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Application of Atomic Absorption for Determination of Metal Nanoparticles in Organic-Inorganic Nanocomposites

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1. Introduction

The Pd-catalyzed Suzuki cross-coupling reaction has been shown as an efficient method for the construction of C-C bonds and plays an important role in pharmaceutical industry and organic synthesis (Makhubela et al., 2010; Venkatesan & Santhanalakshmi, 2010; Zhao et al., 2011). Numerous Pd complexes, such as palladacycles (Mu et al., 2011) and N-heterocyclic carbine (Chanjuan et al., 2008), have been developed for use in these reactions. However, these Pd(0) or Pd(II) complexes cause difficulties in the synthesis and purification of the final product. Another class of catalysts for these reactions, namely heterogeneous catalysts, is easy to prepare and readily separated from the products (Jana et al., 2009; Tamami & Ghasemi, 2010)

In catalytic applications, a uniform dispersion of nanoparticles and an effective control of particle size are usually expected. However, nanoparticles frequently aggregate to yield bulk-like materials, which greatly reduce the catalytic activity and selectivity. Therefore, they must be embedded in a matrix such as polymer or macromolecular organic ligands (Sanchez-Delgado et al., 2007; Luo & Sun, 2007). However, nanoparticle-polymer composites usually suffer from disadvantages such as absence of complete heterogeneity and high temperature annealing, which generally causes thermal degradation of organic polymers. In addition, to avoid the problems associated with metal nanoparticles such as homogeneity, recyclability and the separation of the catalyst from reaction system, some other works have focused on immobilizing metal nanoparticles on suitable support materials such as immobilization in pores of heterogeneous supports (Thomas et al., 2003; Jacquin et al., 2003), like ordered mesoporous silica. Although nanoparticle-mesoporous materials are completely heterogeneous, the hydrophilicity of these catalysts causes a reduction in the activity of such catalysts in organic reactions. Therefore, preparation of organic-inorganic hybrid catalysts with a hydrophobe-hydrophile nature is interesting.

The discovery of M41S-type ordered mesoporous materials opened a new class of periodic porous solids (Huo et al. 1996). Mesoporous silica structures have been regarded as ideal

supports for heterogeneous catalysts due to their high surface area, tunable pore size, and alignment. In particular, the SBA-15 framework synthesized by Zhao et al. (Zhao et al., 1998) has a highly ordered hexagonal mesostructure with parallel channels and adjustable pore size in the range of 2-10 nm (Kalbasi et al, 2010). This size regime is relevant to catalysis, since the catalytically active components are metal particles in the 2-10 nm size range. SBA-15 is well suited as a structure that can contain individual metal particles within its mesopores, and the pores are wide enough to permit facile diffusion of reactants and products.

Hybrid organic–inorganic polymers have received increasing interest from research groups because of their unique properties (Mark, 2006; Zheng et al., 2008; Chung, 2002). Nevertheless, among the different researches on these materials, there are relatively a few reports on the application of organic-inorganic hybrid polymer as a heterogeneous catalyst (Morales et al., 2010; Ma et al., 2010; Alves et al., 2009). Recently, in our previous studies (Kalbasi et al., 2010; Kalbasi et al., 2010; Kalbasi et al., 2011; Kalbasi & Mosaddegh, 2011), Hybrid organic–inorganic polymers were used as catalysts. The hybrid materials could be obtained by combining organic polymers with inorganic materials (Run et al., 2007). These organic–inorganic hybrid materials could be prepared by various methods, depending on what kind of interaction is employed between organic polymers and inorganic elements, or on how organic moieties are introduced to inorganic phases. An in situ polymerization, which is the simultaneous polymerization of organic monomers in the presence of mesoporous materials, is an important method for the preparation of composite materials without chemical interaction.

There are a lot of methods for characterization of these nanoparticles supported on hybrid materials. However, one of the best methods for determination the amounts of the metal nanoparticles is atomic absorption spectrometry (AAS). For many years, atomic absorption spectrometry (AAS), both flame (FAAS) and electrothermal (ETAAS), has been widely used for the determination of metals in various materials (Ghanemi et al., 2011). At present, AAS is the most widely used method for determination of metal as long as the sample can be dissolved in acids. Separation, pre-concentration and dissolution of samples are the vital steps in many procedures, owing to the very low concentration of these metals in many samples and the complexity of the matrix. Among the AAS methods developed, the determinations for Pd and Rh are relatively sensitive (Scaccia & Goszczynska, 2004). Efforts have been made to make methods reliable and practical.

In this study, Pd nanoparticle-poly(N-vinyl-2-pyrrolidone)/SBA-15 (Pd-PVP/SBA-15) nanocomposite was prepared as a highly efficient catalyst by in situ polymerization method. The sample was studied by XRD, FT-IR, UV-Vis, TG, BET, TEM and AAS techniques. The main goal of this catalytic synthesis was to introduce a novel and efficient organic-inorganic composite to expand the use of these types of composites for carbon-carbon coupling reaction. This nanocomposite was tested for catalytic activity for Suzuki-Miyaura cross-coupling reactions between phenylboronic acid and several aryl halides. The reaction was carried out in the presence of water at room temperature. The amount of Pd nanoparticles has critical effect on the catalytic activity of the catalyst. So the effect of metal amounts for the synthesis of Pd-PVP/SBA-15 has been investigated. In addition, the effects of reaction temperature, the amount of catalyst, amount of support and solvent, were investigated as well as recyclability of the heterogeneous composite. The catalyst used for this synthetically

useful transformation showed considerable level of reusability besides very good activity. Reusability of the catalyst is very important. So in this study we introduce a catalyst that can be reused up to 5 times without losing its catalytic efficiency. For determination of the amount of remained Pd after each cycle of the reaction on the catalyst structure, atomic absorption spectroscopy was used.

2. Experimental method

2.1 Catalyst characterization

The samples were analyzed using FT-IR spectroscopy (using a Perkin Elmer 65 in KBr matrix in the range of 4000–400 cm^{-1}). The BET specific surface areas and BJH pore size distribution of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Series BEL SORP 18. The X-ray powder diffraction (XRD) of the catalyst was carried out on a Bruker D8Advance X-ray diffractometer using nickel filtered Cu Kα radiation at 40 kV and 20 mA. Moreover, scanning electron microscope (SEM) studies were performed on Philips, XL30, SE detector. The thermal gravimetric analysis (TGA) data were obtained by a Setaram Labsys TG (STA) in a temperature range of 30–650 ˚C and heating rate of 10 ˚C/min in N_2 atmosphere. Transmission electron microscope (TEM) observations were performed on a JEOL JEM.2011 electron microscope at an accelerating voltage of 200.00Kv using EX24093JGT detector in order to obtain information on the size of Pd nanoparticles. The DRS UV-Vis spectra were recorded with JASCO spectrometer, V-670 from 190 to 2700 nm. Moreover, Pd content of the catalyst was estimated using atomic absorption spectroscopy (AAS) (Perkin-Elmer, AAnalyst 300).

2.2 Catalyst preparation
2.2.1 Preparation of SBA-15

Mesoporous silica SBA-15 was prepared using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) template as a structure directing agent and tetraethylorthosilicate (TEOS) as the silica precursor. In a typical synthesis, Pluronic P123 (2 g) was dissolved at room temperature in H_3PO_4 (4.16 mL, 85%) and deionized water (75.37 mL), then TEOS (4.58 mL) was added to the solution and synthesis was carried out by stirring at 35 ˚C for 24 h in sealed Teflon breakers, and it was subsequently placed at 100 ˚C for 24 h. Then, the solution was filtered, washed with deionized water, and finally dried at 95 ˚C for 12 h in air. Template removal was performed by calcination in air using two successive steps; first heating at 250 ˚C for 3 h and then at 550 ˚C for 4 h.

### 2.2.2 Preparation of poly(N-vinyl-2-pyrrolidone)/SBA-15 (PVP/SBA-15)

N-vinyl-2-pyrrolidone (NVP) (0.5 mL, 4.6 mmol) and SBA-15 (0.5 g) in 7 mL tetrahydrofuran (THF) were placed in a round bottom flask. Benzoyl peroxide (3 % mol, 0.034 g) was added and the mixture was heated to 65-70°C for 5 h while being stirred under N_2 gas. The resulting white fine powder composite (PVP/SBA-15) was collected by filtration, washed several times with THF, and finally dried at 60 ˚C under reduced pressure.

2.2.3 Preparation of Pd nanoparticle-poly(N-vinyl-2-pyrrolidone)/SBA-15 (Pd-PVP/SBA-15)

Pd-PVP/SBA-15 nanocomposite was synthesized as follows (Scheme 1): PVP/SBA-15 (0.1 g) and 10 mL of an aqueous acidic solution (C_{HCl} = 0.09 M) of Pd(OAc)$_2$ (0.025 g, 0.111 mmol)

were placed in a round bottom flask. The mixture was heated to 80 °C for 5 h while being stirred under N_2 gas. Then, 0.6 mL (9.89 mmol) aqueous solution of hydrazine hydrate (80 vol.%) was added to the mixture drop by drop in 15-20 minutes. After that, the solution was stirred at 60 °C for 1 h. Afterwards, the solution was filtered and precipitated, and was washed sequentially with chloroform and methanol to remove excess $N_2H_4.H_2O$ and was dried in room temperature to yield palladium nanoparticle-poly(N-vinyl-2-pyrrolidone)/SBA-15 composite (Pd-PVP/SBA-15).

In order to specify the amount of Pd, the composite should be decomposed by perchloric acid, nitric acid, fluoric acid and hydrochloric acid. For this purpose, Pd-PVP/SBA-15 nanocomposite (0.1 g), perchloric acid (0.5 mL), nitric acid (0.5 mL) and the known amount of water were placed in a round bottom flask. The mixture was heated for 1 h to evaporate the liquids. Then, to the precipitated, hydrofluoric acid (2.5 mL) and hydrochloric acid (2.5 mL) were added and the mixture was heated again for 2 h to evaporate the liquids. In the last step, hydrochloric acid (0.5 mL) and water (5 mL) were added to the precipitated and the mixture was heated for 30-60 minutes. Then, the Pd content of the catalyst was estimated by Atomic Absorption Spectroscopy (AAS). The Pd content of the catalyst estimated by AAS was 0.56 mmol g^{-1}.
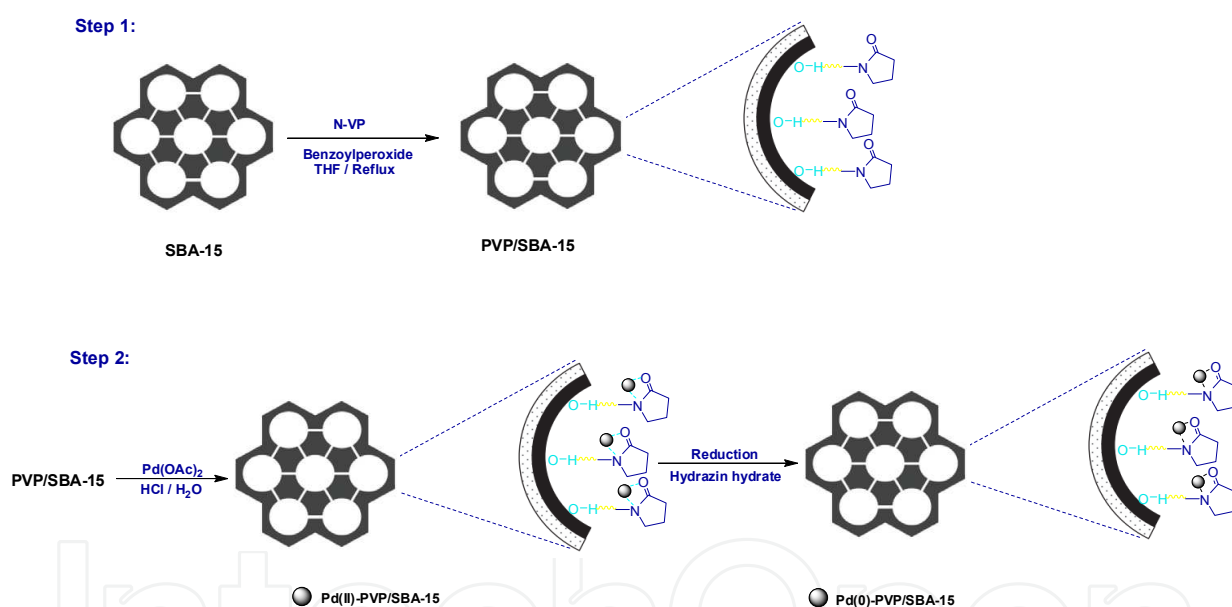
Scheme 1. Preparation of Pd-PVP-SBA-15

2.3 General procedure for Suzuki-Miyaura coupling reaction

The general procedure was as follows (Scheme 2): In the typical procedure for Suzuki-Miyaura coupling reaction, a mixture of iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), and catalyst (0.12 g, Pd-PVP/SBA-15) in H_2O (5 mL) was placed in a round bottom flask. The suspension was stirred at room temperature for 8 h. The progress of reaction was monitored by Thin Layer Chromatography (TLC) using n-hexane as eluent. After completion of the reaction (monitored by TLC), for the reaction work-up, the catalyst was removed from the reaction mixture by filtration, and then the reaction products were extracted with CH_2Cl_2 (3×5 mL). The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the desired coupling product (98% isolated yield).
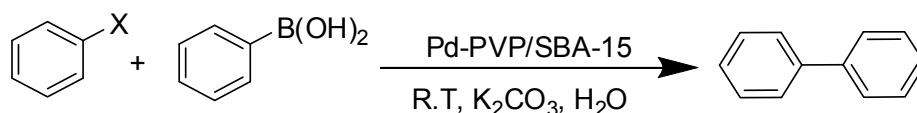
Scheme 2. Suzuki-Miyaura coupling reaction

3. Results and discussion

3.1 Catalyst characterization
3.1.1 XRD

The small angle XRD patterns of the SBA-15, PVP/SBA-15 and Pd-PVP/SBA-15 are shown in the Fig. 1. One intense peak at about 0.9–0.95° and two weak peaks at about 1.5–1.65° and 1.7–1.9° can be indexed as (100), (110), and (200) reflections associated with two-dimensional hexagonal symmetry (*P6mm*) (Kalbasi et al., 2010). The PVP/SBA-15 and Pd-PVP/SBA-15 (2Θ = 0.7-6) samples show the same pattern indicating that the structure of the SBA-15 (100) is retained even after the support of the surface of the SBA-15 with PVP and Pd (Fig. 1). However, the intensity of the characteristic reflection peaks of the PVP/SBA-15 and Pd-PVP/SBA-15 (2Θ = 0.7-6) samples are found to be reduced (Fig. 1). This may be attributed to the symmetry destroyed by the hybridization of SBA-15 which is also found in the ordered mesoporous silica loading with guest matter (Kalbasi et al., 2010). In addition, composites contain much less SBA-15 due to the dilution of the siliceous material by PVP and Pd; therefore, this dilution can also account for a decrease in the peak intensity.
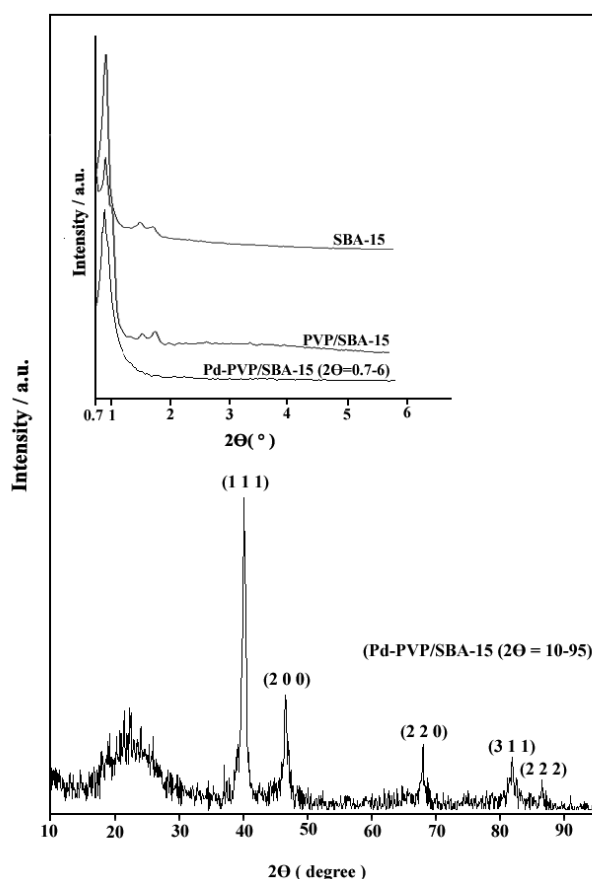

Fig. 1. The powder XRD pattern of (a) mesoporous silica SBA-15, (b) PVP/SBA-15 and (c) Pd-PVP/SBA-15.

The wide angle XRD pattern of the Pd-PVP/SBA-15 nanocomposite is shown in Fig. 1. All diffraction peaks in the XRD pattern are from the *fcc* Pd (Harish et al., 2009). The average grain sizes of the Pd nanoparticles in the nanocomposite were estimated from the full width at half maximum of the diffraction peaks using Scherrer equation. The average grain size of the Pd nanoparticles is about 7 nm for Pd-PVP/SBA-15. The average grain size of the Pd nanoparticles is the same as the average particle size of the Pd nanoparticles determined by the TEM observations, which indicates that the Pd nanoparticles are single crystals.

3.1.2 TEM

The morphologies of SBA-15 (Fig. 2a), Pd-PVP/SBA-15 nanocomposite (Fig. 2b) and the distribution of Pd nanoparticles in the Pd-PVP/SBA-15 (Fig. 2c) were studied by the TEM observations. The typical TEM micrographs (Fig. 2) clearly show that the Pd-PVP/SBA-15 nanocomposite have a hexagonal pore array structure. In the side view micrographs of the nanocomposite (Fig. 2b), the dark spots are the Pd nanoparticles. It can be seen in Fig. 2 that most of the Pd nanoparticles are distributed within the channels of the mesoporous silica. The particle sizes of the Pd nanoparticles in Pd-PVP/SBA-15 are between 3 and 5 nm (Fig. 2c).
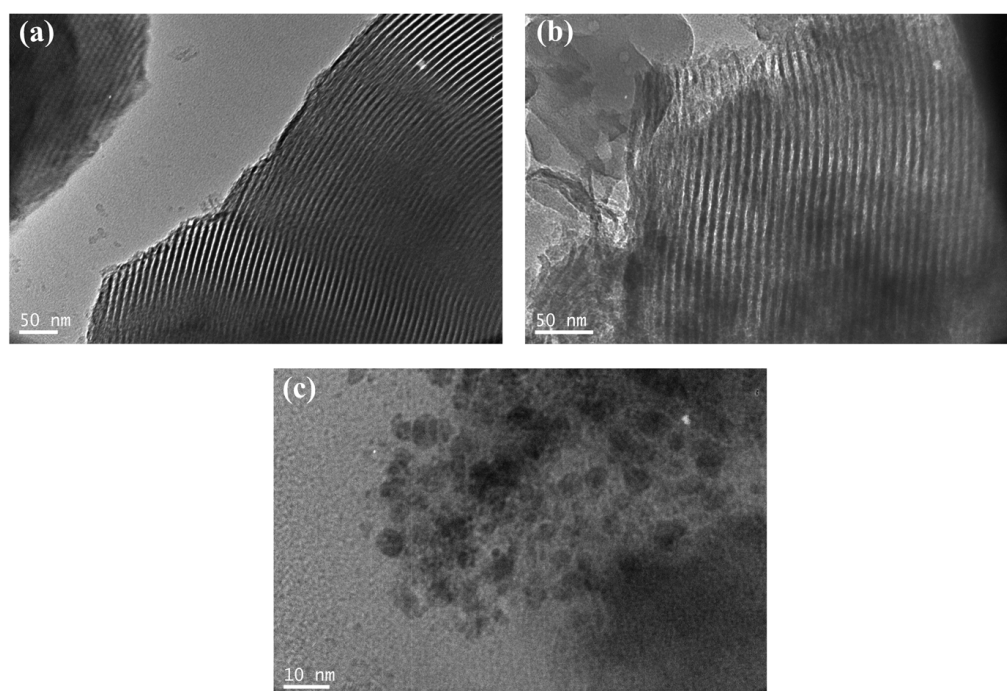

Fig. 2. TEM images for (a) SBA-15 and (b,c) Pd-PVP/SBA-15.

3.1.3 FT-IR

Fig. 3 shows the FT-IR spectra of SBA-15 (a), PVP/SBA-15 (b), and Pd-PVP/SBA-15 (c). The characteristic bands at around 1080, 810 and 480 cm^{-1} may be assigned to Si–O–Si asymmetrical stretching vibration, symmetrical stretching vibration and bending vibration, respectively, which is seen in the Fig 3. a,b,c. In addition, the band at around 950-965 cm^{-1} is related to Si–OH vibrations of the surface silanols (Fig. 3), which is characteristic of mesoporous silica. The existence of PVP in the PVP/SBA-15 composite is evidenced by the appearance of typical PVP vibration on the FT-IR spectrum (Fig. 3b). In the FT-IR spectrum

of PVP/SBA-15 (Fig. 3b), the new band at 1666 cm^{-1} is corresponds to the carbonyl bond of PVP (Iwamoto et al., 2009). Moreover, the presence of peaks at around 2800-3000 cm^{-1} corresponds to the aliphatic C–H stretching in PVP/SBA-15 (Fig. 3b). The appearance of the above bands showed that PVP has been attached to the surface of SBA-15 and the PVP/SBA-15 has been obtained. As shown in Pd-PVP/SBA-15 spectrum (Fig. 3c), the band around 1666 cm^{-1} which corresponds to carbonyl bond of PVP, is shifted to lower wave numbers (1639 cm^{-1}) (red shift). Moreover, the peak intensity of the carbonyl bond in the spectrum of Pd-PVP/SBA-15 is lower than that of PVP/SBA-15. This may be due to the interaction between the Pd nanoparticles and C=O groups. This means that the double bond CO stretches become weak by coordinating to Pd nanoparticles. Thus, it is confirmed that PVP molecules exist on the surface of the Pd nanoparticles, and coordinate to the Pd nanoparticles (Metin et al., 2008; Hirai et al.,1985).
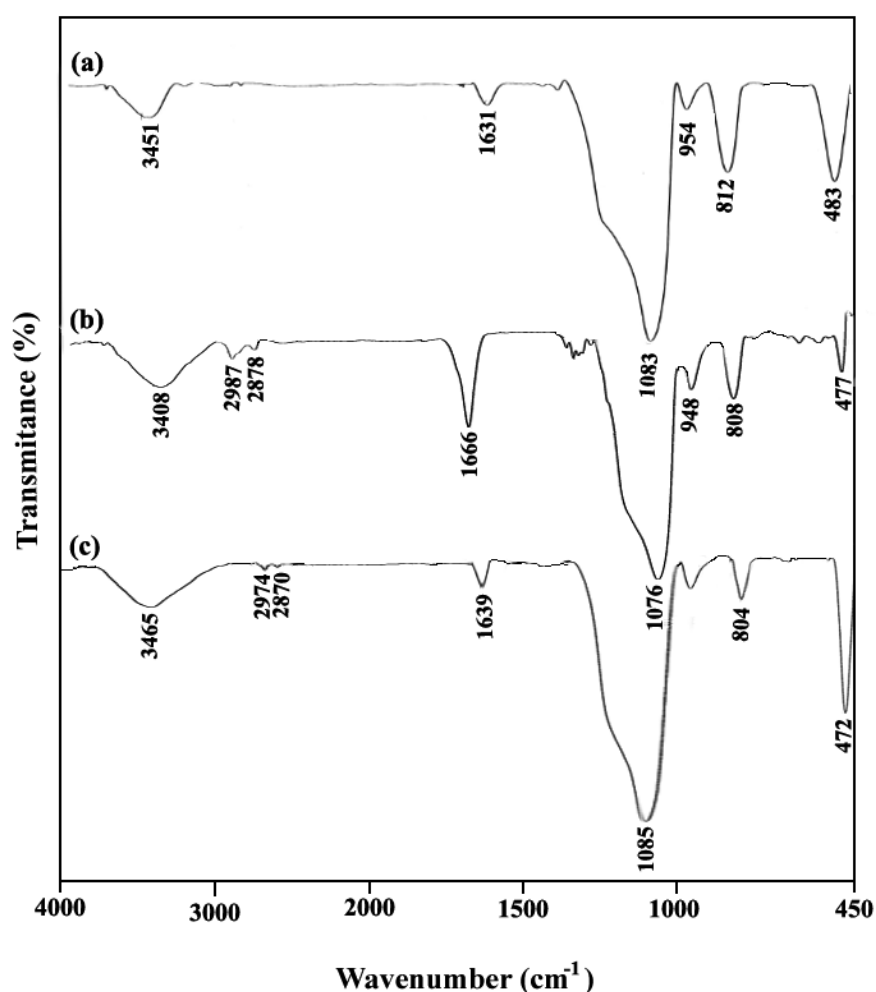

Fig. 3. FT-IR spectra of (a) mesoporous silica SBA-15, (b) PVP/SBA-15 and (c) Pd-PVP/SBA-15

3.1.4 BET
The representative N_2 adsorption–desorption isotherms of the SBA-15 (a), PVP/SBA-15 (b) and Pd-PVP/SBA-15 (c) are shown in Fig. 4. The mesoporous materials all exhibit clear H1-

type hysteresis loops indicative of mesoporous materials with one-dimensional cylindrical channels (Kalbasi et al., 2010) and narrow pore size distributions. The BET surface areas, the BJH pore diameters, and the pore volumes for the SBA-15, PVP-SBA-15 and Pd-PVP/SBA-15 nanocomposite are summarized in Table 1. A specific surface area of 1430 m^2/g, a pore volume of 1.9 cm^3/g, and a pore diameter of 9.9 nm are obtained from the isotherm of SBA-15. After hybridization with PVP through in situ polymerization, PVP/SBA-15 exhibits a smaller specific area, pore size and pore volume in comparison with those of pure SBA-15, which might be due to the presence of polymer on the surface of the SBA-15 (Table 1 and Fig. 4). However, there is a noticeable increase in pore diameter for Pd-PVP/SBA-15, and the pore volume of Pd-PVP/SBA-15 is smaller than that of PVP/SBA-15. It might be due to the incorporation of Pd nanoparticles into the pores of PVP/SBA-15 composite (Chytil et al., 2005).

According to the results, Pd-PVP/SBA-15 still has a mesoporous form with reasonable surface area and it is suitable to act as a catalyst.

Sample	BET surface area ($m^2\ g^{-1}$)	V_P ($cm^3\ g^{-1}$) [a]	BJH pore diameter (nm)
Mesoporous silica SBA-15	1430	1.09	9.90
PVP/SBA-15	465	0.93	4.03
Pd-PVP/SBA-15	102	0.13	4.61

[a] Total pore volume.

Table 1. Surface area analyses of mesoporous silica SBA-15, PVP/SBA-15 and Pd-PVP/SBA-15 samples obtained from N_2 adsorption.
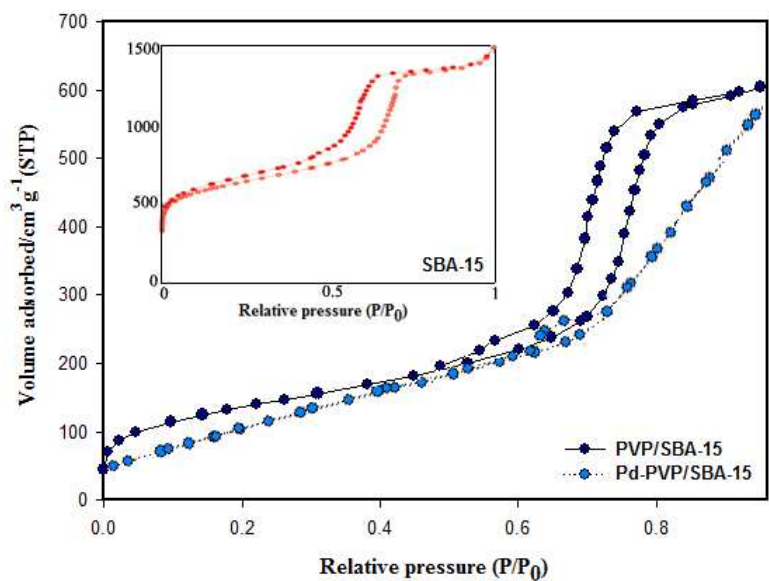

Fig. 4. N_2 adsorption-desorption isotherms of mesoporous silica SBA-15, PVP/SBA-15 and Pd-PVP/SBA-15.

3.1.5 TG-DTA

Fig. 5 presents the TGA curves of SBA-15 (a), PVP (b), PVP/SBA-15 (c) and Pd-PVP/SBA-15 (d) under N_2 atmosphere. The mass loss at temperature <100 °C (around 6%, w/w) is attributed to desorption of water present in the surfaces of the SBA-15 (Fig. 5a). The TGA curves of PVP show a small mass loss (around 7.5%, w/w) in the temperature range 50–150 °C, which is apparently associated with adsorbed water (Fig. 5b). At temperatures above 200 °C, PVP shows one main stage of degradation. The mass loss for PVP in the second step is equal to 80% (w/w) which corresponds to the effective degradation of the polymer (Fig. 5b). Thermo analysis of PVP/SBA-15 shows two steps of mass loss (Fig. 5c). The first step (around 3%, w/w) that occurs at temperature <150 °C is related to desorption of water. The second step (around 9%, w/w) which appeared at 220 °C is attributed to degradation of the polymer, and the degradation ended at 400 °C (Fig. 5c). By comparing the PVP and PVP/SBA-15 curves, one can find that PVP/SBA-15 has higher thermal stability and slower degradation rate than PVP (Fig. 5b,c). Therefore, after hybridization, the thermal stability is enhanced and this is very important for the catalyst application. However, for Pd-PVP/SBA-15 sample, two separate weight loss steps are seen (Fig. 5d). The first step (around 5%, w/w) appearing at temperature <100 °C corresponds to the loss of water. The second weight loss (about 200–500 °C) amounts around 6% (w/w) is related to the degradation of the polymer. Obviously, the hybrid Pd-PVP/SBA-15 shows higher thermal stability than PVP/SBA-15. It may be attributed to the presence of Pd nanoparticles in the composite structure. Therefore, it is very important for the catalyst application that the thermal stability was enhanced greatly after hybridization.
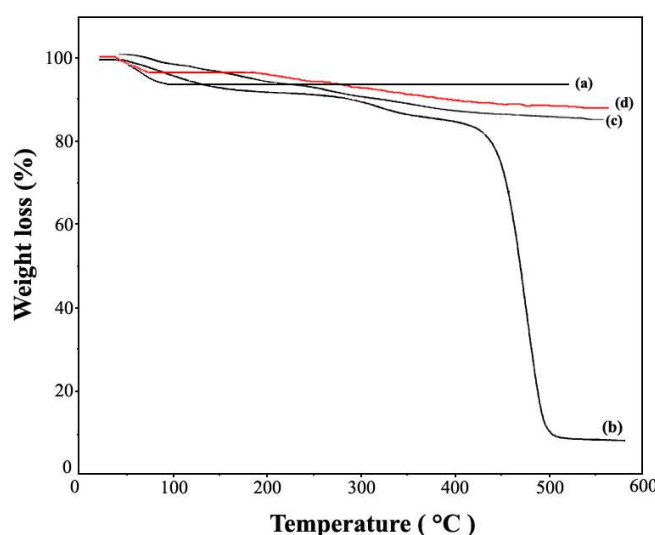

Fig. 5. TGA curves of (a) mesoporous silica SBA-15, (b) PVP, (c) PVP/SBA-15 and (d) Pd-PVP/SBA-15.

3.1.6 Uv-Vis

Fig. 6 displays the result of UV-Vis spectra of Pd-PVP/SBA-15. The UV-Vis spectra of Pd(OAc)$_2$ which reveal a peak at 400 nm refer to the existence of Pd(II) (Ahmadian et al.,2007). As mentioned in the experimental section, and according to scheme 1, Pd nanoparticle-PVP/SBA-15 was prepared by adding hydrazine hydrate to the Pd (II)-PVP/SBA-15. However, as can be seen in Fig. 6, there isn't any peak at 400 nm in the UV-Vis

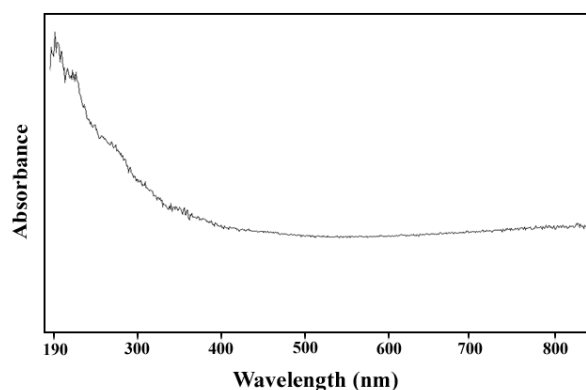spectra of Pd-PVP/SBA-15, which indicates complete reduction of Pd(II) to Pd nanoparticles.

Fig. 6. UV-Vis spectra of Pd-PVP/SBA-15.

3.2 Catalytic activity

In this section, we firstly investigated the corresponding parameters for the Suzuki cross-coupling reaction. It includes different solvents and bases for the room-temperature Suzuki reaction, of iodobenzene, and phenylboronic acid in the presence of 0.12 g (Pd-PVP/SBA-15) catalyst. The molar ratio of iodobenzene to phenylboronic acid was set at 1:1.5 for the Suzuki cross-coupling reaction. Solvent plays a crucial role in the rate and the product distribution of Suzuki-Miyaura coupling reactions. Since water is known to increase the activity of the Suzuki–Miyaura catalyst (Bedford et al., 2003), two kinds of solvents were used: H_2O or $MeOH/H_2O$ (3:1 v/v). In recent years, a large number of studies have been devoted by academic and industrial research groups to the development of environmentally friendly processes. In this context, the use of water as a reaction medium in transition metal-catalyzed processes has merited increasing attention and is currently one of the most important targets of sustainable chemistry (Anastas et al., 2000). Water, an inexpensive, readily available, non-in flammable, non toxic solvent, provides remarkable advantages over common organic solvents both from an economic and an environmental point of view. The experimental results show that the time the reaction is completed is rarely shorter in the case of using $MeOH/H_2O$ (3:1 v/v) as a solvent, but neat H_2O was chosen because of the advantages of using water that were mentioned above.
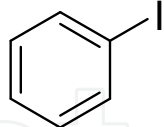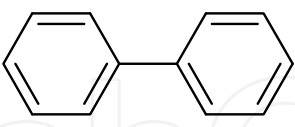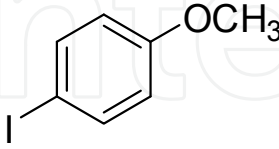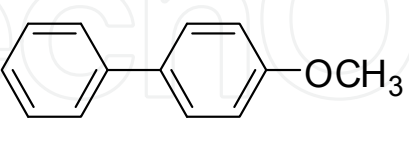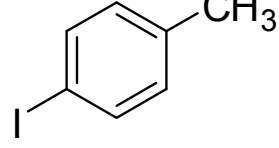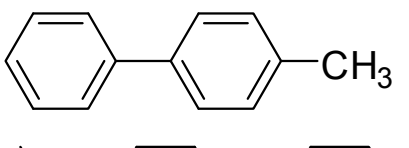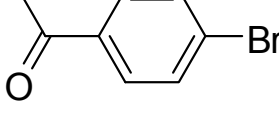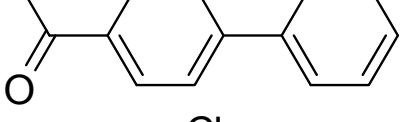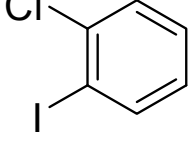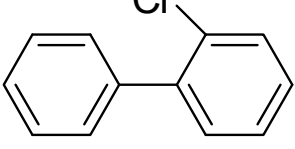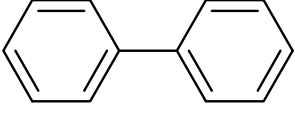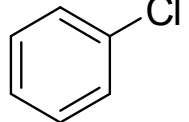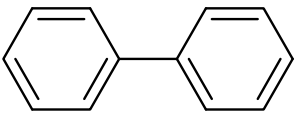
We then examined the effect of bases for the Suzuki reaction. The inorganic bases including K_2CO_3 and Na_3PO_4 afforded high yields of 70–98%, as shown in Table 2. However, the organic base NEt_3 gave a lower yield of 30% as shown in Table 2, entry 3. Thus, K_2CO_3 was selected as the base and H_2O as the solvent.

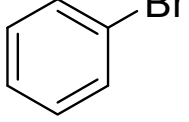| Base	Yield (%) [b]
K_2CO_3	98
Na_3PO_4	70
Et_3N	30

[a] Reaction conditions: Pd-PVP/SBA-15 (0.12 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), base (5 eq), H_2O (5 mL), room temperature, 8 h.
[b] Isolated Yield.

Table 2. Effect of different bases on Suzuki-Miyaura reaction [a]

Entry	Substrate	Product	Yield (%) [b]	Time (h)	Mp (°C)	
					Found	Reported ref
1	(iodobenzene)	(biphenyl)	98	8 [c]	71-73	70-72 Xu et al.
2	(4-iodoanisole, OCH₃)	(4-methoxybiphenyl, OCH₃)	90	12 [c]	92-94	91-92 Xu et al.
3	(4-iodotoluene, CH₃)	(4-methylbiphenyl, CH₃)	90	8 [d]	47-49	45-50 Xu et al.
4	(4-bromoacetophenone, Br)	(4-acetylbiphenyl)	60	12 [d]	121-123	120-122 Xu et al.
5	(1-chloro-2-iodobenzene, Cl)	(2-chlorobiphenyl, Cl)	96	4 [c]	31-35	32.5-33.5 Xu et al.
6	(bromobenzene, Br)	(biphenyl)	95	10 [c]	71-73	70-72 Xu et al.
7	(chlorobenzene, Cl)	(biphenyl)	90	14 [d]	71-73	70-72 Xu et al.

[a] Reaction conditions: Pd-PVP/SBA-15 (0.12 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 eq), H_2O (5 mL).
[b] Isolated yield.
[c] R.T.
[d] 95 °C.

Table 3. Suzuki-Miyaura reaction of aromatic aryl halides and phenylboronic acid catalyzed by Pd-PVP/SBA-15 [a]

Using our optimized reaction conditions, we selected a series of aryl iodides, some aryl bromides and aryl chloride in the Suzuki reaction. All reactions were performed using 1:1.5 stoichiometric ratios of aryl halides and phenylboronic acid in air. The results are summarized in Table 3. Reactions were carried out in water at different times. In some cases, coupling reactions with aryl iodide (entry 3), aryl bromide (entry 4) and aryl chloride (entry 7) required higher temperature (95 °C) in order to obtain excellent yields. The results are listed in Table 3. It is well known that activation of C-Cl bond is much more difficult than C-Br and C-I bonds, and in general requires harsher reaction conditions in a heterogeneous

catalysis system (Yin & Liebscher, 2007; Martin & Buchwald, 2008). Thus, the catalyst afforded average to excellent yields of biaryl products even at room temperature. In the literature, only a few catalysts are known for affecting the Suzuki-Miyaura cross-coupling reactions under mild conditions (Littke et al., 2000; Cuia et al., 2007; Marion et al., 2006, Navarro et al., 2006; Fairlamb et al., 2004).

The catalyst reuse and stability were checked using Suzuki reaction of iodobenzene with phenylboronic acid at room temperature in present water as solvent. The catalyst was separated from the reaction mixture after each experiment by simple filtration, washed with diethylether and acetone and dried carefully before using it in the subsequent run. The results showed that this catalyst could be reused without any modification, 5 times. It should be mentioned that there was rarely low catalyst leaching (4.5%) (Pd content of the catalyst was determined by AAS after each cycle) during the reaction and the catalyst exhibited high stability until 5 recycles (Table 4).

Cycle	Yield (%) [b]	Pd content of catalyst (mmol in 0.12 g catalyst) [c]
fresh	98	0.0672
1	98	0.0670
2	95	0.0661
3	93	0.0659
4	91	0.0651
5	87	0.0643

[a] Reaction conditions: Pd-PVP/SBA-15 (0.12 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3
(5 eq), H_2O (5 mL), room temperature.
[b] Isolated yield.
[c] Estimated by AAS.

Table 4. The catalyst reusability for the Suzuki-Miyaura reaction [a]

4. Conclusion

In this chapter, we demonstrated a facile palladium nanoparticle-PVP preparation inside modified mesoporous silica and the utilization of this nanocomposite as a new heterogeneous organic hybrid catalyst system. The catalytic activity of this catalyst was excellent for Suzuki-Miyaura cross-coupling reaction of aryl chloride, bromide and iodides at room temperature under aerobic conditions. Further, easy catalyst recovery and reasonable recycling (at least 5 times) efficiency of the catalyst made it an ideal system for coupling reactions in the aqueous phase. For determination of the amount of remained Pd on the catalyst structure, atomic absorption spectroscopy was used.

There are various methods such as XRD, BET, TEM, FT-IR, UV-Vis and etc. for characterization of solid catalysts. Estimation of the stability of the catalysts is one the important factors for the performance of the catalysts. The stability of the catalysts is directly related to the amounts leaching of the active species of the catalysts. AAS is the best technique for determination of the metal leaching in the catalysts containing metal nanoparticles.

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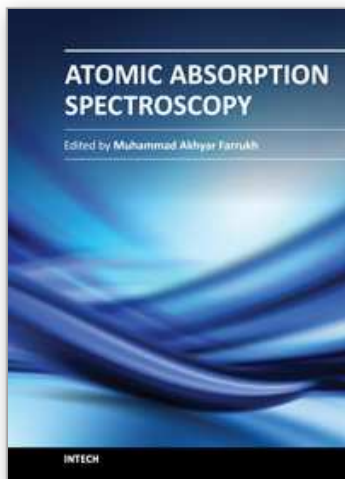
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Atomic Absorption Spectroscopy is an analytical technique used for the qualitative and quantitative determination of the elements present in different samples like food, nanomaterials, biomaterials, forensics, and industrial wastes. The main aim of this book is to cover all major topics which are required to equip scholars with the recent advancement in this field. The book is divided into 12 chapters with an emphasis on specific topics. The first two chapters introduce the reader to the subject, it's history, basic principles, instrumentation and sample preparation. Chapter 3 deals with the elemental profiling, functions, biochemistry and potential toxicity of metals, along with comparative techniques. Chapter 4 discusses the importance of sample preparation techniques with the focus on microextraction techniques. Keeping in view the importance of nanomaterials and refractory materials, chapters 5 and 6 highlight the ways to characterize these materials by using AAS. The interference effects between elements are explained in chapter 7. The characterizations of metals in food and biological samples have been given in chapters 8-11. Chapter 12 examines carbon capture and mineral storage with the analysis of metal contents.

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