

Microreactor of Pd Nanoparticles Immobilized Hollow Microspheres for Catalytic Hydrodechlorination of Chlorophenols in Water

Yang Lan, Li Yang, Minchao Zhang, Wangqing Zhang,* and Shengnan Wang

Key Laboratory of Functional Polymer Materials of Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

ABSTRACT A microreactor of Pd nanoparticles immobilized shell-corona hollow microspheres of poly[styrene-*co*-2-(acetoacetoxy)ethyl methacrylate-*co*-acrylamide] has been designed for catalytic hydrodechlorination (HDC) of chlorophenols in the sole solvent of water. The strategy of the combined use of the shell-corona hollow microspheres as microcapsule and catalyst scaffold endues the microreactor several advantages. First, the microreactor can be dispersed in the sole solvent of water and acts as a quasi-homogeneous catalyst for catalytic HDC of chlorophenols. Second, the reactant of chlorophenols can be highly concentrated within the hollow microspheres of the microreactor in the sole solvent of water. Third, the resultant product of phenol can be favorably excreted off the microreactor into water because of the polar difference between the reactant of chlorophenols and the product of phenol. Ascribed to the combined advantages, catalytic HDC of chlorophenols can be performed efficiently within the microreactor in the sole solvent of water at room temperature under atmosphere pressure.

KEYWORDS: hollow microspheres • Pd nanoparticles • microcapsule • chlorophenols • hydrodechlorination

1. INTRODUCTION

Chlorophenols, which are widely used in manufacture of pesticides, herbicides, dyes, and fungicides, represent a major group of pollutants in wastewater because of their acute toxicity and resistance to degradation (1–3). Widespread and increasing contamination in water attributable to chlorophenols has spurred an intense drive to find efficient and cost-effective treatment. The existing strategies to deal with the chlorophenol contamination mainly includes three forms: (1) “end-of-pipe” treatment, e.g., adsorption (4) and incineration (5); (2) catalytic/chemical oxidation (6) and advanced oxidation (7), such as photolysis (8), and ozonation (9); and (3) catalytic hydrodechlorination (HDC) (10–17). The treatment of adsorption offers a means of concentration rather than transformation and the adsorbate is always a mixture of pollutants; it therefore often requires an additional destructive waste treatment. Incineration requires high temperature and those products resulted from incomplete combustion such as polychlorodibenzodioxins and polychlorodibenzofurans are far more toxic than the chlorophenols themselves (6). The catalytic oxidation is preferable to incineration for lower energy demand, yet generates unwanted CO₂ and pollutants such as CO, Cl₂, and COCl₂ in air. The efficiency of the advanced oxidation processes is unproven and this oxidation process is also hampered

against practical considerations in terms of high energy demands. The catalytic hydrodechlorination (HDC) reaction, in which chlorine is replaced by hydrogen, is a promising route to abate the toxicity of chlorophenols in wastewater (10–15). The advantages of catalytic HDC reaction compared with the other two kinds of strategies include high conversion at low temperature and pressure, reusable raw material of phenol being generated, and no toxic products being produced. Up to now, palladium (Pd) has been identified as the best catalyst for catalytic HDC reaction with regard to high activity under lower temperature and pressure and resistance to deactivation (16, 17).

Chemical conversion within a confined microreactor or nanoreactor is of growing interest to chemists because it is expected to increase conversion due to high local concentration of reactants (18–21). Up to now, various microreactors or nanoreactors have been designed. For example, Ueno et al. (20) describe a microreactor of Pd nanocluster encapsulated in the apo-ferritin cavity for size-selective olefin hydrogenation. Vriezema et al. (21) assemble enzymes in a polymersome nanoreactor that greatly promotes the reaction of glucose oxidation. Polymeric hollow microspheres can be used as microcapsules because hollow microspheres can provide a compartmentalization to encapsulate and conserve guest molecules (22–24). For example, Kim et al. (24) realize encapsulation and release of a fluorescent dye in solvent-responsive polymer nanocapsules by controlled swelling or deswelling of the nanocapsules in different solvents. However, the combined use of hollow microspheres as microcapsule to encapsulate reactants and scaf-

* Corresponding author. E-mail: wqzhang@nankai.edu.cn. Tel: 86-22-23509794. Fax: 86-22-23503510.
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fold to immobilize catalyst of noble metal nanoparticles is scarcely studied, although the separate application of polymeric hollow microspheres as microcapsule (22–24) or catalyst scaffold is studied (25–27). Recently, we combined the use of hollow microspheres as microcapsule to encapsulate and concentrate reactants in water and the scaffold to immobilize catalyst of noble metal nanoparticles, and propose a microreactor of Pd-anoparticle-immobilized hollow microspheres for organic/aqueous biphasic catalysis (28).

In the present study, the Pd-nanoparticle-immobilized shell-corona hollow microspheres of poly[styrene-*co*-2-(acetoacetoxy) ethyl methacrylate-*co*-acrylamide] (PS-*co*-PAEMA-*co*-PAM) are further introduced as microreactor for catalytic HDC reaction in the sole solvent of water. The extended application of the microreactor of Pd nanoparticles immobilized shell-corona hollow microspheres from the organic/aqueous biphasic catalysis to the catalytic HDC reaction in the sole solvent of water is due to two concerns: (1) the pollutant of chlorophenols is generally dissolved or dispersed in wastewater, and thus the aqueous quasi-homogeneous catalysis instead of organic/aqueous biphasic catalysis is more feasible and economical for the catalytic HDC reaction; (2) the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres, which act just like a smart pump, can selectively concentrate the reactant of chlorophenol within the hollow microspheres and excrete the product of phenol off the hollow microspheres in water because of the different hydrophilic character between the reactant and product, and thus the catalytic HDC reaction within the microreactor is accelerated. The catalysis demonstrates that the HDC reactions within the microreactor can be efficiently performed in the sole solvent of water at room temperature under atmosphere pressure, and suggests that the proposed microreactor has special advantage for chemical conversions such as HDC reaction in water if the reactant and product have different hydrophilicity.

2. EXPERIMENTAL SECTION

2.1. Materials. Styrene (St, >98 %) and methylacrylic acid (MAA, >99 %) were purchased from Tianjin Chemical Company and distilled under vacuum before being used. Acrylamide (AM, >99 %, Tianjin Chemical Company) was recrystallized from acetone before being used. Divinylbenzene (DVB, >80 %, Alfa Aesar) was washed with 5 % NaOH aqueous solution and water, followed by drying with MgSO₄. 2,2'-Dicyano-2,2'-azopropane (AIBN, 99 %, Tianjin Chemical Company) was purified by recrystallization from ethanol. 2-(Acetoacetoxy) ethyl methacrylate (AEMA, >95 %, Aldrich) was used as received. PdCl₂ (>99 %), NaBH₄ (>98.9 %), K₂S₂O₈ (>99.5 %), 4-chlorophenol (>95 %), 2-chlorophenol (>95 %), 2,4-dichlorophenol (>95 %), and other analytical reagents were purchased from Tianjin Chemical Company and used as received.

2.2. Synthesis of the Microreactor of Pd Nanoparticles Immobilized Shell-Corona Hollow Microspheres.

2.2.1. Synthesis of the Shell-Corona Hollow Microspheres. The shell-corona hollow microspheres of PS-*co*-PAEMA-*co*-PAM were synthesized by template polymerization (29). The typical procedures are introduced as following. First, to a flask MAA (0.430 g, 5.0 mmol) and styrene (5.208 g, 50.0 mmol) were added. The mixture was vigorously stirred at about 300 rpm

for about 30 min at room temperature and degassed under nitrogen purge, and K₂S₂O₈ (0.297 g, 1.10 mmol) was then added. The mixture was degassed again, and polymerization was performed with vigorous stirring at 80 °C for 24 h under nitrogen atmosphere. The resultant template of the PS-*co*-PMAA microspheres was purified by centrifugation and then dispersed in 150.0 mL of water. Second, 45.0 mL of the aqueous dispersion of the resultant PS-*co*-PMAA microspheres, H₂O (55 mL) and K₂S₂O₈ (0.135 g, 0.50 mmol) were added into a flask. The mixture was degassed under nitrogen purge at room temperature and heated to 80 °C; a mixture of styrene (1.043 g, 10.0 mmol), AEMA (2.142 g, 10.0 mmol), AM (0.355 g, 5.0 mmol), and DVB (0.135 g, 1.0 mmol) was then added. The polymerization was performed under a nitrogen atmosphere with vigorous stirring for 24 h at 80 °C. The resultant coated microspheres of PS-*co*-PMAA/PS-*co*-PAEMA-*co*-PAM were purified by centrifugation. Third, the coated microspheres were dispersed in DMF (100 mL) for about 12 h to remove the core template to form the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres. The elimination of the template microspheres can be judged by dropping the DMF solution into water until no turbidity or deposition being optically observed. The resultant shell-corona hollow microspheres were collected by centrifugation and dispersed in 200.0 mL of water for direct use.

2.2.2. Preparation of Microreactor by Immobilization of Pd Nanoparticles on the Shell-Corona Hollow Microspheres.

To a 250 mL conical flask were added 20.0 mL of the aqueous dispersion of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres and the acidic aqueous solution of PdCl₂ (80.0 mL, containing 0.10 mmol Pd). The mixture was stirred and kept at room temperature for 4 h. The pH value was then adjusted to about 7 with NaOH aqueous solution. Subsequently, cool NaBH₄ aqueous solution (10 mL, 0.05 mmol/mL) was slowly added at room temperature. The resultant microreactor of Pd nanoparticles immobilized hollow microspheres was kept for 4 h with stirring and finally dialyzed against water for 7 days to remove the impurities. The final microreactor was dispersed in 120.0 mL of water, wherein the concentration of the Pd catalyst was 0.83 mmol/L and the loading capacity of the shell-corona hollow microspheres for the Pd catalyst was 0.27 mmol/g.

2.3. Encapsulation of 4-Chlorophenol/Phenol within the Shell-Corona Hollow Microspheres. The encapsulation of 4-chlorophenol within the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres in neutral or alkaline aqueous solution at room temperature is typically introduced. The aqueous dispersion of the shell-corona hollow microspheres (0.20 mL, 9.2 mg/mL) and NaOH (3.0 mg, 7.5 × 10⁻² mmol, ONLY for the encapsulation under alkaline aqueous solution) were added into the 4-chlorophenol or phenol aqueous solution (15.0 mL, 5.0 × 10⁻³ mmol/mL). After being stirred for 1 h, the mixture was filtrated with 0.20 μm filter and the concentration of 4-chlorophenol or phenol in the filtrate was measured by high performance liquid chromatography (HPLC) analysis. The amount of 4-chlorophenol or phenol encapsulated within the shell-corona hollow microspheres is calculated from the difference between the fresh 4-chlorophenol or phenol aqueous solution and the filtrate. The volume percent *P* occupied by the encapsulated 4-chlorophenol or phenol within a single hollow microsphere is calculated by the following equation

$$P = \frac{m_a / \rho_a}{(m_b / \frac{4}{3} \pi (R^3 - r^3) \rho_c) \times \frac{4}{3} \pi r^3}$$

where *m_a* and *m_b* are the quality of encapsulated guest molecules and the hollow microspheres, *ρ_a* and *ρ_c* are the density of the encapsulated guest molecules and the wall of the hollow

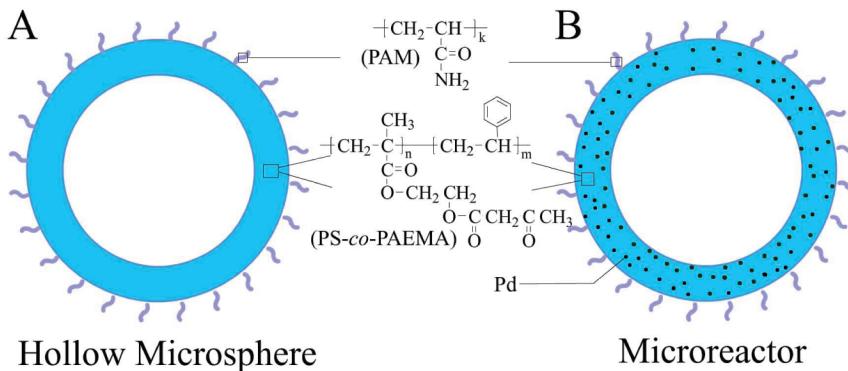


FIGURE 1. Schematic structure of (A) the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres and (B) the microreactor of Pd-nanoparticle-immobilized hollow microspheres.

microspheres, R and r are the average radius of the hollow microspheres and the average radius of the microcavity, respectively. Herein, the density of the wall of the hollow microspheres, ρ_c , is approximately estimated to be equal to that of the bulk polymer materials, 1 g/cm^3 .

The encapsulation of the mixture of 4-chlorophenol and phenol (1:1 by mole) within the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres in neutral or alkaline aqueous solution were carried out and calculated as similar as introduced above.

2.4. General Procedures for Catalytic HDC Reaction. Take the catalytic HDC of 4-chlorophenol as a typical example. A given amount of 4-chlorophenol (0.257 g, 2.0 mmol), a given amount of base (5.2 mL of aqueous solution) and the microreactor (4.80 mL of aqueous dispersion containing $4.0 \times 10^{-3} \text{ mmol}$ of Pd catalyst) were added in a 100 mL tubelike glass reactor equipped with a reflux condenser. The catalytic HDC reaction was started by bubbling H_2 at 25°C under atmospheric pressure. The catalytic HDC reaction was monitored by HPLC. To test the reusability of the microreactor just after the catalytic HDC reaction was completed in 2 h, we collected the microreactor by centrifugation and used it for the next run of catalytic HDC reaction with the same amounts of 4-chlorophenol and NaOH being added and under the same reaction conditions as those of the fresh run.

2.5. Characterization. Transmission electron microscopy (TEM) measurements were performed using a Philips T20ST electron microscope at an acceleration of 200 kV, whereby a small drop of the aqueous dispersion was deposited onto a piece of copper grid and then dried at room temperature under vacuum. HPLC analysis was performed on a LabAlliance PC2001 system equipped with a C18 column and a UV-vis detector using the mixture of CH_3CN and water (6:4 by volume) as eluent. The dynamic light scattering (DLS) measurements were performed with a Brookhaven 90Plus laser particle size analyzer and all the measurements were carried out at a scattering angle of 90° at room temperature.

3. RESULTS AND DISCUSSIONS

3.1. Synthesis and Characterization of the Shell-Corona Hollow Microspheres. Figure 1A schematically shows the structure of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres. The PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres are composed of three parts: (1) the hydrophilic corona of polyacrylamide (PAM); (2) the cross-linked and hydrophobic shell of poly[styrene-*co*-2-(acetooxy)-ethylmethacrylate] (PS-*co*-PAEMA); (3) the microcavity. The functions of each component of the shell-corona hollow microspheres are elucidated as follows. The hydrophilic PAM corona makes the hollow microspheres

or the microreactor keep suspending in aqueous solution. The shell-forming segment of PAEMA is used since it contains chelate ligands of β -diketone to immobilize catalyst of Pd nanoparticles (30–32). As to the PS segment, since the glass transition temperature (T_g) of the shell-forming PAEMA segment is very low ($\sim 3^\circ\text{C}$) (32), it is introduced into the shell to increase the thermal stability of the shell-corona hollow microspheres.

The PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres are synthesized by template polymerization (29). First, the sacrificial template of PS-*co*-PMAA microspheres is synthesized by one-stage soap-free emulsion polymerization as described in our recent manuscript (33). Polymerization of the mixture monomers of styrene, AEMA, AM, and the cross-linker of DVB on the template of the PS-*co*-PMAA microspheres results in formation of coated microspheres. Lastly, the sacrificial template is removed with DMF, and therefore, the shell-corona hollow microspheres of PS-*co*-PAEMA-*co*-PAM are produced. The detailed synthesis and characterization of the shell-corona hollow microspheres can be found in the Supporting Information.

Figure 2A shows the TEM image of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres. Clearly, the average diameter, the extent of the microcavity and the wall thickness are 300, 200, and 50 nm, respectively. Figure 2B shows the hydrodynamic diameter distribution of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres in neutral aqueous solution measured by DLS, which indicates that the size of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres is almost monodispersed. Herein, it should be pointed out that the average hydrodynamic diameter of the shell-corona hollow microspheres measured by DLS, 350 nm, is a little larger than those observed by TEM (300 nm), because the shell-corona hollow microspheres are swollen in water because of the hydrophilic corona of PAM.

3.2. Synthesis of Microreactor by Immobilization of Pd Nanoparticles on Shell-Corona Hollow Microspheres. PAEMA is a kind of typical coordinate polymer, which contains the chelate ligand of β -diketone and has been used as scaffold of transitional metal catalyst or resin to remove heavy metal pollutant in wastewater (30–32). As shown in Figure 1A, the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres contain the shell-

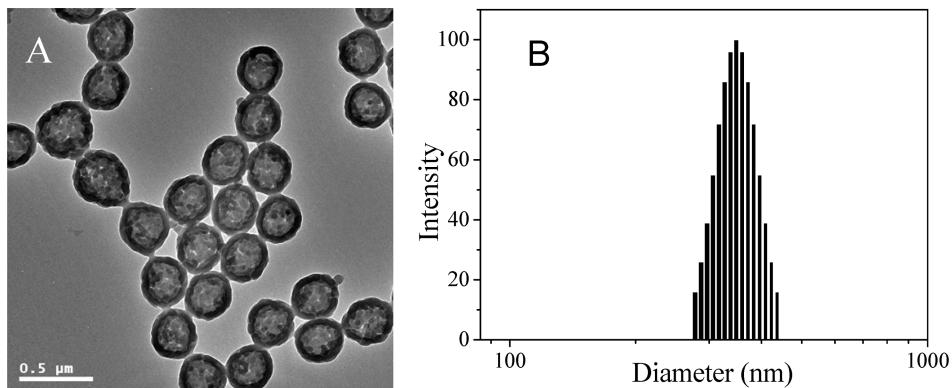


FIGURE 2. (A) TEM image and (B) the hydrodynamic diameter distribution of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres.

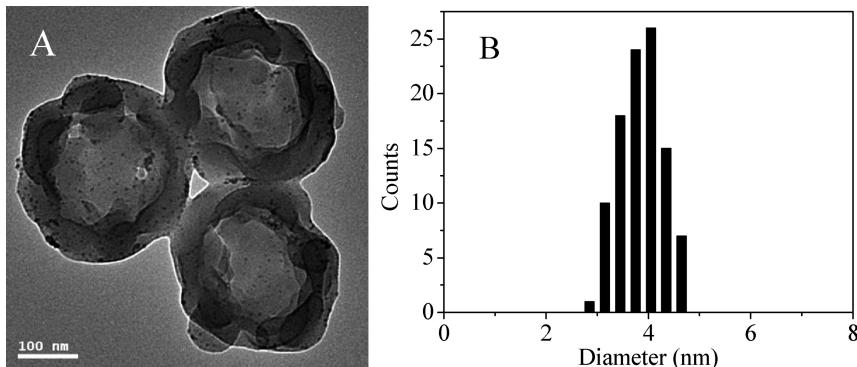


FIGURE 3. (A) TEM image of the microreactor of Pd nanoparticles immobilized hollow microspheres and (B) the size distribution of immobilized Pd nanoparticles.

forming segment of PAEMA. Therefore, when PdCl_2 is added into the aqueous dispersion of the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres, Pd ions are first coordinated with the chelate ligands of β -diketone and then the catalyst of Pd nanoparticles is immobilized on the shell-corona hollow microspheres by reducing with NaBH_4 aqueous solution, and therefore the microreactor of Pd nanoparticles immobilized hollow microspheres as shown in Figure 1B is produced. The TEM image shown in Figure 3A confirms the structure of the microreactor. It is clearly observed that the *in situ* synthesized Pd nanoparticles are uniformly dispersed on the PS-*co*-PAEMA-*co*-PAM hollow microspheres. Figure 3B shows the size distribution of Pd nanoparticles, which shows that the size of Pd nanoparticles is almost monodispersed and the average size is 3.9 nm. Powder X-ray diffraction (XRD) pattern also confirms formation of Pd nanoparticles on the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres (see Figure S5 in the Supporting Information).

3.3. Catalytic HDC of Chlorophenols within the Microreactors in Water. It is well-documented that chemical translation confined within a suitable microreactor can be accelerated partly because of the concentrated reactants (18–21). In a recent communication (28), we have demonstrated that the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres with immobilized Pd nanoparticles can act as efficient microreactor for hydrogenation of olefin under organic/aqueous biphasic condition since the microreactor can greatly encapsulate and concentrate hydrophobic organic molecules within the microcavity of the hollow

microspheres. Herein, we extend the application of the microreactor of Pd nanoparticles immobilized shell-corona hollow microspheres to the catalytic HDC of chlorophenols in the sole solvent of water. To perform catalytic HDC of chlorophenols within the microreactor in water, we should concern with the following advantages of the proposed microreactor.

The first concern is on the dispersion of the microreactor of Pd nanoparticles immobilized shell-corona hollow microspheres in water. Because of the hydrophilic PAM corona, the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres and the microreactor can be easily dispersed in the sole solvent of water (see Figure S1 in the Supporting Information). The easy dispersion of the microreactor suggests that the microreactor is as same as a quasi-homogeneous catalyst (34) and therefore high catalytic efficiency is expected.

The second concern is on the concentrated reactant of chlorophenols within the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres of the microreactor. As similar as general microcapsules (22–24), the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres can encapsulate and concentrate the reactant of chlorophenols due to the hydrophobic character of the microcavity in the hollow microspheres. For example, it is found when the shell-corona hollow microspheres are added into the aqueous solution of 4-chlorophenol, part of 4-chlorophenol is encapsulated within the shell-corona hollow microspheres. The encapsulated 4-chlorophenol occupies about 89 % of vacancy volume of the hollow microspheres and the 4-chlorophenol concentration located in the hollow microspheres, 2.68 mol/L, is about 668

times higher than those in the solvent of water. Therefore we expect that the catalytic HDC reaction within the microreactor can be accelerated because of the highly concentrated reactant of chlorophenols.

The third concern is on the diffusion of the product of phenol off the microreactor. With the progress of the HDC reaction within the microreactor, the product is gradually accumulated within the microreactor. Clearly, only if the product diffuses off the microreactor, the chemical balance will be transferred to the product. As discussed above, the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres contain a hydrophilic PAM corona and a hydrophobic PS-*co*-PAEMA shell, therefore the microcavity of the hollow microspheres is generally hydrophobic. In the hydrogenation of olefin within the microreactor under organic/aqueous biphasic condition, the driven force for the resultant hydrocarbon diffusion off the microreactor is mainly ascribed to the extraction caused by the organic phase, whereas in the present catalytic HDC reaction within the microreactor in water, the resultant product of phenol can be favorably excreted off the microreactor into water because the product of phenol is more hydrophilic than the reactant of chlorophenols. That is to say, the microreactor can selectively concentrate the reactant of chlorophenols within the microreactor but exclude the phenol product off the microreactor in water; therefore, the balance of catalytic HDC reaction is transferred to the product and the HDC reaction is accelerated. To confirm this hypothesis, we first added the shell-corona hollow microspheres into the aqueous solution of phenol. It is found that phenol can also be encapsulated within the shell-corona hollow microspheres; however, the encapsulated phenol occupies just about 52% of vacancy volume of the hollow microspheres, which are much lower than that of the encapsulation of 4-chlorophenol, 89%. In addition, the shell-corona hollow microspheres are further added into the aqueous solution of the 4-chlorophenol/phenol mixture (1:1 by mole), and it is found that the amount of the encapsulated 4-chlorophenol within the hollow microspheres is 1.3 times higher than those of the encapsulated phenol. In basic aqueous solution, the selective encapsulation of 4-chlorophenol is further improved and the amount of the encapsulated 4-chlorophenol within the hollow microspheres is 1.6 times higher than those of the encapsulated phenol. Therefore, it is concluded that the microreactor is just like a smart pump, which can selectively concentrate the reactant of chlorophenols and excrete the product of phenol.

On the basis of the structure and the corresponding advantages of the microreactor introduced above, the entire concept of catalytic HDC reaction within the microreactor in the sole solvent of water is pictorially shown in Figure 4. At the beginning of the HDC reaction, chlorophenols, which are generally hydrophobic, are encapsulated and concentrated within the shell-corona hollow microspheres of the microreactor, within which HDC reaction takes place and a more hydrophilic product of phenol is produced. With the progress of the HDC reaction, the product of phenol is

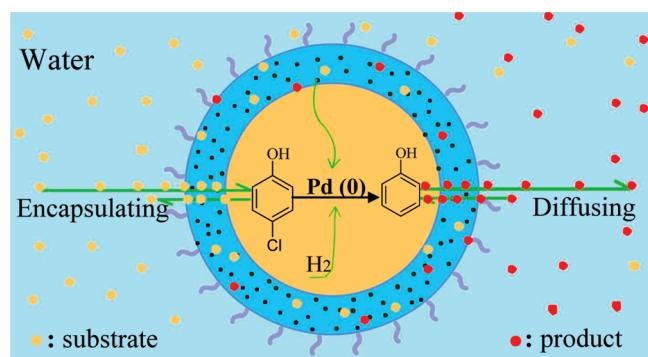


FIGURE 4. Schematic catalytic HDC reaction within the microreactor of Pd nanoparticles immobilized shell-corona hollow microspheres in the sole solvent of water.

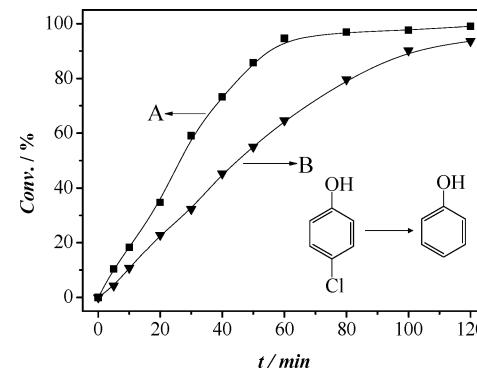


FIGURE 5. Catalytic HDC of (A) 4-chlorophenol within the microreactor and (B) a reference catalyst of 4.1 nm Pd nanoparticles immobilized on the solid microspheres in water at room temperature under atmosphere pressure. Reaction conditions: 4-chlorophenol (2.0 mmol), NaOH (2.0 mmol), and 4.80 mL of the aqueous dispersion of the microreactor or the reference catalyst containing 4.0×10^{-3} mmol of Pd catalyst, bubbling H₂ at 25 °C under atmospheric pressure.

excreted off the microreactor into water and the HDC reaction runs forward. Herein, it should be pointed out that the shell of the shell-corona hollow microspheres is swollen with the reactant and product as schematically indicated by the red and yellow dots on the blue shell layer of the hollow microspheres in Figure 4, which leads to enough accessibility of the Pd nanocatalyst.

Now the research is focused on the catalytic HDC of 4-chlorophenol within the microreactor in water at room temperature under atmosphere pressure. As similar as the general catalytic HDC reaction employing Pd catalyst (35, 36), the catalytic HDC of 4-chlorophenol within the microreactor is greatly affected by addition of a suitable base possibly because of catalyst deactivation caused by the byproduct of HCl. Of all the bases such as Na₂CO₃, NaHCO₃, and NaOH, the equivalent NaOH to 4-chlorophenol is most suitable for the catalytic HDC of 4-chlorophenol within the microreactor and the most efficient catalytic HDC reaction is achieved (see Figure S6 in the Supporting Information).

Figure 5A shows the time-dependent catalytic HDC conversion of 4-chlorophenol within the microreactor in water at room temperature under atmosphere pressure. As shown in Figure 5A, 95% of 4-chlorophenol is converted into phenol in 1 h and almost all 4-chlorophenol is converted in 2 h within the microreactor employing 0.20 mol % Pd catalyst.

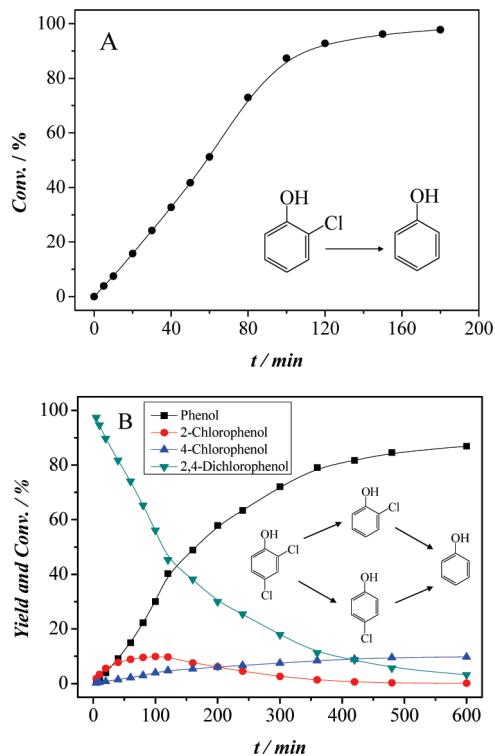


FIGURE 6. Catalytic HDC of (A) 2-chlorophenol and (B) 2,4-dichlorophenol within the microreactor in water at room temperature under atmospheric pressure. Reaction conditions: 2-chlorophenol (2.0 mmol) or 2,4-dichlorophenol (2.0 mmol), NaOH (2.0 mmol), and 4.80 mL of the aqueous dispersion of the microreactor containing 4.0×10^{-3} mmol of Pd catalyst, bubbling H₂ at 25 °C under atmospheric pressure.

The present microreactor offers a turnover frequency (TOF) value of 628 h⁻¹ in the catalytic HDC of 4-chlorophenol (TOF is measured as moles product per molar Pd per hour in the initial 5 min). To further evaluate the microreactor, we used a reference catalyst of Pd nanoparticles. The reference catalyst is prepared by immobilizing 4.1 nm Pd nanoparticles, the size of which is very close to those of the microreactor, on solid microspheres of the coated microspheres. The solid microspheres are composed of the PS segment and the chelate PAEMA segment and the hydrophilic PAM segment similar with the PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres, but they do not have hollow or porous structure (seeing the TEM image of the reference catalyst in the Supporting Information). As shown in plots A and B in Figure 5, the present microreactor is much more efficient than the reference catalyst (TOF 628 h⁻¹ vs 260 h⁻¹) under the same HDC reaction conditions. We think that the selective concentration of 4-chlorophenol within the hollow microspheres of the microreactor contributes the efficient HDC conversion. In addition, compared with several reference Pd nanocatalysts (37), the microreactor is very competitive because it can realize the catalytic HDC reaction efficiently on mild conditions such as at room temperature under atmosphere pressure.

The microreactor can also be employed for the catalytic HDC of 2-chlorophenol and 2,4-dichlorophenol in water at room temperature under atmosphere pressure. For the catalytic HDC of 2-chlorophenol (Figure 6A), the conversion

Table 1. Catalyst Recycling of the Microreactor for the Catalytic HDC of 4-Chlorophenol in Water at Room Temperature under Atmospheric Pressure.^a

	run			
	first	second	third	fourth
yield (%)	99	100	99	98

^a Reaction conditions: 4.80 mL of the aqueous dispersion of the microreactor containing 4.0×10^{-3} mmol of Pd catalyst (ONLY for the 1st run), 4-chlorophenol (2.0 mmol), NaOH (2.0 mmol), bubbling H₂ at 25 °C under atmospheric pressure for 2 h.

of 2-chlorophenol increases almost linearly along with time in the initial 90 min; therefore the reaction shows a quasi-zero-order kinetics to 2-chlorophenol concentration. All 2-chlorophenol can be catalytically converted into phenol in 3 h. The TOF value of 233 h⁻¹ in the HDC of 2-chlorophenol is lower than that of 4-chlorophenol, which may be ascribed to the steric hindrance from the ortho substituent of the hydroxyl group. For the catalytic HDC of 2,4-dichlorophenol (Figure 6B), two intermediates of 2-chlorophenol and 4-chlorophenol are detected and the catalytic HDC of 2,4-dichlorophenol is expected to be a stepwise dechlorination process as described in the inset of Figure 6B. The mole fraction of the 2-chlorophenol intermediate in solution exhibits a time-dependent maximum at 100 min and then declines continuously with the increase in the conversion of 2,4-dichlorophenol. The 4-chlorophenol intermediate seems a little abnormal, the mole fraction of which almost slightly increases and keeps a constant of 9%, even when 90% conversion of 2,4-dichlorophenol is achieved. This possibly suggests that formation of the 4-chlorophenol intermediate is the primary dechlorination of 2,4-dichlorophenol in the present study. The TOF value of 157 h⁻¹ in the HDC of 2,4-dichlorophenol is lower than that of 4-chlorophenol or 2-chlorophenol. The reason is partly ascribed to the steric hindrance and partly to the low electron density associated with the phenyl ring of 2,4-dichlorophenol.

The reusability of the microreactor of Pd nanoparticles immobilized shell-corona hollow microspheres is also tested employing the HDC of 4-chlorophenol as a typical example. When the catalytic HDC reaction is just completed in 2 h, the microreactor is collected by centrifugation and used for the next cycle of HDC reaction. It is found that the microreactor can be used at least four times without significant loss of activity as shown in Table 1. The centrifuged aqueous phase is further analyzed by atomic absorption spectroscopy (AAS) and the Pd catalyst leaching in aqueous phase is not detected. These results suggest good reusability and low catalyst leaching of the microreactor of Pd-nanoparticle-immobilized hollow microspheres for the catalytic HDC reactions in water.

4. CONCLUSIONS

A microreactor for catalytic hydrodechlorination of chlorophenols in the sole solvent of water has been prepared by immobilizing Pd nanoparticles on shell-corona hollow polymeric microspheres. The PS-*co*-PAEMA-*co*-PAM shell-corona hollow microspheres, which are synthesized by template

polymerization, are composed of three parts: (1) the hydrophilic PAM corona; (2) the cross-linked and hydrophobic wall of PS-*co*-PAEMA; (3) the microcavity. The microreactor of 3.9 nm Pd nanoparticles immobilized shell-corona hollow microspheres are prepared first through coordination between the chelate PAEMA segment with PdCl_2 and then by reduction. The unique structure of the shell-corona hollow microspheres endue the microreactor advantages including easy dispersion in the solvent of water as similar as a quasi-homogeneous catalyst, selective concentration of the chlorophenol reactant and excretion of the phenol product. Because of the combined advantages, efficient catalytic hydrodechlorination of chlorophenols can be realized within the microreactor in water at room temperature under atmosphere pressure. The microreactor of Pd-nanoparticle-immobilized shell-corona hollow microspheres is also demonstrated to be recyclable and low-leaching palladium catalyst for HDC reaction in water.

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Supporting Information Available: Synthesis and characterization of the shell-corona hollow microspheres, TEM image of the reference catalyst of Pd-nanoparticle-immobilized coated microspheres, and base effect on the catalytic HDC reaction (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Ramamoorthy, S.; Ramamoorthy, S. *Chlorinated Organic Compounds in the Environment*; CRC Press: Boca Raton, FL, 1997.
- Juhler, R. K.; Sorensen, S. R.; Larsen, L. *Water Res.* **2001**, *35*, 1371.
- Keane, M. A. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1211.
- Keane, M. A. *Green Chem.* **2003**, *5*, 309.
- Addink, R.; Altwicker, R. E. *Carbon* **2004**, *42*, 2661.
- Gonzalez-Velasco, J. R.; Aranzabal, A.; Lopez-Fonseca, A.; Ferret, R.; Gonzalez-Marcos, J. A. *Appl. Catal., B* **2000**, *24*, 33.
- Pera-Titus, M.; Garcia-Molina, V.; Banos, M. A.; Gimenez, J.; Espugas, S. *Appl. Catal., B* **2004**, *47*, 219.
- Fabbri, D.; Biancano, P. A.; Pramauro, E. *Appl. Catal., B* **2004**, *49*, 233.
- Piera, E.; Calpe, J. C.; Brillas, E.; Domenech, X.; Peral, J. *Appl. Catal., B* **2000**, *27*, 169.
- Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2002**, *102*, 4009.
- Yuan, G.; Keane, M. A. *Ind. Eng. Chem. Res.* **2007**, *46*, 705.
- Liu, J.; He, F.; Durham, E.; Zhao, D.; Roberts, C. B. *Langmuir* **2008**, *24*, 328.
- Liu, Q.; Cui, Z.; Ma, Z.; Bian, S.; Song, W. *J. Phys. Chem. C* **2008**, *112*, 1199.
- Babu, N. S.; Lingaiah, N.; Gopinath, R.; Reddy, P. S. S.; Prasad, P. S. *S. J. Phys. Chem. C* **2007**, *111*, 6447.
- Schuth, C.; Reinhard, M. *Appl. Catal., B* **1998**, *18*, 215.
- (a) Gomez-Quero, S.; Cardenas-Lizana, F.; Keane, M. A. *Ind. Eng. Chem. Res.* **2008**, *47*, 6841. (b) Xu, J.; Bhattacharyya, D. *Ind. Eng. Chem. Res.* **2007**, *46*, 2348. (c) Jin, Z.; Yu, C.; Wang, X.; Wan, Y.; Li, D.; Lu, G. *Chem. Commun.* **2009**, 4438.
- Diaz, E.; Casas, J. A.; Mohedano, A. F.; Calvo, L.; Gilarranz, M. A.; Rodriguez, J. J. *Ind. Eng. Chem. Res.* **2008**, *47*, 3840.
- Vriezema, D. M.; Aragones, M. C.; Elemans, J. A. A. W.; Cornelissen, J. L. M.; Rowan, A. E.; Nolte, R. J. M. *Chem. Rev.* **2005**, *105*, 1445.
- Leeder, S. M.; Gagné, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 9048.
- Ueno, T.; Suzuki, M.; Goto, T.; Matsumoto, T.; Nagayama, K.; Watanabe, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 2527.
- Vriezema, D. M.; Garcia, P. M. L.; Oltra, N. S.; Hatzakis, N. S.; Kuiper, S. M.; Nolte, R. J. M.; Rowan, A. E.; Hest, J. C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7378.
- For reviews on polymeric capsules, see: (a) Lensen, D.; Vriezema, D. M.; van Hest, J. C. M. *Macromol. Biosci.* **2008**, *8*, 991. (b) Meier, W. *Chem. Soc. Rev.* **2000**, *29*, 295. (c) Sukhorukov, G.; Fery, A.; Mohwald, H. *Prog. Polym. Sci.* **2005**, *30*, 885.
- (a) Marinakos, S. M.; Anderson, M. F.; Ryan, J. A.; Martin, L. D.; Feldheim, D. L. *J. Phys. Chem. B* **2001**, *105*, 8872. (b) Caruso, F.; Yang, W.; Trau, D.; Renneberg, R. *Langmuir* **2000**, *16*, 8932. (c) Marinakos, S. M.; Novak, J. P.; Brousseau III, L. C.; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518. (d) Ghan, R.; Shutava, T.; Patel, A.; John, V. T.; Lvov, Y. *Macromolecules* **2004**, *37*, 4519. (e) Koo, B.-M.; Jung, J.-E.; Han, J.-H.; Kim, J.-W.; Han, S.-H.; Chung, D. J.; Suh, K.-D. *Macromol. Rapid Commun.* **2008**, *29*, 498. (f) Zelikin, A. N.; Becker, A. L.; Johnston, A. P. R.; Wark, K. L.; Turatti, F.; Caruso, F. *ACS Nano* **2007**, *1*, 63.
- Kim, E.; Lee, J.; Kim, D.; Lee, K. E.; Han, S. S.; Lim, N.; Kang, J.; Park, C. G.; Kim, K. *Chem. Commun.* **2009**, 1472.
- Miao, S.; Zhang, C.; Liu, Z.; Han, B.; Xie, Y.; Ding, S.; Yang, Z. *J. Phys. Chem. C* **2008**, *112*, 774.
- Ng, Y. H.; Ikeda, S.; Harada, T.; Higashida, S.; Sakata, T.; Mori, H.; Matsumura, M. *Adv. Mater.* **2007**, *19*, 597.
- Ikeda, S.; Ishino, S.; Harada, T.; Okamoto, N.; Sakata, T.; Mori, H.; Kuwabata, S.; Torimoto, T.; Matsumura, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7063.
- Lan, Y.; Zhang, M.; Zhang, W.; Yang, L. *Chem.—Eur. J.* **2009**, *15*, 3670.
- (a) Sun, Q.; Deng, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8274. (b) Xu, X.; Asher, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7940. (c) Marinakos, S. M.; Shultz, D. A.; Feldheim, D. L. *Adv. Mater.* **1999**, *11*, 34. (d) Li, G.; Liu, G.; Kang, E. T.; Neoh, K. G.; Yang, X. *Langmuir* **2008**, *24*, 9050. (e) Fleming, M. S.; Mandal, T. K.; Walt, D. R. *Chem. Mater.* **2000**, *12*, 3481. (f) Feng, Z.; Wang, Z.; Gao, C.; Shen, J. *Chem. Mater.* **2007**, *19*, 4648. (g)
- Zheng, P.; Zhang, W. *J. Catal.* **2007**, *250*, 324.
- Kaliyappan, T.; Kannan, P. *Prog. Polym. Sci.* **2000**, *25*, 343.
- Krasia, T.; Soula, R.; Börner, H. G.; Schlaad, H. *Chem. Commun.* **2003**, 558.
- Wen, F.; Zhang, W.; Zheng, P.; Zhang, X.; Yang, X.; Wang, Y.; Jiang, X.; Wei, G.; Shi, L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1192.
- (a) Ren, N.; Yang, Y.-H.; Zhang, Y.-H.; Wang, Q.-R.; Tang, Y. *J. Catal.* **2007**, *246*, 215. (b) Biffis, A.; Cunial, S.; Spontoni, P.; Prati, L. *J. Catal.* **2007**, *251*, 1. (c) Zhang, J.; Zhang, W.; Wang, Y.; Zhang, M. *Adv. Synth. Catal.* **2008**, *350*, 2065.
- Urbano, F. J.; Marinas, J. M. *J. Mol. Catal. A* **2001**, *173*, 329.
- Jong, D. V.; Louw, R. *Appl. Catal., A* **2004**, *271*, 153.
- (a) Hara, T.; Mori, K.; Oshiba, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Green Chem.* **2004**, *6*, 507. (b) Nakao, R.; Rhee, H.; Uozumi, Y. *Org. Lett.* **2005**, *7*, 163. (c) Hara, T.; Kaneta, T.; Mori, K.; Mitsudome, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Green Chem.* **2007**, *9*, 1246. (d) Shindler, Y.; Matatov-Meytal, Y.; Sheintuch, M. *Ind. Eng. Chem. Res.* **2001**, *40*, 3301.

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