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Article

Immobilized Pd nanoparticles on Tris-modified SiO₂: Synthesis, characterization, and catalytic activity in Heck cross-coupling reactions

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ABSTRACT

The preparation of supported Pd nanoparticles on Tris (tris(hydroxymethyl)aminomethane)-modified SiO₂ gel and their catalytic application in Heck coupling are investigated. The catalyst was characterized using a combination of X-ray diffraction, transmission electron microscopy, field-emission scanning electron microscopy, and scanning electron microscopy/energy-dispersive X-ray spectroscopy. The supported Pd nanoparticles were found to be a highly active and reusable catalyst for the Heck reaction at a low Pd loading (0.02 mol%) because of stabilization by the Tris moieties. Several reaction parameters, including the type and amount of solvent, base, and temperature, were evaluated. The heterogeneity of the catalytic system was investigated using different approaches, and showed that slight Pd leaching into the reaction solution occurred under the reaction conditions. Despite this metal leaching, the catalyst can be reused seven times without significant loss of its activity.

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1. Introduction

Metal nanoparticles have attracted attention in the field of catalysis because they can catalyze many organic reactions effectively as a result of their high surface area to volume ratio [1]. However, these naked nanoparticles tend to aggregate to form larger metal particles because of the effect of high surface energy, resulting in decreased catalytic activity. A useful way of preventing agglomeration is to immobilize the metal nanoparticles on suitable supports, and many methods have been developed for this purpose [2]. Catalytic C–C cross-coupling reactions are extensively used in both the academic [3] and industrial [4] communities, making Pd the most widely used metal catalyst for the synthesis of a wide variety of organic compounds. One of the most successful methods for C–C bond for-

mation is Heck coupling [5–9], which involves the reaction of an olefin with an aryl halide. Various efficient homogeneous Pd catalyst precursors have been developed for effective coupling of aryl halides with olefins. However, because the reactions are typically catalyzed by homogeneous Pd complexes or colloidal Pd, the possibility of reuse in successive reactions is limited. Much effort has therefore been made to immobilize Pd complexes [10–17] or Pd nanoparticles [18–29] on various supports. SiO₂ gel has emerged as a robust, readily available, and high surface area heterogeneous catalyst support. In particular, much attention has been focused on ligand functionalization, because ligands are well known to stabilize nanoparticles against aggregation without affecting their desirable properties, and are also known to increase the catalytic activity [30]. Several nonporous and porous SiO₂ supports have therefore

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been used for Heck reactions [31].

In this paper, we report the preparation and testing of a semi-heterogeneous metal Pd catalyst stabilized on the surface of Tris (tris(hydroxymethyl)aminomethane)-functionalized SiO₂ particles.

2. Experimental

2.1. General

Palladium chloride (99%) was purchased from Sigma-Aldrich. Tris, NaHCO₃, methyl acrylate (MA), NaI, acetonitrile, toluene, dimethylformamide (DMF), and aryl halides were purchased from Merck. X-ray diffraction (XRD) powder patterns were obtained using an X'PERT MPD, with Cu K α radiation (40 kV, 30 mA). Infrared (IR) spectra were recorded with a Jasco Fourier-transform (FT)-IR spectrometer (400–4000 cm⁻¹, resolution 2 cm⁻¹), using samples diluted with KBr. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance DPXS spectrometer (400 or 300 MHz), in CDCl₃ with tetramethylsilane as the internal standard. Transmission electron microscopy (TEM) images were obtained using a Philips CM10 microscope. The Pd content in the catalyst was measured using atomic absorption spectroscopy (AAS; Perkin-Elmer 2380 spectrophotometer).

2.2. Catalyst preparation

Scheme 1 summarizes the preparative route to the catalyst. First, 3-chloropropyltrimethoxysilane was converted to the more reactive 3-iodopropyltrimethoxysilane. NaI (0.0457 g, 2.5 mmol) was dissolved in acetone (50 mL) in a dry 100-mL round-bottomed flask equipped with a reflux condenser. Chloropropyltrimethoxysilane (0.50 g, 2.5 mmol) was added, and the mixture was refluxed overnight under Ar. After centrifugation to remove NaCl, the acetone was removed by evaporation, and the residue was dissolved in CH₂Cl₂ to precipitate NaI. After centrifugation, the CH₂Cl₂ was removed by evaporation, and replaced with 50 mL of dry toluene for further reaction with SiO₂ gel. Activated SiO₂ was prepared by soaking SiO₂ gel S (150–230 mesh; 5 g) in concentrated HCl overnight to hydrolyze the surface Si–O–Si bonds to Si–OH, and then resuspended in fresh deionized water several times until the pH of the filtrate was higher than 6. The acid-treated SiO₂ was dried at 150 °C overnight and cooled in a desiccator. 3-Iodopropyltrimethoxysilane supported on SiO₂ gel was prepared by sus-

pending activated silica gel (1 g) in the above solution of 3-iodopropyltrimethoxysilane in toluene. The suspension was refluxed for 72 h. After cooling, the particles were collected by filtration, exhaustively washed with CH₂Cl₂, and dried under reduced pressure to give iodopropyl-SiO₂ gel (elemental analysis C 5.9 mmol/g, I 1.7 mmol/g). The iodopropyl-SiO₂ gel was resuspended in 30 mL of acetonitrile, Tris (0.605 g, 5 mmol) was added, and the mixture was refluxed for 12 h. The solids were extracted with ethanol in a Soxhlet apparatus for 5 h and dried under reduced pressure (elemental analysis C 13.5 mmol/g, N 1.5 mmol/g, I trace). Finally, Tris-supported SiO₂ (1 g) and Pd(OAc)₂ (9 mg, 0.04 mmol) were stirred in acetone overnight. After washing with acetone, the resulting light brown solid was stirred in ethanol overnight. The obtained black solid was washed with CH₂Cl₂ and acetone, and dried under vacuum (elemental analysis C 12.8 mmol/g, N 1.3, I trace, Pd 0.035 mmol/g).

Another catalyst with a lower Pd loading was prepared similarly, from Pd(OAc)₂ (0.9 mg, 0.004 mmol) and the Tris-modified support (1 g; elemental analysis C 12.8 mmol/g, N 1.5 mmol/g, I trace, Pd 0.0038 mmol/g). The catalyst is denoted by SiO₂-Tris-PdNPs (Fig. 1).

2.3. Catalytic tests

The samples for the Heck reaction (Scheme 2) were prepared using the following reaction conditions. Iodobenzene (1 mmol), MA (1.2 mmol), NaHCO₃ (2 mmol), benzonitrile (0.1 mmol, internal standard in the optimization and kinetic studies), and the catalyst (50 mg, 0.02 mol%) were stirred in DMF (1.5 mL) at 140 °C. Samples (1 μ L) were withdrawn periodical-

Fig. 1. Schematic diagram of SiO₂-Tris-PdNPs.

Scheme 1. Synthetic route for preparation of SiO₂-Tris-PdNP catalyst.

Scheme 2. Representative Heck coupling reaction.

ly using a high-performance liquid chromatography (HPLC) syringe, and analyzed by GC after dilution with acetone. The isolated products obtained in separate experiments were analyzed using ^1H NMR to confirm the GC analysis (HP5 column, 30 m $\times$ 0.32 mm $\times$ 0.25 μm , flame-ionization detector). The Pd amount that leached into the solution was measured using AAS. After completion of the reactions, the mixture was cooled to room temperature and the product was extracted with hexane (3 $\times$ 10 mL) and dried over CaCl_2 . The extract was filtered and evaporated to dryness to give the products. In the case of reactions with < 95% conversion, the column chromatography (hexane/EtOAc; 80/20) was used for further purification.

2.4. Catalyst reusability

Catalyst recycling was examined for the coupling reaction of iodobenzene with MA under the optimized reaction conditions (1 mmol iodobenzene, 1.2 mmol MA, 2 mmol NaHCO_3 , 50 mg catalyst, 1.5 mL DMF, 140 $^\circ\text{C}$). After the first run, the reaction mixture was allowed to cool to room temperature and the catalyst was separated by centrifugation, washed with H_2O and acetone (three times), and allowed to dry at room temperature for 15 min under vacuum. The recycled catalyst was then used without any regeneration under the same reaction conditions as for the first run.

3. Results and discussion

3.1. Characterization results of Pd catalyst

The FT-IR spectra of the SiO_2 gel before and after modification with Tris are shown in Fig. 2. It can be seen that new absorption peaks at 1590 (N–H bending), 1470 (CH_2 bending), 1400, 1285 (C–N stretching), 1030 (C–O stretching), 890 (N–H out-of-plane bending), and 627 cm^{-1} appeared after treatment of the SiO_2 gel with Tris. The other Tris bands were covered by strong SiO_2 bands.

Figure 3 shows typical TEM and FE-SEM images of SiO_2 -Tris-PdNPs. The TEM image shows particles with diameters in the nanometer range. The size distribution is between 4 and 24 nm, with most being around 11 nm. Unambiguous evidence of Pd nanoparticles on SiO_2 -Tris was provided by FE-SEM/EDX and XRD.

The XRD pattern in Fig. 4(1) shows characteristic peaks of amorphous SiO_2 at $2\theta = 22^\circ$; Figure 4(2) shows the appearance of new peaks at $2\theta = 40.1^\circ$, 46.5° , 68.0° , and 86° , attributed to Pd species. The results indicate that the Pd nanoparticles have been successfully immobilized on SiO_2 particle surfaces. The SEM/EDX analytical results for SiO_2 -Tris-PdNPs are shown in Fig. 5.

Fig. 2. FT-IR spectra of SiO_2 -Tris and SiO_2 .

Fig. 3. TEM (a) and FE-SEM (b) images of SiO_2 -Tris-PdNPs.

3.2. Catalyst testing in Heck reaction

The reactions were performed in the presence of two catalyst samples with different Pd loadings. A comparison of the

Fig. 4. XRD patterns of SiO_2 (1) and Pd/SiO_2 (2).

Fig. 5. SEM (a) and EDX (b) analysis of SiO₂-Tris-PdNP catalyst.

reactions showed that the catalytic performance is strongly affected by the N/Pd ratio. The catalyst with a lower Pd loading (0.0038 mmol/g) and higher N/Pd ratio (421) achieved 98% conversion of iodobenzene at 140 °C in the reaction with MA, whereas the catalyst with a higher Pd loading (0.035 mmol/g) and lower N/Pd ratio (37) led to 67% conversion, at the same conditions. We therefore chose the catalyst with 0.0038 mmol/g of Pd for further studies.

We explored the catalytic properties of SiO₂-Tris-PdNPs by using it in the Heck reaction under various conditions. The initial experiments were carried out with iodobenzene as the substrate. The bases, solvents, and reaction temperatures were varied in the experiments (Fig. 6). The results show that these parameters are critical to the outcome of the reaction. The highest yields were obtained with DMF or NMP and NaHCO₃ at 140 °C.

We chose DMF as the solvent because of its lower boiling point and GC retention time compared with NMP. An excess of MA was used (1.2 equiv.) to suppress double arylation. Neither double arylation nor any other side products such as biphenyl and *cis* isomers were detected by GC analysis of the reaction mixtures. This not only indicated that the Heck coupling proceeded cleanly, but also enabled the amount of reacted olefin to be directly related to the Heck product. The optimized amount of catalyst was 50 mg (0.0002 mmol Pd).

The efficiency of this catalyst was studied in the Heck reactions of various aryl halides and olefins under the optimized reaction conditions. The results are summarized in Table 1. A range of activity was observed, with yields from 48% to 99%,

Fig. 6. Optimization of Heck reaction of iodobenzene and MA under various conditions.

depending on the nature of the aryl bromo/iodo or chloro derivatives and olefins. For both styrene and MA, short reaction time was observed for 4-bromobenzonitrile, 4-bromonitrobenzene, and 4-bromoacetophenone, but longer reaction time was observed for bromobenzene and 4-bromoanisole. When MA was used as the olefin, the reactions proceed faster than with styrene.

Figure 7 shows the kinetic behavior of aryl iodide with different substituents. The results show that an electron-withdrawing –NO₂ substituent enhances coupling product formation, whereas electron-donating –OMe has a negative influ-

Table 1

Heck reactions of olefins with various aryl halides.

$\text{R}^1\text{-C}_6\text{H}_4\text{-X} + \text{R}^2\text{-CH=CH}_2 \xrightarrow[\text{NaHCO}_3, \text{DMF}, 140^\circ\text{C}]{\text{catalyst}} \text{R}^1\text{-C}_6\text{H}_4\text{-CH=CH-R}^2$					
Entry	X	R ¹	Olefin	Time (h)	Isolated yield (%)
1	I	H	MA	2.0	99
2	Br	4-CHO	MA	4.0	92
3	I	4-NO ₂	MA	1.6	97
4	I	4-OMe	MA	6.6	87
5	Br	3-Cl	MA	5.8	92
6	Br	4-Cl	MA	6.6	89
7	Br	H	MA	9.5	93
8	1-Bromonaphthalene		MA	16	85
9	Br	4-CN	MA	1.9	99
10	Br	4-COCH ₃	MA	3.0	96
11	Br	3-COCH ₃	MA	9.0	85
12	Br	4-OMe	MA	4.8	88
13	Br	2-COCH ₃	MA	10	76
14	Br	4-NO ₂	MA	2.2	98
15	9-bromophenanthrene		MA	22	80
17	Br	H	styrene	18	84
18	I	H	styrene	12	94
19	I	4-OMe	styrene	25	76
20	Br	4-CHO	styrene	23	82
21	Br	3-Cl	styrene	9.5	93
22	Br	4-Cl	styrene	9.0	88
23	1-Bromonaphthalene		styrene	24	76
24	Br	4-CN	styrene	8.0	95

(To be continued)

Table 1 (Continued)

Entry	X	R ¹	Olefin	Time (h)	Isolated yield (%)
25	Br	4-COCH ₃	styrene	10	90
26	Br	3-COCH ₃	styrene	21	83
27	Br	2-COCH ₃	styrene	35	62
28	Br	4-NO ₂	styrene	8	90
29	I	H	acrylic acid	3	96
30	I	4-OMe	acrylic acid	4	96
31	Br	4-CHO	acrylic acid	6	92
32	Br	3-Cl	acrylic acid	6	92
33	Br	4-Cl	acrylic acid	6	94
34	1-Bromonaphthalene		acrylic acid	18	71
35	Br	4-CN	acrylic acid	5	90
36	Br	4-COCH ₃	acrylic acid	7	88
37	Br	3-COCH ₃	acrylic acid	12	85
38	Br	2-COCH ₃	acrylic acid	36	82
39	Cl*	H	MA	72	49
40	Cl	NO ₂	MA	72	66
41	Cl	4-COCH ₃	MA	72	57
42	Cl	H	acrylic acid	72	48
43	Cl	NO ₂	acrylic acid	72	60
44	Cl	4-COCH ₃	acrylic acid	72	60

Reaction conditions: aryl halide 1 mmol, styrene 1 mmol, MA 1.2 mmol, acrylic acid 1.2 mmol, Pd catalyst 50 mg (0.0002 mmol Pd), NaHCO₃ 2 mmol, DMF 1.5 mL.

*The reaction performed at 160 °C and 2 equiv. of Cs₂CO₃ as base.

ence on the reaction process, compared with iodobenzene. This figure also shows the kinetics for 4-bromobenzonitrile, which is more reactive than iodobenzene and 4-bromoanisole.

This catalytic system yielded better results at higher temperatures. The increasing activity with increasing temperature could be attributed to standard Arrhenius behavior of the rate-determining reaction step [12]. According to Richardson et al. [32], the increase in activity with increasing temperature can be attributed to increased leaching of immobilized Pd. Figure 8 shows the effect of different temperatures in the Heck reaction of iodobenzene and MA. The results show that a higher temperature gives a higher product yield. We also measured the

Fig. 7. Effects of substituents on kinetics of Heck reaction of MA and aryl halides.

Fig. 8. Effect of reaction temperature on conversion and Pd leaching in reaction of MA and iodobenzene. The reactions were carried out using the same time (2 h) and solvent volumes (3 mL).

extent of Pd leaching from the catalyst surface into the reaction solution. As the temperature increased, the Pd leaching increased (Fig. 8).

We found that the reaction rate is higher in smaller amounts of solvent. Figure 9 shows time-conversion curves for Heck reactions in different amounts of DMF. As can be observed, the reaction rate is higher in 1 mL of DMF than in 2 and 3 mL of DMF.

This is because in a smaller amount of solvent, the interactions between the substrates and catalyst surface are promoted (if the catalyst is heterogeneous), or the concentration of leached Pd is higher. We therefore chose the minimum volume of solvent for further reactions.

3.3. Catalyst heterogeneity

Leaching of metal ions is a serious problem for supported metal catalysts, and prevents catalyst separation and recycling. Leaching was examined for the coupling reaction of iodobenzene with MA under the optimized reaction conditions (1 mmol iodobenzene, 1.2 mmol MA, 2 mmol NaHCO₃, 50 mg catalyst (0.0002 mmol Pd), 140 °C, and 0.1 mmol benzonitrile (internal

Fig. 9. Time-conversion curves for Heck reactions in different amounts of DMF.

standard))), using the hot-filtration and catalyst-poisoning methods.

3.3.1. Hot-filtration test

A catalytic run was started as for a standard reaction, and after reaction for 95 min, corresponding to 57% conversion, the reaction mixture was filtered through a Whatman paper to afford a clear filtrate. The clear filtrate was then treated as a standard catalytic run and its evolution was followed by GC. The results were compared with that of a standard catalytic run. Figure 10 clearly shows that after removal of the heterogeneous catalyst, slow progression of the reaction was observed (< 20% over 1305 min versus 40% for a standard catalytic run of 210 min), leading after 1305 min to a 76% yield compared with the 57% yield observed immediately after filtration.

These results suggest that slight leaching occurred during the reaction because the yield increased slightly when the solid was removed from the reaction medium. In addition, AAS for Pd determination performed on the clear filtrate indicated that some catalytically active Pd was being released from the surface (about 0.5 ppm). The reaction of the filtrate stopped after 76% conversion, because of a lack of supported Pd reservoirs (supported Pd nanoparticles).

3.3.2. Catalyst poisoning

Another useful method that was used to evaluate the homogeneity/heterogeneity of this catalytic system was a catalyst-poisoning test. By addition of materials that are known to act as poisons, soluble reactive Pd species can be removed from a solution by strong coordination of the poison to the Pd species in solution. Pyridine was used in this case, because this ligand is known to bind strongly to Pd [28]. The results presented in Fig. 11 show that pyridine had a significant effect on the reaction rate compared with the normal reaction. These findings indicate that part of the catalytic activity is derived from leached homogeneous Pd species.

3.3.3. AAS analysis

Potential Pd leaching from the catalyst surface into the reac-

Fig. 10. Hot-filtration test for SiO₂-Tris-PdNP-catalyzed Heck reaction of iodobenzene and MA with NaHCO₃ and 3 mL of DMF at 140 °C.

Fig. 11. Influence of catalyst poison (pyridine) on progress of Heck reactions of iodobenzene and MA with NaHCO₃ and DMF at 140 °C.

tion mixture was also investigated using AAS. For this purpose, 1-mL samples of clear reaction solution were taken, using an HPLC syringe, during the standard heterogeneous Heck reaction (reaction temperature 140 °C) and diluted to 10 mL with distilled water. The organic compounds precipitated immediately after the addition of water. The solids were filtered through a filter paper, and the clear filtrate was analyzed using AAS. Standard solutions were prepared with Pd(OAc)₂ in 1 mL of DMF and diluted to 10 mL with distilled water. The analysis of these samples showed that the Pd concentration in the reaction solution was about 0.5 ppm (0.00075 mg Pd or 3.5% of initial Pd).

According to Arai group [33], oxidized Pd species are more resistant to leaching from supports than reduced ones, and complex formation between the solvent and metal is easier with reduced than with oxidized catalysts. They also suggest that the addition of NMP increases the reaction rate. They assumed that NMP molecules produce a more active complex with Pd. It is assumed from these results that Pd leaching is caused by coordination of DMF with Pd to form Pd complexes that are soluble in the reaction solution. The Pd-DMF complexes that leach into the reaction solution and the supported Pd nanoparticles are the active catalytic species, and the Heck reaction proceeds partly homogeneously in the solution, although the catalyst is originally heterogeneous.

Based on the above results, the mechanism for the Heck reaction of iodobenzene and MA with a supported Pd catalyst in DMF solvent and NaHCO₃ as the base is proposed; it is shown in Scheme 3. In the first step, soluble Pd complexes are formed by coordination with the polar solvent, DMF. The supported Pd nanoparticles and leached Pd are catalytically active species. The cycle then proceeds through the traditional mechanism of the Heck reaction.

3.4. Catalyst recyclability

The recyclability of SiO₂-Tris-PdNPs was further investigated. As shown in Fig. 12, there was a little leaching of Pd from the catalyst and loss of surface Pd as a source of active Pd, but it

Scheme 3. Proposed mechanism for Heck reaction of iodobenzene and MA over SiO₂-supported Pd catalyst in DMF in the presence of NaHCO₃.

Fig. 12. Effect of catalyst recycling on conversion in Heck reactions of iodobenzene and MA with NaHCO₃ and DMF at 140 °C.

is worth noting that the catalyst gave complete conversion of iodobenzene, and over 95% conversion was achieved within 2 h in each cycle, without significant loss of activity.

As can be seen, the SiO₂-Tris-PdNP catalyst gives a good recycling performance in the Heck arylation of MA, and can be reused seven times with no significant loss of activity. Even after recycling nine times, a product yield of 76% was obtained. This slight loss of Pd was the major reason for the decrease in activity. The catalyst was easily separated from the reaction mixture, washed three times with water and acetone, and dried for the next run. These results further confirmed the high recyclability of SiO₂-Tris-PdNPs.

4. Conclusions

In summary, it was demonstrated that Pd nanoparticles can be stably immobilized on the surface of modified-SiO₂ gel, and act as highly active and reusable catalysts for the reactions of aryl halides and olefins. The investigations also show that bromoarenes and iodoarenes can be converted in good to excellent

yields with this catalyst, using extremely low Pd concentrations (0.0002 mmol Pd). The experimental results indicate that supported Pd nanoparticles and Pd complexes leached into the reaction solution act as the catalytically active species.

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Graphical Abstract

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Synthesis, characterization, and catalytic activity in Heck
cross-coupling reactions**

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The preparation of palladium nanoparticles supported on tris(hydroxymethyl)aminomethane-modified silica gel and its catalytic application in Heck coupling are investigated.

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