Synthesis and property of polymer nanospheres with Pd/P4VP shells via surface RAFT polymerization

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Abstract. A reversible addition-fragmentation chain transfer (RAFT) agent with carbazole as Z-group was immobilized on the surfaces of the cross-linked poly (4-vinylbenzyl chloride-*co*-styrene) (PVBCS) nanospheres with a diameter of about 70 nm by the reaction of benzyl chloride groups in the PVBCS between carbazole and carbon sulfide. Then surface RAFT polymerization of 4-vinylpyridine (4VP) was used to modify the nanospheres to produce a well-defined and covalently tethered P4VP shell. By surface activation in a PdCl₂ solution and then reduction by hydrazine hydrate (N₂H₄·H₂O), the P4VP composite shells were obtained containing densely palladium metal nanoparticles. The chemical composition of the nanosphere surfaces at various stages of the surface modification was characterized by X-ray photoelectron spectroscopy (XPS). Transmission electron microscopy (TEM) was used to characterize the morphology of the hybrid nanospheres. The Pd/P4VP shell nanospheres were also applied to the catalytic reaction and proved to be efficient and reusable for the Heck reaction.

Keywords: polymer composites, RAFT polymerization, palladium catalyst

1. Introduction

Organic/inorganic hybrid nanoparticles have attracted much attention due to their fascinating optical, electronic, magnetic, photoelectric, biocompatible, and catalytic properties [1–3]. Among the hybrid materials, core-shell nanospheres usually consist of polymer shells and inorganic cores. The organic polymer shell mainly determines the chemical properties of nanoparticles, while the physical properties of nanoparticles are governed by both the size and shape of inorganic cores. There have been a number of methods to prepare core-shell nanospheres with different sizes, structures and compositions, such as sol-gel process [4], layer-by-layer assembly [5], encapsulation of different nanoparticles in cross-linked shell [6] and so on [7, 8]. Recently, rapid progress in the field of

controlled/living radical polymerizations [9–11] has paved the way to prepare well-defined core-shell nanospheres by grafting the polymer chains to the solid nanoparticles [12–14]. Among the major controlled polymerization strategies developed, reversible addition-fragmentation chain transfer (RAFT) [11] polymerization has become one of the most promising techniques to prepare polymer grafted solid supports because this technique can adapt to a wide range of reaction conditions, provides a procedure for the simple preparation of various of block copolymers, and has the compatibility with a wide range of functional monomers [15–17]. Until now, RAFT polymerization has been successfully utilized to graft various polymeric chains onto solid supports to form core-shell systems such as functionalized silica particles [18], gold nano-

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particles [19], CdSe nanoparticles [20], carbon nanotubes [21], Merrifield resins [22] and silica wafers [23]. Recent progress in this field also involves the preparation of hybrid nanoparticles coated with functional polymer brushes [24–26]. For example, Nishi and Kobatake prepared gold nanoparticles covered with photochromic diarylethene polymer that expressed a bright red color via RAFT polymerization [25]. However, there have been few reports on procedures to graft functional polymer chains onto solid supports and the properties, such as catalytic properties, of the shell modified materials.

Palladium is a highly active and selective catalyst in C–C bond formation reactions [27–30]. However, the problem that concerns many researchers is to combine high efficiency of the catalyst with the possibility of its easy separation from the reaction products. To the best of our knowledge, the synthesis of palladium (Pd)/polymer nanospheres with core-shell structure via RAFT technique and the investigation of their catalytic properties have not been reported till now. In this work, hybrid nanospheres with a well-dispersed Pd/poly (4-vinylpyridine) (P4VP) composite shell and a cross-linked poly (4-vinylbenzyl chloride-*co*-styrene) (PVBCS) core were prepared via the surface-RAFT technique. Cross-linked PVBCS nanospheres were synthesized by emulsion copolymerization of 4-vinylbenzyl chloride (VBC) and styrene in the presence of a cross-linking agent, *p*-divinylbenzene (DVB). The PVBCS nanosphere surfaces were then converted into polymer-supporting RAFT agents by the reaction of the benzyl chloride groups in the PVBCS with carbazole and carbon sulfide. The surface RAFT polymerization of 4VP produced a well-defined and covalently tethered P4VP shell on the surface of the nanospheres. The Pd/P4VP composite shells were obtained by activating P4VP shells in a PdCl₂ solution and then reducing Pd²⁺ by hydrazine hydrate (N₂H₄·H₂O). The nanospheres with the Pd/P4VP shells were used as catalysts for the Heck reaction between iodobenzene and methyl acrylate; and the results demonstrated that the catalysts were efficient and reusable for the Heck reaction.

2. Experimental

2.1. Materials

4-Vinylbenzyl chloride (VBC, 90%), *p*-divinylbenzene (DVB, 80%), iodobenzene (98%) were supplied by Acros. Styrene (St) and methyl acrylate (MA, analytical reagent, Shanghai Chemical Reagent Co., Ltd, China) were distilled before use. 4-Vinylpyridine (4VP, 95%) was obtained from Acros, distilled under reduced pressure and then stored at –15°C. Azobisisobutyronitrile (AIBN, 99%, Shanghai Chemical Reagent Co., Ltd, China) was recrystallized twice from ethanol. Benzyl bromide (98%), 2-propanol (analytical reagent), palladium(II) chloride (PdCl₂, analytical reagent), sodium dodecyl sulfate (SDS, analytical reagent), potassium persulfate (KPS, analytical reagent), triethylamine (Et₃N, analytical reagent), carbazole (analytical reagent), carbon disulfide (CS₂, analytical reagent), hydrazine hydrate (N₂H₄·H₂O, 50%) and dimethyl sulphoxide (DMSO, analytical reagent) were purchased from Shanghai Chemical Reagent Co., Ltd, China. 2-Propanol was dried with activated molecular sieve (4 Å). All other reagents were analytical quality reagents and used as received without further purification.

2.2. Preparation of cross-linked PVBCS nanosphere

The cross-linked PVBCS nanospheres were prepared by emulsion copolymerization of VBC, St and DVB at 65°C, using KPS as an initiator and SDS as a surfactant. About 150 mg of SDS was dissolved in 75 ml of deionized water. The monomers, VBC (1.5 ml, 9.6 mmol), St (4.0 ml, 34.8 mmol) and DVB (1.5 ml, 9.0 mmol) were well-mixed and dropped into the SDS solution under stirring, to give rise to a milky emulsion. Then the emulsion was kept in an ultrasonic bath for 10 min. The above emulsion was then placed in a three-necked round-bottom flask and purged with argon for 30 min. After KPS (50 mg, 0.18 mmol) was added at room temperature, the reaction mixture was kept under an argon atmosphere in an oil bath at 65°C for 12 h. After polymerization, the PVBCS nanospheres were purified by subjecting them to successive centrifugation/redispersion cycles in deionized water, ethanol, and finally tetrahydrofuran (THF). The obtained nanospheres were dispersed and stored in THF.

2.3. Synthesis of chain transfer agent (CTA): benzyl 9H-carbazole-9-carbodithioate (BCBD)

A suspension of KOH (0.24 g, 4.2 mmol) in DMSO (20 ml) was prepared, and carbazole (0.71 g, 4.2 mmol) was added under vigorous stirring. The solution was stirred for 2 h at room temperature and then carbon sulfide (0.38 g, 5.0 mmol) was added dropwise. The resultant reddish red solution was stirred for 5 h at room temperature, and then benzyl bromide (0.86 g, 5.0 mmol) was added. After the mixture was stirred overnight, the mixture was precipitated in a large amount of water, and a yellow solid was obtained. After being recrystallized twice from alcohol, yellow crystals of benzyl 9H-carbazole-9-carbodithioate (BCBD) were obtained. BCBD: Yield: 75%. ^1H NMR (CDCl_3): δ 4.73 (s, 2H), 7.32–7.47 (m, 9H), 8.00, 7.98 (d, 2H), 8.44, 8.46 (d, 2H). ELEM. ANAL. Calcd: C 72.03%, H 4.53%, N 4.20%, S 19.23%; found: C 72.15%, H 4.53%, N 4.18%, S 19.14%.

2.4. Synthesis of PVBCS supporting chain transfer agent (CTA): PBCBD

A suspension of potassium hydroxide (0.24 g, 4.2 mmol) in DMSO (20 ml) was prepared, and carbazole (0.71 g, 4.2 mmol) was added under vigorous stirring. The solution was stirred for 2 h at room temperature and then carbon sulfide (0.38 g, 5.0 mmol) was added dropwise. The resultant reddish solution was stirred for 5 h at room temperature, and then the suspension of the PVBCS nanospheres (2.0 g) in THF (50 ml) was added. After stirring at room temperature for 36 h, the nanospheres were isolated by centrifugation at 7200 rpm, and purified by subjecting them to successive centrifugation/redispersion cycles in THF and finally in 2-propanol. The obtained yellow product, PVBCS supporting RAFT agents (PBCBD), was dispersed and stored in 2-propanol. Elemental analysis: S, 2.41% (CTA loading: 0.376 mmol/g PBCBD nanospheres).

2.5. Synthesis of PVBCS-g-P4VP nanosphere (PVBCS-1)

In a 25 ml glass tube, 4VP (3 ml, 26 mmol), AIBN (2 mg, 0.012 mmol), 2-propanol (10 ml, containing 0.2 g PBCBD, 0.074 mmol CTA), and free BCBD

(0.024 g, 0.074 mmol) were added. The suspension was dispersed by ultrasonic and then purged with argon for 15 min. Polymerization was carried out under vigorous stirring for a predetermined time at 50°C. At the end of the polymerization, the surface modified PVBCS-1 nanospheres were purified by subjecting them to successive centrifugation/redispersion cycles in 2-propanol. The final product, PVBCS-g-P4VP nanosphere (PVBCS-1), was dispersed and stored in 2-propanol.

2.6. Preparation of Pd/P4VP shell nanosphere (PVBCS-2)

30 ml of aqueous solution containing 0.1 wt% PdCl_2 and 5 ml of 2-propanol suspension containing 0.1 g PVBCS-1 were added to a 50 ml glass tube. After stirring for 30 min, the nanospheres were purified by subjecting them to successive centrifugation/redispersion cycles in deionized water. The purified nanospheres were finally dispersed in 20 ml of deionized water. After adjusting pH to 14 with 1 M NaOH, excess $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added to the above suspension. The reaction was carried out at 50°C for 1 h to enable the Pd(II) to be converted entirely into palladium metal nanoparticles. The nanospheres were purified by subjecting them to successive centrifugation/redispersion cycles in deionized water. The final black product, Pd/P4VP shell nanosphere (PVBCS-2), was dried under reduced pressure at room temperature.

2.7. Heck reaction

Iodobenzene (5.0 mmol), methyl acrylate (7.5 mmol), triethylamine (Et_3N , 7.5 mmol), *N,N*-dimethylformamide (DMF, 20 ml), and the PVBCS-2 (15 mg) were added into a Schleck flask equipped with a constant temperature oil bath, and the mixture was stirred for 8 h at 90°C. After cooling to ambient temperature, the suspension was separated and the precipitate was washed by DMF and diethyl ether. To check its reusability, the precipitate was dried and reused in the next experiment. The filtrate was poured in water (30 ml) and extracted with CH_2Cl_2 (3×20 ml). The combined organic phases were dried over MgSO_4 , filtered and evaporated in vacuum. The products were purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 10:1 (v:v) as eluent.

^1H NMR (CDCl_3): δ 3.81 (s, 3H), 6.43, 6.47 (d, 1H), 7.39 (m, 3H), 7.53 (m, 2H), 7.68, 7.72 (d, 1H).
 ELEM. ANAL. Calcd: C 74.06% H 6.21%; found: C 73.23%, 5.97%.

2.8. Characterizations

Elemental analysis of C, H, N and S were measured with an EA1110 instrument. Surface compositions were measured by X-ray photoelectron spectroscopy (XPS). XPS was collected on an XSAM800 spectrometer at a pressure of about $2 \cdot 10^{-8}$ torr using $\text{Mg K}\alpha$ radiation as the exciting source, which was operated at 12 kV and 11 mA. All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. In peak synthesis, the line width (full width at half maximum) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Transmission electron microscopy (TEM) images were recorded on FEI TecnaiG220 transmission electron microscopy at 200 kV. The sample was prepared by mounting a drop of the nanosphere dispersion on a carbon-coated Cu grid, and allowing the sample to dry in air. The atomic absorption spectroscopy (AAS) (Varian Duo-220) was used to determine the percentage of palladium in PVBCS-1 nanospheres. The sample was prepared by removing organic substance in a muffle furnace at 700°C and then dissolving in aqua regia. ^1H NMR was recorded on an Inova 400 MHz nuclear magnetic resonance instrument with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard.

3. Results and discussion

3.1. Synthesis of PVBCS nanosphere with Pd nanoparticle/P4VP composite shells

Figure 1 shows the synthetic pathway for the preparation of core-crosslinked PVBCS nanospheres with Pd nanoparticle/P4VP composite shells. The process involves (i) preparation of cross-linked PVBCS nanospheres by emulsion copolymerization of VBC and St in the presence of DVB [31], (ii) immobilization of CTA, PBCBD, on the surface of PVBCS nanospheres via reaction of benzyl chloride group in PVBCS nanospheres with carbazole and carbon sulfide [32], (iii) synthesis of PVBCS-g-P4VP nanosphere (PVBCS-1) via RAFT polymerization of 4VP, and (iv) preparation of Pd/P4VP shell nanosphere (PVBCS-2) via activation with PdCl_2 solution and then reduction with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

Crosslinked PVBCS nanospheres with an average diameter of about 70 nm were obtained by this method (see later). Subsequently, the key step of this work is to attach RAFT agent to the PVBCS surfaces. In general, the attachment of the RAFT agent to the surfaces of nanoparticles can be accomplished through either the Z or the R group [33, 34]. However, in the R-group approach, where the solid support is a part of the leaving R groups, higher molecular weight of grafted polymers and grafting density can be achieved [34]. These advantages inspired us to design RAFT agents anchored onto PVBCS nanosphere surfaces through the method of R group moiety. In this work, the benzyl chloride groups on the PVBCS nanosphere surfaces were further reacted with carbazole and carbon sul-

Figure 1. Schematic diagram illustrating the process for the preparation of polymer nanospheres with palladium nanoparticle/P4VP composite shells

fide, leading to the polymer-supporting chain transfer agent (PBCBD). Elemental analysis of the polymer-supporting PBCBD shows that it contains 2.41% of S element (CTA loading: 0.376 mmol/g). The PBCBD was then used as a macro-RAFT agent to mediate RAFT polymerization of 4VP to produce P4VP brushes on the PVBCS nanosphere surfaces. The polymerizations ([4VP]:[PBCBD]:[BCBD]:[AIBN] = 2000:6:6:1) were conducted in the presence of a free RAFT agent BCBD in 2-propanol at 50°C for different reaction times. The thickness of P4VP brushes grafted onto PVBCS nanosphere surfaces can be controlled by the polymerization time, as shown in Table 1. It can be seen from the table, an increase in thickness of grafted P4VP shells from 0 to 3.5 nm is observed when the polymerization time increases from 0 to 24 h, which indicates that the polymerization of 4VP can be well controlled under the present polymerization conditions. At the same time, the content of Pd on different thickness P4VP shells are also increased, which indicates that we can also control the content of Pd loading (from 0–10.1 wt%) in the nanospheres by adjusting the polymerization time. The chemical composition of the nanosphere surfaces at various stages was determined by XPS. Figure 2(a–c) shows the XPS wide scan, C 1s, and Cl 2p spectra of the PVBCS nanosphere surfaces. The peak components in C 1s at the BEs of about 284.6 and 286.3 eV are attributable to the $\underline{\text{C}}\text{--C}/\underline{\text{C}}\text{--H}$ and $\underline{\text{C}}\text{--Cl}$ species [35, 36], respectively. The Cl 2p

Figure 2. XPS a) wide scan, b) C 1s, and c) Cl 2p core-level spectra of the PVBCS nanosphere surface

core-level spectrum consists of Cl 2p_{3/2} and Cl 2p_{1/2} doublet at the BEs of about 200.4 and 202.0 eV, respectively [35], attributable to the covalently bonded chlorine ($\underline{\text{C}}\text{--Cl}$) species. Figure 3(a–c) shows the XPS wide scan, C 1s and S 2p spectra of the PBCBD nanosphere surfaces after surface modification of PVBCS. The XPS wide scan spectrum shows four peak component at the BEs of about 163, 200, 284 and 400 eV, attributable to S 2p, Cl 2p, C 1s and N 1s species of the PBCBD nanospheres, respectively. The peak components in C 1s core-level spectrum at the BEs of about 284.6, 284.9 and 286.6 eV are attributable to the $\underline{\text{C}}\text{--C}/\underline{\text{C}}\text{--H}$, $\underline{\text{C}}\text{--S}/\underline{\text{C}}\text{=S}$, and $\underline{\text{C}}\text{--Cl}$ species [33, 34], respectively. The S 2p core-level spectrum can be curve-fitted with two peak component with BEs at about 162.9 and 164.2 eV, attributable to the

Table 1. Chemical composition, diameter, and layer thickness of the PVBCS-1 nanospheres

Entry	Polymerization time ^a [h]	N ^b [wt %]	Diameter (D) ^c [nm]	Shell thickness ^d [nm]	Content of Pd ^e [wt %]
1	0	0.00	70	0.0	0.0
2	12	2.20	74	2.0	8.9
3	15	2.44	75	2.5	9.9
4	24	2.90	76	3.0	10.0
5	36	3.43	77	3.5	10.1

^aPolymerization conditions: 4VP (3 ml), 2-propanol (10 ml, containing 0.2 g PBCBD), AIBN (2 mg), BCBD (0.074 mmol), [M]:[PBCBD]:[BCBD]:[AIBN] = 2000:6:6:1, temperature = 50°C

^bPercentage of nitrogen of PVBCS-1 nanospheres, deduced from elemental analysis

^cDiameter of the PVBCS-1, calculated from bulk nitrogen composition and according to Equation (1):

$$D = \left[\frac{\left(\frac{D_0}{2} \right)^3 \cdot 13.32\%}{13.32\% - \%N} \right]^{\frac{1}{3}} \cdot 2 \tag{1}$$

where D_0 is the diameter of the PVBCS (70 nm); 13.32% is the theoretical wt% of nitrogen in P4VP; %N is the nitrogen composition in the sample.

^dThickness of the P4VP shell in PVBCS-1

^ePercentage of palladium in PVBCS-1 nanospheres, deduced from the atomic absorption spectroscopy (AAS)

Figure 3. XPS a) wide scan, b) C 1s, and c) S 2p core-level spectra of the PBCBD nanosphere surface

C=S and C-S species [23, 36], respectively. It is a key step that the immobilization of RAFT agent on the surfaces of PVBCS nanospheres for this work. Generally, the reaction of benzyl chloride group with carbazole and carbon sulfide is very active and the substitution efficiency of chlorine atoms was reported to be close to 100% [37, 38]. However, the chloride signal can still be discernible in the XPS wide scan spectrum, indicating that there are chlorine atoms in the range of the XPS probing. It is well known that the probing depth of the XPS technique is about 8 nm in an organic matrix [39]. In addition, the XPS-derived surface [Cl]/[C] ratio of 1/100 (after reaction) in PBCBD nanospheres is much lower than that of 1/20 (before reaction) in PVBCS nanospheres, indicating that the most of the benzyl chloride groups have been transferred into the dithioester groups; at the same time, the thickness of CTA layer immobilized on the surfaces of PVBCS nanosphere should be less than 8 nm. All these results demonstrated that the RAFT agent BCBD was successfully anchored onto the PVBCS nanosphere surfaces.

Figure 4(a–c) shows the XPS wide scan, C 1s, and N 1s spectra of the surfaces of PVBCS-1 nanospheres obtained by the surface RAFT polymerization of 4VP for 24 h (as shown in entry 4 of Table 1). The XPS wide scan spectrum shows two dominant peak component at the BEs of about 284 and 400 eV, attributable to C 1s, and N 1s species of the PVBCS-1 nanospheres, respectively. In addition, a sulfur signal is also discernable though it is weaker, as shown in Figure 4d. The C 1s core-level spectrum of the PVBCS-1 surface can be curve-fitted into three peak components with BEs at 284.6,

Figure 4. XPS a) wide scan, b) C 1s, c) N 1s, and d) S 2p core-level spectra of the P4VP-grafted PVBCS or PVBCS-1 nanosphere surface from 24 h of surface RAFT polymerization

285.5, and 286.5 eV, attributable to the C-C/C-H, C-N/C-S/C-S, and C-Cl species, respectively. The N 1s core-level spectrum shows a predominantly peak component at BEs of 398.9 eV, attributable to the imine moiety (–N=) of the pyridine rings [40]. The results indicate that the P4VP shells were successfully immobilized onto the PVBCS nanosphere surfaces.

Poly(vinylpyridine) is the most used polymer for nanoparticle stabilization because it fulfils ligand requirements [41]. In this work, the PVBCS-1 nanospheres were activated in the PdCl₂ solution, and then hydrazine hydrate was used as the reducing agent for the PdCl₂-activated nanospheres. The nanospheres gradually turned from light-yellow to black, indicating the formation of palladium metal nanoparticles in the P4VP shell (PVBCS-2). Figure 5(a–d) shows the XPS wide scan, C 1s, N 1s, and Pd 3d spectra of the PVBCS-2 nanosphere surfaces. The XPS wide scan shows five peak components at the BEs of about 162, 200, 284, 335, and 398 eV, attributable to S 2p, Cl 2p, C 1s, Pd 3d, and N 1s species, respectively. The C 1s core-level spectrum of the PVBCS-2 surface can be curve-fitted into three peak components with BEs at about 284.6, 285.5, and 286.5 eV, attributable to the C-C/C-H, C-N/C-S/C-S, and C-Cl species, respectively. The peak component at the BEs of 398.9 eV in the N 1s core-level spectrum is attributable to the imine moiety (–N=) of the pyridine rings. The XPS spectrum of Pd 3d can be curve-fitted into two spin-orbit-split doublets, as illustrated in Figure 5d. The two peak components at the BEs

Figure 5. XPS a) wide scan, b) C 1s, c) N 1s, d) Pd 3d, and e) Cl 2p core-level of the Pd/P4VP composite shell nanosphere (PVBCS-2 nanosphere) surface

of about 335.4 and 340.7 eV are attributable to the Pd 3d_{5/2} and Pd 3d_{3/2} species, which can be indexed to the Pd (0) state [36, 42]. The other set of peaks at 337.7 eV (Pd 3d_{5/2}) and 342.9 eV (Pd 3d_{3/2}) is ascribed to the Pd²⁺ [38, 43]. Calculating the integration areas of these two doublets using XPS-PEAK software, it can be estimated that the atomic ratio of Pd⁰/Pd²⁺ was about 59:41. The oxidation form of Pd is possibly palladium oxide, which may result from the surface oxidation of palladium nanoparticles when they are exposed to air. A similar phenomenon was also reported by others [42, 43].

3.2. Activity for the heck reaction of the PVBCS-2 nanospheres

It is well-known that Pd is effective in catalyzing C–C bond formation reactions [27–30]. Among palladium-catalyzed couplings, the Suzuki-Miyaura [29], Sonogashira [27] and Heck [28] reactions are the most widely used. In this work, the catalytic activity of the PVBCS-2 nanospheres for Heck reaction was investigated using the model reaction of iodobenzene and methyl acrylate (Figure 6). The reaction of iodobenzene (1.0 equiv) and methyl acrylate (1.5 equiv) with 15 mg of PVBCS-2 nanos-

Figure 6. Schematic diagram illustrating Heck reaction using iodobenzene and methyl acrylate as the model reagents

pheres was performed at 90°C in DMF containing triethylamine (1.5 equiv). The results are listed in Table 2.

The freshly synthesized PVBCS-2 nanospheres exhibit a higher activity. Although the activity of the catalyst gradually decreases somewhat after subsequent recycling, the catalyst still shows a good activity even if it was used three times. XPS spectroscopy technique was also used to check the chemical composition of the recycled catalyst (PVBCS-2A) surfaces after being used four times. Figure 7(a–d) shows the XPS wide scan, C 1s,

Table 2. Results of Heck reaction catalyzed by PVBCS-2 nanosphere

Run ^a	1	2	3	4
Isolated yield [%] ^b	97	95	94	94

^aReaction performed with 5.0 mmol of iodobenzene, 7.5 mmol of methyl acrylate, 7.5 mmol of triethylamine, 20 ml of DMF, PVBCS-2 (15 mg, Pd% = 8.9 wt%)

^bIsolated yield after filtration of crude reaction mixture on silica gel

Figure 7. XPS a) Wide scan, b) C 1s, c) N 1s, and d) Pd 3d core-level spectra of the recycled PVBCS-2 nanosphere (PVBCS-2A nanosphere) surface

N 1s, and Pd 3d spectra of the PVBCS-2A nanosphere surfaces. The XPS wide scan, C 1s, and N 1s spectra of the PVBCS-2A nanosphere surfaces have no significant changes as compared with the PVBCS-2 nanosphere surfaces. The XPS wide scan shows five peak components at the BEs of about 162, 200, 284, 335, and 398 eV, attributable to S 2p, Cl 2p, C 1s, Pd 3d, and N 1s species, respectively. The C 1s core-level spectrum of the PVBCS-2 surface can be curve-fitted into three peak components with BEs at about 284.6, 285.5, and 286.5 eV, attributable to the C-C/C-H , C-N/C=S/C-S , and C-Cl species, respectively. The peak component at the BEs of 398.9 eV in the N 1s core-level spectrum is attributable to the imine moiety ($-\text{N}=\text{}$) of the pyridine rings. As illustrated in Figure 7d, the doublet with a binding energy at 335.4 eV ($\text{Pd } 3d_{5/2}$) and 340.7 eV ($\text{Pd } 3d_{3/2}$) can be indexed to the Pd^0 . The other set of peaks at 337.6 eV ($\text{Pd } 3d_{5/2}$) and 342.3 eV ($\text{Pd } 3d_{3/2}$) is ascribed to the Pd^{2+} . Different from the result of original PVBCS-2 nanospheres, the atomic ratio of $\text{Pd}^0/\text{Pd}^{2+}$ is about 33:67 by calculating the integration areas of these two doublets using XPSPEAK software after four times catalytic cycles, being lower than the ratio (59:41) of the initial catalyst.

The increased oxidation form of Pd possibly results from the surface oxidation of palladium nanoparticles during the Heck reaction [42, 43].

3.3. Morphology of the PVBCS nanospheres

The morphologies of the PVBCS nanospheres at different stages of surface functionalization were observed by TEM. PVBCS nanospheres with an average diameter of about 70 nm, as determined by TEM (Figure 8(a, b)), were obtained. After surface functionalization, the PVBCS-supporting chain transfer agent (PBCBD) was obtained, and the size and morphology of the nanospheres are almost identical to these of the PVBCS nanospheres (Figure 8c). Figure 8d shows the TEM image of the P4VP grafted PVBCS nanospheres (PVBCS-1) with a 76 nm of diameter after RAFT polymerization for 24 h. Figure 8e shows the TEM images of the Pd/P4VP shell nanospheres (PVBCS-2). The small dark spots representing the palladium metal nanoparticles are dispersed throughout the surface of the PVBCS-2 nanospheres in the P4VP shell. The surface of the nanoparticles becomes a little rough after being recycled four times, as shown in Figure 8f. During the reaction process, most of the

Figure 8. TEM images of a), b) the cross-linked PVBCS nanosphere, c) the PVBCS supporting chain transfer agent: PBCBD nanosphere, d) the PVBCS-*g*-P4VP nanosphere (PVBCS-1 nanosphere) obtained by the surface RAFT polymerization of 4VP for 24 h, e) the Pd/P4VP composite shell nanosphere (PVBCS-2 nanosphere), and f) the Pd/P4VP composite shell nanosphere (PVBCS-2A nanosphere) used in the Heck reaction after four times

leached Pd species can be adsorbed on the polymer support [42], so the catalyst remains good in activity and is stable after being recycled several times.

4. Conclusions

A four-step method for preparing core-crosslinked polymer nanospheres with Pd/P4VP inorganic/organic hybrid shells via RAFT polymerization was developed. This method allows the control over shell thickness by simply adjusting the RAFT polymerization time, and therefore the content of palladium. The Pd/P4VP shell nanospheres can serve as an efficient and reusable catalyst for the Heck reaction.

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