful method for the construction of new carbon–carbon bonds in the synthesis of fine chemicals, agrochemicals, and active pharmaceutical intermediates as well as functional materials [1]. And the Heck reaction is normally catalyzed by palladium complexes in organic solvents under homogeneous conditions. Homogeneous systems are known to often suffer from some drawbacks: it is difficult to separate the coupling product from the catalyst and organic solvent, the expensive palladium catalyst cannot be recycled, and the organic solvent can cause potential environmental contamination when it is volatilized. Therefore, it is desirable to develop an efficient, recyclable catalytic system that uses a green solvent.

Recently, great progress has been achieved with the use of heterogeneous palladium catalysts for Heck reactions using supercritical carbon dioxide (scCO₂). These include silica-supported Pd nanoparticles [2], polyureaencapsulated Pd [3], and polymer-supported Pd [4]. However, heterogeneous palladium catalysts act as reservoirs for highly active soluble forms of Pd in many cases, which may lead to the leaching of active catalyst species [5].

In this paper, we report our preliminary results on the preparation and application of a SBA-15-supported palladium catalyst for Heck reaction in scCO₂ for the first time (Scheme 1). The mesoporous materials, Ph-SBA-15 and Ph-SBA-15-PPh₃, as well as the desired catalyst, Ph-SBA-15-PPh₃-Pd, were synthesized. This newly formed SBA-15-supported palladium catalyst (Ph-SBA-15-PPh₃-Pd) is expected to act as a nanoreactor, in which catalysis can occur. Even if the palladium species breaks off from one phosphine ligand, it may attach to another phosphine ligand inside the SBA-15.

1. Experimental

Mesoporous material Ph-SBA-15-PPh₃ was synthesized according to the modified method (Scheme 1) [6,7]. A mixture of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, 4.0 g), diluted HCl solution (6 wt%, 120 g), and deionized water (30 mL)

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Scheme 1. Schematic illustration for the preparation of SBA-supported palladium catalyst.

was stirred at room temperature untill the Pluronic P123 template was dissolved completely. After the temperature of the resulting solution was enhanced to 40 °C, 8.4 g of Si(OEt)₄ was added dropwise to the solution. After stirring for 24 h, the resultant suspension was transferred into an autoclave. The autoclave was placed under static conditions at 100 °C for 24 h. After the temperature was reduced to room temperature, the precipitated solid was isolated by filtration, successively washed with deionized water (100 mL) and ethanol (25 mL), and dried at 80 °C under vacuum for 5 h. The solid (2.0 g) obtained was treated with (MeO)₃SiPh (2.0 mL) in toluene (50 mL) in the presence of pyridine (2.0 mL) at 115 °C for 2 h. After the mixture was cooled to room temperature, white precipitates were isolated by filtration. Then, it was successively washed with ethanol, ethyl ether, and acetone, and dried at 80 °C under vacuum for 5 h. The Pluronic P123 template was removed by an extraction with scCO₂ to obtain Ph-SBA-15 (1.6 g). The mesoporous materials Ph-SBA-15 (1.5 g) such obtained was treated with ligand (MeO)₃SiCH₂CH₂CH₂SCH₂ C₆H₄PPh₂ (1.5 g) in toluene (80 mL) in the presence of pyridine (1.5 mL) at reflux under N₂ atmosphere for 24 h. The mixture was slowly cooled to room temperature, and then the precipitated white solid was isolated by a filtration, washed with methanol, ethyl ether, acetone, and hexane successively, and dried at 80 °C under vacuum for 5 h. The mesoporous materials Ph-SBA-15-PPh₃ was eventually obtained as white powders (1.4 g).

Mesoporous materials Ph-SBA-15-PPh₃ (1.0 g) was treated with a solution of $Pd_2(dba)_3$ (0.1 g) in CH_2Cl_2 (50 mL) at room temperature under N₂ atmosphere for 24 h. Such palladium species were tethered within the cavity of the mesoporous materials Ph-SBA-15-PPh₃ *via* ligand-exchange reaction. The content of Pd in the mesoporous materials was determined by inductively coupled plasma (ICP) analysis to be 1.04 wt% after the resultant khaki solid was filtrated and washed with CH_2Cl_2 (10 mL × 2) as well as dried at 80 °C under vacuum for 2 h.

The supported palladium catalyst Ph-SBA-15-PPh₃-Pd (153.6 mg, 3 mol% Pd), 4-nitrobromobenzene (101.0 mg, 0.5 mmol), methyl acrylate (172.2 mg, 2.0 mmol), and (*n*-Bu)₄NOAc (180.9 mg, 0.6 mmol) were placed in a 25 mL stainless steel pressure vessel with a magnetic stir bar under nitrogen atmosphere. The vessel was purged with carbon dioxide three times, and then 13 g of carbon dioxide was filled into this vessel. It was then heated to 120 °C for 24 h. The pressure increased to 23 MPa at this temperature. The vessel was allowed to cool to room temperature and was then vented into ethyl acetate (30 mL). The crude product was purified by flash chromatography using silica gel column to give the desired product (101.5 mg, 98%). (E)-Methyl 3-(4-nitrophenyl) acrylate: ¹H NMR (400 MHz, CDC1₃/DMSO-*d*₆): δ 8.25 (d, 2H, *J* = 8.8 Hz), 7.72 (d, 1H, *J* = 16.0 Hz), 6.67 (d, 2H, *J* = 8.8 Hz), 6.56 (d, 1H, *J* = 16.0 Hz), 3.84 (s, 3H). The catalyst was collected, washed with water, ethanol, and dichloromethane, then dried in a vacuum and reused.

2. Results and discussion

Fig. 1 shows the UV–vis spectra of the SBA-15 and Ph-SBA-15. Compared with SBA-15, Ph-SBA-15 has an obvious absorption peak attributed to the benzene ring at 263 nm. This reveals that the external surface of SBA-15 has been successfully modified with (MeO)₃SiPh.

The N₂ sorption isotherms of Ph-SBA-15 and Ph-SBA-15-PPh₃-Pd are displayed in Fig. 2. Both materials exhibit a type-IV isotherm pattern with an H2 hysteresis loop, which is characteristic of the mesoporous structure. The ordered mesoporous structure of Ph-SBA-15, Ph-SBA-15-PPh₃, and Ph-SBA-15-PPh₃-Pd were further confirmed by X-ray diffraction (XRD, Fig. 3). All three curves obtained display an intense peak and two weak peaks, which match well with the pattern of SBA-15 silica reported in literature [8].



Fig. 1. UV-vis spectra of SBA-15 and Ph-SBA-15.



Fig. 2. N2 adsorption-desorption isotherms for Ph-SBA-15 and Ph-SBA-15-PPh3-Pd.

The transmission electron microscopy (TEM) shows well-ordered hexagonal pore channels in the Ph-SBA-15-PPh₃-Pd catalyst (Fig. 4, left). The TEM image also reveals arrays in the Ph-SBA-15-PPh₃-Pd catalyst when viewed perpendicular to the channel axis (Fig. 4, right). Finally, inductively coupled plasma (ICP) analysis indicates that the ratio of Pd on the Ph-SBA-15-PPh₃-Pd catalyst is 1.04 wt%.



Fig. 3. XRD patterns of Ph-SBA-15, Ph- SBA-15-PPh₃, and Ph-SBA-15-PPh₃-Pd.



Fig. 4. TEM image of Ph-SBA-15-PPh₃-Pd: (left) taken along the parallel channels; (right) vertical to the parallel channels.



Scheme 2. Heck reaction of 4-nitrobromobenzene with methyl acrylate.

The SBA-15-supported palladium catalyst was then employed in a Heck reaction involving 4-nitrobromobenzene and methyl acrylate to evaluate its catalytic activity and stability. The results are shown in Scheme 2 [9]. The reaction of 4-nitrobromobenzene with methyl acrylate proceeded smoothly under optimized conditions (3.0 mol% Pd, 0.5 mmol of 4-nitrobromobenzene, 2.0 mmol of methyl acrylate, 0.6 mmol of $^{n}Bu_4NOAc$, scCO₂, 120 °C, 24 h) to give the desired product in 98% yield (run 1). The SBA-15-supported palladium catalyst was also repeatedly used in the reaction of 4-nitrobromobenzene with methyl acrylate. The same 96% yield of product was obtained in runs 2 and 3.

In conclusion, we have presented a new method for preparing SBA-15-supported palladium catalyst for Heck reaction in $scCO_2$. Our study on the catalyst reuse suggests that the Ph-SBA-15-PPh₃-Pd catalyst is very stable and can be reused several times without a loss of catalytic activity. It was considered that this newly formed catalyst acts as expected as a nanoreactor, in which catalysis occurred, and even if the palladium species breaks off from one phosphine ligand, it may attach to another phosphine ligand inside the SBA-15. Therefore, our catalyst is very stable and reusable in comparison with previously reported heterogeneous palladium catalyst.

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