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The effect of framework functionality on the catalytic activation of supported Pd nanoparticles in the Mizoroki–Heck coupling reaction

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ABSTRACT

Palladium nanoparticles (Pd-NPs) were supported on functional and nonfunctional Co-coordination polymers ($Pd/CoBDCNH_2$ and Pd/CoBDC). Advanced analytical techniques revealed that Pd-NPs are supported on the external surface of the polymer framework and the functionalized framework possesses effective influence to prevent Pd-NP aggregation. Supported Pd-NPs were effectively applied as heterogeneous recyclable catalysts in the Mizoroki–Heck C–C cross coupling reactions of iodobenzene and either aromatic or aliphatic terminal alkenes. Catalytic results exhibited that highly dispersed Pd-NPs with low loading (1%) on the functional polymer ($Pd/CoBDCNH_2$) are more effective than aggregated Pd-NPs with high loading (9%) on the nonfunctional polymer (Pd/CoBDC). Both catalysts can simultaneously provide high activity and selectivity to E-coupled products, high efficiency in low amounts, easy separation of heterogeneous catalyst and appropriate performance in the recycling reaction without addition of a reducing agent.

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1. Introduction

There has recently been considerable interest in research on the fabrication of metal nanoparticles with high stability and controllable size distribution. This is largely due to their potential application in many fields, especially in catalysis [1–3]. Among catalytically active nanoparticles, palladium nanoparticles (Pd-NPs) have extensively been utilized for the formation of C–C bonds [4–6] that play significant roles in modern synthetic chemistry. The Pd-NPs exhibit suitable catalytic activity. Moreover, heterogeneous metal nanocatalysts provide considerable advantages such as easy isolation of products, efficient recovery and recyclability of catalysts, good thermal and chemical stabilities, and good dispersion of the active catalytic site [7–9].

A number of solid materials as supports have broadly been investigated for the immobilization of palladium such as clay [10], carbon nanofibers [11], carbon nanotubes [12], graphene [13], ionic liquids [14,15], mesoporous silica [16], zeolites [17], SBA-15 [18], metal oxides [19,20] and polymers [21]. Among these solid supports, metal–organic frameworks (MOFs) or porous coordination polymers can be considered as a suitable solid material for the stabilization of ligand-free metal nanoparticles [22,23]. On the other hand, finding a suitable support to immobilize Pd-NPs without agglomeration is still a tempting challenge in the field of heterogeneous catalysis.

Here, we report the comparative study on the functional effect of polymers on the dispersion and catalytic activity of supported Pd-NPs. We used functional and nonfunctional

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Co-coordination polymers, Pd/CoBDCNH$_2$ and Pd/CoBDC, respectively, as a support for Pd-NPs where CoBDCNH$_2$ = [Co$_3$(BDCNH$_2$)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$, CoBDC = [Co$_3$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$, H$_2$BDCNH$_2$ = 2-amino-1,4-benzenedicarboxylic acid and H$_2$BDC = 1,4-benzendicarboxylic acid. Catalytic activity of these supported Pd-NPs was examined in the Mizoroki–Heck coupling reactions of iodobenzene with terminal alkenes.

2. Experimental

2.1. Materials and instruments

All reagents for synthesis and analysis were obtained commercially and of analytical grade and used without further purification. The elemental analysis (CHN) of compound was performed using a Carlo ERBA Model EA 1108 analyzer. Fourier transform infrared (FT-IR) spectroscopy was carried out by utilizing a Unicam Matson 1000 FT-IR spectrophotometer using KBr disks at room temperature. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 analyzer in a N_2 atmosphere with a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku D-max C III and X-ray diffractometer using Ni-filtered Cu Kα radiation. Inductively coupled plasma–mass spectroscopy (ICP-MS) was performed by using an ICP-MS HP 4500. The morphology and size of palladium nanoparticles in Pd/MnBDC were investigated by incorporating scanning electron microscopy (SEM, S-4160, Hitachi) and high-resolution transmission electron microscopy (HR-TEM, Philips CM30) at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PerkinElmer PHI 5000CESCA system with a base pressure of 10^{-9} Torr. The products of the coupling reaction were determined and analyzed by using an HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenylmethylsiloxane 30 m × 320 μm × 0.25 μm) and a flame-ionization detector.

2.2. Synthesis of the [Co$_3$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$ framework

The [Co$_3$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$ coordination polymer (CoBDC) was synthesized based on our previous study [24] by adding a solution of 1,4-benzenedicarboxylic acid (H$_2$BDC) (166 mg, 1 mmol) in 5 mL of DMF to CoCl$_2$·6H$_2$O (291 mg, 1 mmol) solution (DMF, 5 mL). The solution was heated for 48 h at 80 °C. After 2 days, purple crystals of [Co$_3$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$ (85% yield based on H$_2$BDC) were collected. Anal. Calcd: for Co$_3$C$_{30}$H$_{24}$N$_2$O$_{16}$: C, 42.42; H, 3.32; N, 3.30. Found: C, 42.63; H, 2.86; N, 3.28. FT-IR (KBr 4000–400 cm^{-1}): 3491 (br), 2931 (w), 1663 (s), 1619 (s), 1559 (s), 1418 (s), 1254 (w), 1115 (m), 855 (m), 813 (m), 760 (s), 693 (s), 655 (m), 468 (m).

2.3. Synthesis of the [Co$_3$(BDCNH$_2$)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$ framework

A DMF solution (5 mL) of CoCl$_2$·6H$_2$O (291 mg, 1 mmol) was added to a solution of 2-amino-1,4-benzene dicarboxylic acid (H$_2$BDCNH$_2$) (182 mg, 1 mmol) in 5 mL of DMF in a small sample vessel. The solution was heated for 24 h at 90 °C. A light cream powder of [Co$_3$(BDCNH$_2$)$_3$(DMF)$_2$(H$_2$O)$_2$]$_n$ (named CoBDCNH$_2$, 85% yield based on H$_2$BDCNH$_2$) was obtained as an amino-functionalized polymer. The crystals were washed with DMF (3 mL, 2 times) and dried at 80 °C. Anal. Calcd: for Co$_3$C$_{30}$H$_{33}$N$_5$O$_{16}$: C, 40.19; H, 3.71; N, 7.81. Found: C, 40.72; H, 3.70; N, 7.75. FT-IR (KBr 4000–400 cm^{-1}): 3491 (br), 2931 (w), 1663 (s), 1619 (s), 1559 (s), 1418 (s), 1254 (w), 1115 (m), 855 (m), 813 (m), 760 (s), 693 (s), 655 (m), 468 (m).

2.4. Synthesis of supported palladium nanoparticles on the CoBDC polymer framework

The prepared CoBDC polymer (0.15 g) was added to an orange solution of PdCl$_2$ (0.04 g, 0.2 mmol) and NaCl (0.58 g, 1.0 mmol) in DMF (10 mL) under vigorous stirring. Upon adding hydrazine hydrate (4 mL, excess), the mixture immediately turned gray. After stirring for 15 min, the solid was isolated by centrifugation, washed with DMF and dried in an oven at 90 °C. Supported Pd nanoparticles on the Co-coordination polymer (Pd/CoBDC) was obtained as a gray powder. The Pd contents (9 wt %) in the samples were determined by ICP-MS. FT-IR (KBr 4000–400 cm^{-1}): 3475 (br), 3332 (br), 2935 (w), 1659 (w), 1560 (s), 1555 (m), 1419 (s), 1358 (m), 1142 (m), 855(m), 828 (w), 807 (w), 732 (s), 695 (s), 529 (w), 480 (w).

2.5. Synthesis of supported palladium nanoparticles on the CoBDCNH$_2$ polymer framework

The supported Pd-NPs on the amino-functionalized Co-coordination polymer (Pd/CoBDCNH$_2$) was obtained as a gray powder by the addition of an orange solution of PdCl$_2$ (0.04 g, 0.2 mmol) and NaCl (0.58 g, 1.0 mmol) in DMF (10 mL) to prepare CoBDCNH$_2$ (0.15 g) in the presence of hydrazine hydrate (4 mL, excess). After stirring for 15 min, the solid was isolated by centrifugation, washed with DMF and dried in an oven at 90 °C. The Pd contents (1 wt %) in the samples were determined by ICP-MS. FT-IR (KBr 4000–400 cm^{-1}): 3485 (br), 2930 (w), 1659 (s), 1620 (s), 1550 (m), 1420(s), 1250 (w), 1102 (m), 850 (m), 810 (m), 765 (s), 690 (s), 650 (m), 460 (m).

2.6. General procedure for Heck coupling reactions catalyzed by Pd/CoBDC and Pd/CoBDCNH$_2$ catalysts

The heterogeneous C–C coupling reaction was conducted in a two-necked round-bottom flask fitted to a condenser and magnetic stirrer and placed in a temperature-controlled oil bath. Typically, 1.1 mmol of the substrate was taken in 2 mL of solvent, followed by the addition of 13 mg Pd/CoBDC (0.11 mol % Pd) or 5 mg Pd/CoBDCNH$_2$ (0.05 mol % Pd) catalyst, 1 mmol iodobenzene and 1.5 mmol base. The flask was kept at 90 °C and stirred at appropriate times. The products from the reaction mixture were analyzed by gas chromatography and were identified by comparison to known standards.

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