Palladium nanoparticles supported on a poly(*N*-vinyl-2-pyrrolidone)-modified mesoporous carbon nanocage as a novel heterogeneous catalyst for the Heck reaction in water

Roozbeh Javad Kalbasi [a,*], Neda Mosaddegh [a], Alireza Abbaspourrad [b]

[a] Department of Chemistry, Shahreza Branch, Islamic Azad University, 311-86145 Shahreza, Isfahan, Iran
[b] School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States

ARTICLE INFO

ABSTRACT

Palladium nanoparticles supported on poly(*N*-vinyl-2-pyrrolidone)/CKT-3 (a mesoporous carbon nanocage) were employed effectively as novel heterogeneous catalyst for the Heck coupling reaction. The results showed that aryl halides (–Cl, –Br, –I) underwent coupling with a variety of alkenes at 60 °C in water under aerobic conditions. The very stable nanocomposite catalyst was easily recovered, showed negligible Pd leaching, and retained good activity for at least ten successive runs without any additional activation.

Palladium-catalyzed cross-coupling reactions are a versatile tool for the generation of C–C bonds.[1–5] Among various methods, the coupling of aryl halides with olefinic compounds (Heck reaction) is an excellent procedure for the synthesis of useful organic compounds.[6,7] Many Pd complexes have been used in these reactions,[8–15] and although some have the potential to be recycled,[11,12] most suffer from problems such as deactivation and difficulties in separating them from solution due to the aggregation of Pd nanoparticles formed in situ during the Heck reaction. Thus, it is necessary to develop supported catalysts which can easily be recovered from the reaction system and reused.

Porous materials such as alumina, silica, and zeolites have many advantages as supports due to their high surface areas and easy separation from reaction mixtures. After the successful preparation of mesoporous silica crystals, the synthesis of mesoporous carbon crystals was developed by Ryoo and co-workers using silica mesoporous crystals as a hard template.[16] This new group of materials designated as ordered mesoporous carbons (OMCs) possess several advantages compared to mesoporous silica molecular sieves, for example high thermal stability up to 1600 °C under an N_2 atmosphere, high stability in strong acids and bases, high mechanical stability, electrical conductivity, etc. These interesting properties result from their high surface areas, narrow pore size distributions and regular frameworks.[17] Therefore, mesoporous carbons are of

interest for adsorption, catalysis, catalyst supports, electronic applications, and host-guest chemistry.[18–20] Carbon-based catalysts have several advantages as solid catalysts because of their high surface area and large porosity as well as hydrophobic surface nature. As a result of these advantages, research has increased using carbon-based catalysts.[21–25]

Our present paper reports the synthesis and application of Pd nanoparticles supported on poly(*N*-vinyl-2-pyrrolidone)/mesoporous carbon nanocage (CKT-3) using three dimensional large cage-type face-centered cubic *Fm3m* mesoporous silica materials (KIT-5)[26] as inorganic templates. This novel heterogeneous nanocomposite was used effectively for the Heck reaction in water under aerobic conditions.

Pd-poly(*N*-vinyl-2-pyrrolidone)/CKT-3 (Pd-PVP/CKT-3) nanocomposite was prepared via a procedure similar to that reported in our previous work[27] using $Pd(OAc)_2$ as the palladium source and hydrazine hydrate ($N_2H_4 \cdot H_2O$) as the reducing agent in the presence of PVP/CKT-3 as the stabilizer.

The surface morphologies of the obtained CKT-3 and Pd-PVP/CKT-3 were observed by SEM, as shown in Figure 1. By comparing the SEM images of CKT-3 and Pd-PVP/CKT-3, we can see that there are many agglomerate particles on the outer surface of Pd-PVP/CKT-3 which are related to the Pd nanoparticles distributed on the outer surface of the support.

The TEM micrograph of Pd-PVP/CKT-3 is depicted in Figure 2. The regions with darker contrast are assigned to the presence of Pd particles with different dispersions (5–40 nm). The small dark

* Corresponding author. Tel.: +98 321 3213211; fax: +98 321 3213103.
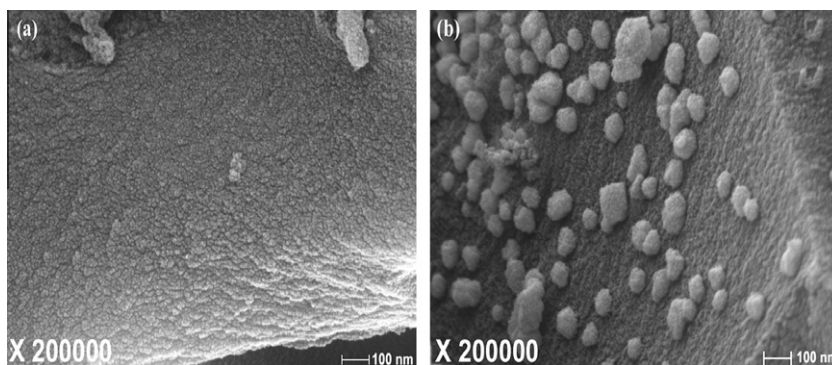*E-mail address:* rkalbasi@iaush.ac.ir (R.J. Kalbasi).

Figure 1. Scanning electron microscopy (SEM) photographs of (a) CKT-3 and (b) Pd-PVP/CKT-3.
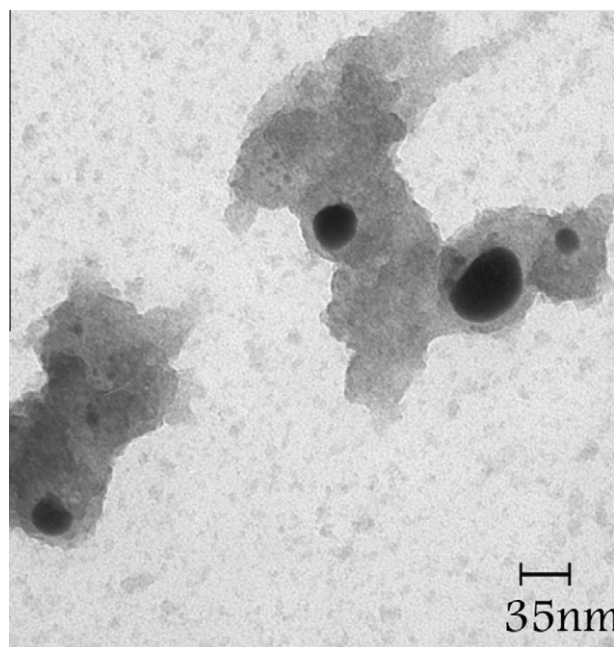

Figure 2. Transmission electron microscopy (TEM) of Pd-PVP/CKT-3 nanocomposite.

spots in the image are ascribed to Pd nanoparticles with average diameters of ~5 nm, probably located in the support channels. The larger dark areas over the channels most likely correspond to Pd nanoparticle agglomerates on the external surface with average diameters of ~12–40 nm (Fig. 2).

The XPS spectrum of the Pd nanoparticles, dispersed on PVP/CKT-3 for the Pd 3d region is presented in Figure 3. The results show that for the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ two peaks are observed at about 334.5 and 339.6 eV, respectively. This indicates that the Pd nanoparticles are stable in the metallic state on PVP/CKT-3 [the XPS spectrum of Pd(II) ions revealed two peaks at about 337 and 342 eV which refer to Pd $3d_{5/2}$ and $3d_{3/2}$].[28,29]

Heck reactions are generally performed at relatively high temperatures, thus we conducted our reactions at 60 °C. In addition, the solvent plays a crucial role in the rate and the product distribution of Heck coupling reactions. Since water is known to increase the activity of the Heck catalyst, two different solvents were used: H_2O and MeOH/H_2O (3:1 v/v). The reaction was catalyzed using 0.12 g of Pd-PVP/CKT-3 (containing about 11.6 wt % palladium) in the presence of 5 equiv of base and with an iodobenzene/styrene ratio of 1–2 (Table 1). The time required for completion of the reaction was shorter when using H_2O as the solvent.

Careful selection of the base in terms of its solubility and basicity in the reaction mixture was crucial. The role of the base in the mechanistic cycle is to re-activate the Pd species in solution, mak-
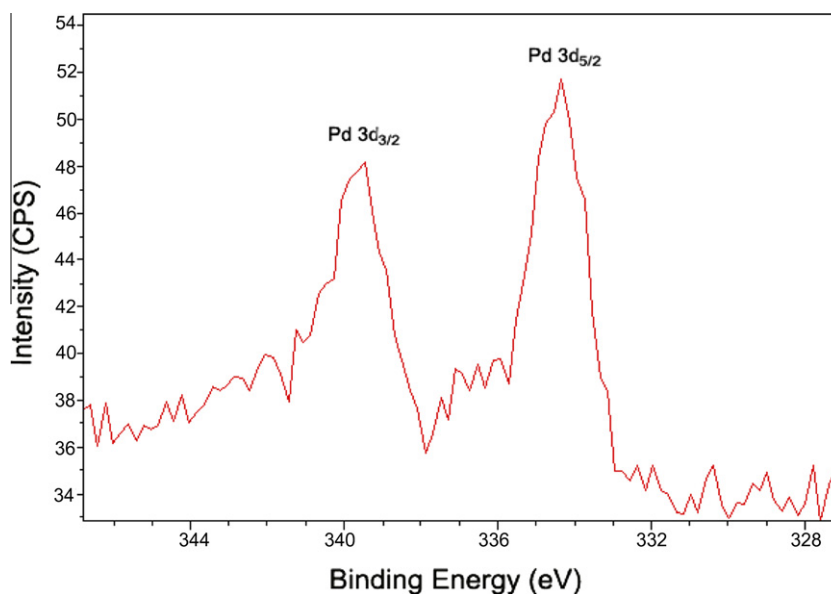

Figure 3. XPS spectrum of Pd 3d region of Pd-PVP/CKT-3.

Table 1
Effect of different bases and solvents on the Heck reaction[a,b]

Base	Time (h)	Yield[c] (%)
K$_2$CO$_3$[d]	1	98
K$_2$CO$_3$[e]	5	84
Na$_3$PO$_4$[d]	1	65
Et$_3$N[d]	1	40

[a] Reaction conditions: Pd-PVP/CKT-3 (0.12 g), iodobenzene (1 mmol), styrene (2 mmol), base (5 mmol), 60 °C.
[b] E/Z stereoselectivity was higher than 99:1 (determined by ^{1}H NMR spectroscopy).
[c] Isolated yield of the E isomer.
[d] Solvent: H$_2$O (5 mL).
[e] Solvent: MeOH/H$_2$O (3:1 v/v) (5 mL).

ing it available to be recycled.[30] The results revealed that the inorganic bases used were more effective than Et$_3$N (Table 1), most probably due to their complete solubility in water. Hence, cheaper K$_2$CO$_3$ was chosen as the base for the coupling reactions. From the data obtained, it can be concluded that the nature of the base played a significant role in the conversion using Pd nanoparticle-PVP/CKT-3 as the catalyst. These observations agree with a previous report in the literature.[31]

In order to study the effect of the support (PVP/CKT-3), the reaction was run over palladium nanoparticles in water as a reference reaction using the same reaction conditions, and no activity was observed. This result showed the important role of the support in this reaction.

Next, the Heck reactions of different aryl halides and styrene over Pd-PVP/CKT-3 as the catalyst were investigated (Table 2). The turnover frequency (TOF) value indicates that Pd-PVP/CKT-3 was a good candidate for this reaction. TOF is defined as the mol product/(mol catalyst/h); and this was calculated from the isolated yield, the amount of palladium used, and the reaction time. The results are shown in Table 2. The Heck reaction of iodobenzene with styrene reached complete conversion within one hour. In addition, bromobenzene (entry 5) and chlorobenzene (entry 7) gave relatively high yields of the desired products, albeit longer reaction times were needed. The more easily accessible and cheaper aryl chlorides have not been employed to any great extent in palladium-catalyzed coupling reactions, primarily because oxidative addition of the C–Cl bond to the Pd(0) species is usually difficult. Few heterogeneous Pd catalysts have been found to convert activated aryl chlorides at high temperature.[32–35]

Aryl iodides with electron-donating substituents (entries 2 and 3) as well as iodobenzene (entry 1) afforded excellent yields of coupled products at 60 °C. The coupling of 4-bromoacetophenone with styrene resulted in a moderate yield (63%) at 60 °C and the yield did not improve at elevated temperature. Thus, the catalyst afforded average to excellent yields of the stilbene products.[36,37]

Another important issue concerning the application of a heterogeneous catalyst is its reusability and stability under the reaction conditions employed. To gain insight into this issue, catalyst recycling experiments were carried out using the Heck reaction of iodobenzene and styrene over Pd-PVP/CKT-3. The results are

Table 2
Heck reaction of aromatic aryl halides and styrene catalyzed by Pd-PVP/CKT-3[a,b]

Entry	Substrate	Product	TOF[c] (h^{-1})	Time (h)	Yield[d] (%)	Mp (°C)	
						Found	Rep. [Ref.]
1			7.66	1	98	122–124	121–123[36]
2			0.63	12	97	136–138	135–137[36]
3			1.48	5	95	117–119	116–118[36]
4			3.75	6	98	38–40	38–39[37]
5			0.94	10	98	122–124	121–123[36]
6			0.41	12	63	142–144	142–145[36]
7			0.62	14	98	122–124	121–123[36]

[a] Reaction conditions: Pd-PVP/CKT-3 (0.12 g), iodobenzene (1 mmol), styrene (2 mmol), K$_2$CO$_3$ (5 mmol), H$_2$O (5 mL), 60 °C.
[b] E/Z stereoselectivity was higher than 99:1 (determined by ^{1}H NMR spectroscopy).
[c] Turn-over frequency.
[d] Isolated yield of the E isomer.

Table 3
Catalyst reusability for the Heck reaction[a,b]

Cycle	Yield[c] (%)	Pd content of catalyst[d] (mmol)
Fresh	98	0.1280
1	98	0.1280
2	98	0.1280
3	98	0.1280
4	98	0.1280
5	97	0.1279
6	97	0.1279
7	96	0.1279
8	96	0.1279
9	96	0.1279
10	95	0.1278

[a] Reaction conditions: Pd-PVP/CKT-3 (0.12 g), iodobenzene (1 mmol), styrene (2 mmol), K_2CO_3 (5 mmol), H_2O (5 mL), 60 °C, 1 h.
[b] E/Z stereoselectivity was higher than 99:1 (determined by ^1H NMR spectroscopy).
[c] Isolated yield of the E isomer.
[d] Measured by ICP-AES.

shown in Table 3. After each cycle the catalyst was filtered, rinsed with water (10 mL), diethyl ether and acetone (3 × 5 mL), and then dried in an oven at 60 °C before reuse in the Heck reaction. The results showed that Pd-PVP/CKT-3 could be reused at least 10 times without any significant loss of activity/selectivity. The catalyst also exhibited high stability over the 10 recycles (Table 3).

The amount of leached Pd in the reaction solution was measured by the ICP-AES technique (Table 3). The Pd content of the catalyst (after 10 cycles) measured by ICP-AES was 1.065 mmol g^{-1}, which was about 1% lower than in the fresh catalyst (Table 3).

In conclusion, we have described the application of a cubic mesoporous carbon as an ideal support for poly(N-vinyl-2-pyrrolidone) and Pd nanoparticles. A novel polymer–organic hybrid material, Pd nanoparticle-PVP/CKT-3, was prepared by a simple method. The catalytic activity of this catalyst proved excellent for the Heck reactions of various aryl halides at 60 °C under aerobic conditions. Additionally, water was employed as an environmentally benign solvent for this reaction. This heterogeneous catalyst can replace a homogeneous catalyst in view of the following advantages: (a) high catalytic activity under mild reaction conditions, and (b) reusability of the catalyst without any significant loss in the yield.

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