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Reactivity of Pd/Fe Bimetallic Nanotubes in Dechlorination of Coplanar Polychlorinated Biphenyls

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Abstract

A new class of bimetallic materials based on palladium-decorated iron nanotubes is described that demonstrates high reactivity in dechlorination reactions. This high dechlorination efficiency was attributed to the high surface area to volume ratio of the hollow nanotubes structure. Herein, we evaluated the effect of different conditions, such as the nanotube size, and the palladium loading on the efficiency of the dechlorination of PCB 77, a model coplanar polychlorinated biphenyl (PCB), by the Pd/Fe bimetallic nanotubes system. The efficiency of the dechlorination was lowered by decreasing the tube diameter from 200 to 100 nm. In addition, the interior surface as well as the exterior surface of the as-synthesized Pd/Fe bimetallic nanotubes was found to contribute to the high efficiency of the dechlorination of PCB 77. The dechlorination of PCB 77 by Pd/Fe bimetallic nanotubes demonstrated small activation energy indicating diffusion controlled reaction. The as-prepared Pd/Fe bimetallic nanotubes showed extended lifetime activity when used in multiple dechlorination cycles.

Keywords

Polychlorinated Biphenyls; Bimetallic nanotubes; dechlorination; Palladium/Iron

1. Introduction

Polychlorinated biphenyls (PCBs) are a well-defined class of environmental contaminants that have adverse effects on human health as well as the ecosystem.(Ross et al., 2000; Aliyu et al., 2010) Consequently, much attention has been given to the design of methods that lead to the degradation of PCBs.(Venkatachalam et al., 2008; Gorbunova et al., 2010) Several approaches, including traditional, biological, and chemical methods, have been followed for the remediation of PCBs.(Chang et al., 2006; Beyer and Biziuk, 2009; Van Aken et al.,

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Appendix A. Supporting Information

2010) Among the chemical methods, the reductive dechlorination by palladium/iron (Pd/Fe) bimetallic nanoparticles has been proven an effective remediation technology.(Zhang, 2003; Choi et al., 2008) This high efficiency of dechlorination is attributed to the surface area to volume ratio of the nanoscale particles. However, owing to their high reactivity and magnetic properties, nanoparticles tend to aggregate and lose their surface area, which impact the rate of the dechlorination reaction.(Zhang, 2003; Nurmi et al., 2005) Consequently, Pd/Fe nanoparticles are usually produced in the presence of surfactant or embedded in solid supports to achieve high dechlorination efficiency.(Bhattacharyya, 2007; Joo and Zhao, 2008) We addressed this challenge from a different direction based on the hypothesis that the nanotube architecture exhibits higher surface to volume ratio than nanoparticles even when aggregates are formed. We developed a new class of nanostructured material based on bimetallic nanotubes of Fe decorated with Pd nanoparticles that had high surface to volume ratio.(Zahran et al., 2011) The Pd/Fe bimetallic nanotubes demonstrated higher reactivity in dechlorination of PCBs than the comparable nanoparticles.

Various factors affect the efficiency of dechlorination of PCBs by Pd/Fe bimetallic nanostructures.(Liu and Lowry, 2006; Xu and Bhattacharyya, 2008) For instance, decreasing the size of Pd/Fe particles increases the surface to volume ratio, which in turn enhances the efficiency of dechlorination.(Wu et al., 2005) Nanoscale Pd/Fe particles have demonstrated much higher reactivity in dechlorination of PCBs than macroscale particles.(Wang and Zhang, 1997) Further, increasing the palladium loading of the Pd/Fe nanostructures increases the amount of active sites available for catalysis, thereby increasing the dechlorination reaction rate.(Chun et al., 2010) On the other hand, the presence of excessive (more than one monolayer coating) amount of palladium in Pd/Fe nanostructured material passivates the iron surface for further reaction in aqueous medium to produce hydrogen, which leads to low dechlorination efficiency. Thus, when designing new classes of material for catalytic dechlorination reactions, these factors should be evaluated experimentally. The objectives of the work described herein are i) to evaluate the effect of chlorine position in PCB 77 dechlorination by Pd/Fe bimetallic nanotubes, ii) to study the effect of nanotube size on the efficiency of dechlorination of PCB 77, iii) to determine the effect of the hollow interior of the Pd/Fe nanotubes on the efficiency of dechlorination of PCB 77, iv) to investigate the effect of palladium content on the reactivity of Pd/Fe nanotubes, and v) to calculate the activation energy of the dechlorination reaction. The stability of the as-prepared Pd/Fe bimetallic nanotubes for multiple dechlorination cycles was also evaluated.

2. Experimental

2.1. Synthesis of Pd/Fe nanotubes

Pd/Fe bimetallic nanotubes with various outer diameters were prepared according to a procedure described by us previously.(Zahran et al., 2011) Briefly, polycarbonate membranes (PC) of 47 mm diameter and pore sizes of 100, 200 and 400 nm (Millipore, Billerica, MA) were placed between the two compartments of a custom made U-tube reaction cell. In this design, the nanoporous membrane separates the two precursors of the electroless reduction; 1×10^{-3} M ferrous sulfate stabilized with 1×10^{-2} M ascorbic acid and 1×10^{-2} M sodium borohydride. Upon the diffusion of these reaction precursors into the

membrane pores, Fe(0) is deposited on the membrane pore walls as a result of a localized electroless reduction reaction. The as-prepared Fe nanotubes were extracted by dissolving the PC membrane in 10 mL methylene chloride, and washing two times with methylene chloride and two times with ethanol. Palladium nanoparticles were deposited on the surface of the Fe nanotubes by adding 1 mg of palladium acetate to 10 mL Fe nanotubes colloidal solution.

Pd/Fe bimetallic nanorods of 200 nm in outer diameter were prepared by running the U-tube reaction for 10 h. Solid sodium borohydride was added into the reductant side every two hours to replace the loss of borohydride because of its decomposition. This platform ensured ultimate nucleation of the Fe(0) to fill the membrane pores.

In-situ Pd/Fe bimetallic nanotubes were prepared inside the PC membrane. Polycarbonate membranes with 200 nm outer diameter Fe nanotubes were prepared according to the aforementioned procedure. Subsequently, the membrane was washed three times with oxygen-free deionized water and three times with ethanol. Palladium nanoparticles were deposited on the internal surface of the Fe nanotubes by filling the U-tube reaction cell with ethanolic solution of palladium acetate. After washing, these membranes were used as is for dechlorination of PCB 77.

2.2. Characterizations of Pd/Fe nanotubes

A Philips XL30 field-emission environmental scanning electron microscope (Philips XL30 ESEM-FEG) running at 20 kV and equipped with an Oxford energy-dispersive X-ray detector was used for characterization of the morphology of the as-prepared Fe nanotubes. Transmission electron microscopy (TEM) images of Fe nanotubes and Pd/Fe nanotubes were obtained using a JEOL 2010F field emission electron microscope equipped with an energy-dispersive X-ray detector and running at an accelerating voltage of 200 kV. A Varian Vista-Pro CCD Simultaneous ICP-OES was used to determine the metallic composition of the Fe and Pd/Fe nanoparticles and nanotubes.

2.3. Dechlorination experiment

The dechlorination of 3,3',4,4'-tetrachlorobiphenyl (PCB 77), a tetrachlorinated PCB congener, was performed in 65-mL or 20-mL glass vials with PTFE septa caps in which 60 mL or 18 mL of 25 μ M 50/50 (v/v) ethanol/water solution of PCB 77 was added. A calculated amount of Pd/Fe bimetallic nanotubes produced from two PC membranes was added into each vial in order to have consistent metal loading of $\approx$ 0.25 mg/mL. In the case of nanorods, two membranes provided a metal loading of 0.8 mg/mL. The head space in all vials was purged with ultra-high purity nitrogen. All vials were placed on a VX-2500 multi-tube vortexer (VWR, Radnor, PA) at maximum agitation speed for the duration of the reaction. At specific time intervals, the glass vial was placed on a strong magnet to collect the Pd/Fe nanotubes or nanorods at the bottom of the vial, while a sample of 1-mL was withdrawn using a glass syringe. The sample was then combined with 1 mL hexanes in a 5-mL glass vial in order to extract PCB 77 and dechlorination products. The analysis of the samples was achieved using GC-MS (Agilent, Santa Clara, CA); dodecane was used as internal standard. The reuse of the material for multiple dechlorination cycles was conducted

by replacing the reaction solution with a fresh 25 μM 50/50 (v/v) ethanol/water solution of PCB 77 when ultimate dechlorination had been achieved.

3. Results and discussion

The U-tube template based method was used to prepare Fe(0) nanotubes with different outer diameters. Palladium particles were post-deposited on the Fe nanotubes from an ethanolic solution of palladium acetate. Following this procedure, we were able to produce 100, 200, and 400 nm Pd/Fe bimetallic nanotubes (Fig. 1). These nanotubes were found to exhibit body-centered cubic crystalline structure with high degree of metallic properties. (Zahran et al., 2011)

It is well established that the reductive dechlorination of PCBs with metallic iron based particles follows a stepwise mechanism, in which a chlorine atom is replaced by hydrogen at each step of the reaction. (Yak et al., 2000; Agarwal et al., 2009) PCB 77 is a tetrachloro coplanar PCB single congener with one chlorine at the *meta* and one chlorine at the *para* positions on each of the two benzene rings. Accordingly, the stepwise dechlorination mechanism of PCB 77 can be represented by removing one chlorine atom at a time (see Fig. 1SI in Supporting Information). (Yak et al., 2000) All daughter dechlorination products of PCB 77 were detected, and their amounts were determined during the course of the dechlorination reaction using Pd/Fe bimetallic nanotubes. It has been noted previously in the literature that the selectivity of the dechlorination reaction depends on the position of the chlorine atom, and it follows the order *para* > *meta* >> *ortho*. (Greaves et al., 1994; Miyoshi et al., 2000) Accordingly, the ratios of all daughters along with PCB 77 and biphenyl produced from the dechlorination of 25 μM PCB 77 using 0.25 mg/mL Pd/Fe bimetallic nanotubes were calculated relative to the carbon balance. These results are depicted in Fig. 2. It is evident from the data that dechlorination takes place preferentially at the *para* substituted chlorines over the *meta* ones. For instance, the measured amount of PCB 35 with two *meta*-substituted chlorines is about 15-fold higher than that of PCB 37, which has two *para* substituted chlorines. Similar *meta/para* substituted chlorines preference was noticed among the di- and mono-chloro-biphenyl products. This trend is consistent with previous reports that used zerovalent iron in subcritical water at 250 °C and 10 MPa to dechlorinate PCBs. (Yak et al., 2000) However, the *meta/para*-substituted chlorines selectivity noticed here is 10-fold higher than the reported value, indicating a high reactivity of the Pd/Fe bimetallic nanotubes toward meta-substituted chlorines.

3.1. Effect of nanotube size

As shown in Fig. 1, we synthesized Pd/Fe bimetallic nanotubes that had outer diameters of 400, 200, and 100 nm. The synthesized nanotubes had a length, L , of 3–7 μm . Assuming an outer nanotube diameter of $2R$ and an inner diameter of $2r$, the surface area A_{NT} of a nanotube can be calculated from the following equation:

$$A_{NT} = 2\pi L(R + r) + 2\pi(R^2 - r^2)$$

Because $L \gg R$, $2\pi L(R + r) \gg 2\pi(R^2 - r^2)$, and therefore

$$A_{NT} \approx 2\pi L(R+r)$$

The volume of this tube can be calculated from the following equation:

$$V_{NT} = \pi L(R^2 - r^2)$$

Thereby, the surface-to-volume ratio, $\frac{A_{NT}}{V_{NT}}$, is equal to $\frac{2}{R-r}$. In other words, the surface-to-volume ratio does not change with L as long as $L \gg R$ of the tube, yet depends on the thickness ($R-r$) of the nanotube wall. Therefore, if there is no other factor affecting the dechlorination reaction, nanotubes of different diameters but having the same wall thickness should demonstrate similar dechlorination efficiencies. To investigate this hypothesis, the dechlorination of a 25 μM solution of PCB 77 was carried out using Pd/Fe bimetallic nanotubes having outer diameter of 400, 200 and 100 nm. As shown in Fig. 3, complete dechlorination of PCB 77 was achieved within 10 or 24 h of the reaction using 400 or 200 and 100 nm Pd/Fe bimetallic nanotubes, respectively. The plots of $-\ln(C/C^0)$ vs time were linear for the first 3 h, indicating a pseudo-first order kinetic behavior.

$$\ln \frac{C_{\text{PCB}}}{C_{\text{PCB}}^0} = -k_{\text{obs}}t$$

Mass-normalized rate constants, k_1 , were calculated for different Pd/Fe bimetallic nanotubes based on the observed rate constant, k_{obs} , and the metal loading according to the following equation:

$$\ln \frac{C_{\text{PCB}}}{C_{\text{PCB}}^0} = -k_{\text{obs}}t = -k_1\rho_m t$$

In this approach, the values of k_1 reflect the difference in the surface area to volume ratio between different nanotubes. (Fang and Al-Abed, 2008) It was found that there was no significant difference between the rates of the dechlorination reactions when using 400 or 200 nm nanotubes with rate constants, k_1 , of 3.96 and 4.12 $\text{L g}^{-1} \text{h}^{-1}$, respectively (Fig. 3 inset). On the other hand, the 100 nm Pd/Fe nanotubes demonstrated a slower dechlorination rate with k_1 of 2.84 $\text{L g}^{-1} \text{h}^{-1}$. This decline in the efficiency of the dechlorination is attributed to an increase of the nanotube wall thickness. It might be also attributed to limited diffusion of the reactants into the internal surface of the nanotube as the tube inner diameter becomes smaller.

The hollow interior of the nanotube architecture provides with high surface-to-volume ratio for the catalytic reaction. In order to evaluate the effect of the internal surface of the nanotube on the efficiency of the dechlorination reaction, Pd/Fe bimetallic nanotubes were prepared inside the PC membrane. In such architecture, the external surface of the Fe nanotube is obstructed by the PC membrane template, and only the internal surface is

available for palladium deposition and dechlorination reaction. On the other hand, in order to evaluate the effect of the external surface of the Pd/Fe bimetallic nanotubes on the efficiency of the dechlorination reaction, Pd/Fe nanorods of 200 nm diameter were also synthesized. The dechlorination results of 25 μM PCB 77 using 200 nm Pd/Fe bimetallic nanotubes, 200 nm Pd/Fe bimetallic nanotubes in membrane, and 200 nm Pd/Fe bimetallic nanorods are shown in Fig. 2SI (Supporting Information). The free Pd/Fe bimetallic nanotubes displayed high dechlorination rate with 95% degradation of PCB 77 in the first 5 h of the batch reaction. On the other hand, the Pd/Fe bimetallic nanorods and the Pd/Fe bimetallic nanotubes in membrane (i.e, those that had Pd only in the interior surface) exhibited much slower rates, with about 90% and 75% degradation in 24 h for nanorods and nanotubes in membrane, respectively. Rate constants k_I were calculated from the linear best fit line in the first 2 h of the reactions to be 4.8, 0.68, and 1.72 $\text{L g}^{-1} \text{h}^{-1}$ for free nanotubes, nanorods, and nanotubes in membrane, respectively. These values indicate that both the internal and the external surface of the hollow tube contribute to the high efficiency of dechlorination of the synthesized Pd/Fe bimetallic nanotubes.

3.2. Effect of palladium loading

The amount of the catalyst plays a vital role in the dechlorination reaction. Therefore, the optimum amount of the catalyst should be identified experimentally. As described previously, (Zahran et al., 2011) palladium particles were deposited as a uniformly distributed monolayer on the surface of Fe nanotubes. This architecture provides high concentration of active sites for the catalytic hydrodechlorination reaction between PCB 77 molecules and active hydrogen. To study the effect of palladium content on the reactivity of the as-synthesized Pd/Fe bimetallic nanotubes, four batches of nanotubes were synthesized with different palladium content. The Pd wt% in these batches was determined by ICP-AES analysis as 0.9, 1.9, 3.2, and 5.1 wt%. Four batch dechlorination reactions of 25 μM PCB 77 solutions were conducted using consistent metal loading of 0.25 mg/mL of Pd/Fe bimetallic nanotubes with different contents (Fig. 4). k_{obs} values of 0.58, 1.22, 1.84, and 2.25 h^{-1} were determined for Pd/Fe nanotubes with 0.9, 1.9, 3.2, 5.1 Pd wt%, respectively. A batch reaction with iron nanotubes (0 wt% Pd) showed insignificant dechlorination of PCB 77. Plotting the values of the rate constant, k_{obs} , against the Pd wt% (Fig. 4, inset) indicated linear relationship between k_{obs} and Pd content in the Pd/Fe bimetallic nanotubes. The deviation from linearity after 3 wt% Pd might be attributed to the number of catalytic active sites becoming more than that required for the reaction. In addition, high palladium coverage on the Fe(0) surface of the nanotube blocks Fe(0) from reacting with water to produce the hydrogen required for the dechlorination.

3.3. Effect of temperature

For most chemical processes, temperature is a factor that influences the rate of the reaction. For instance, the dechlorination of PCBs with zerovalent iron particles has demonstrated very slow reaction rates. Therefore, severe conditions of pressure and temperature (400 °C) were required to achieve complete dechlorination. (Chuang et al., 1995) Generally, a catalyst is used to decrease the activation energy, E_a , of a chemical process. Doping the zerovalent iron with catalytic metal particles such as palladium or nickel made the dechlorination of PCBs accessible at ambient conditions. (Schreier and Reinhard, 1995; Siantar et al., 1996)

Evaluation of the activation energy of the reaction provides insight on the mechanism of the reaction. (Su and Puls, 1999; Xu and Bhattacharyya, 2007) It is generally accepted that reactions that involve a physical process as the rate determining step exhibit small activation energies ($E_a < 30 \text{ kJ mol}^{-1}$). (Laidler, 1987) On the other hand, high activation energy indicates that the reaction is controlled by reaction at the metal-water interface. (Laidler, 1987) For instance, Xu and Bhattacharyya reported $E_a = 24.5 \text{ kJ mol}^{-1}$ for the dechlorination of dichlorobiphenyl by membrane-supported Pd/Fe nanoparticles suggesting a diffusion-controlled reaction. (Xu and Bhattacharyya, 2007) On the other hand, Tratnyek and co-workers found that the dechlorination of CCl_4 by zerovalent iron particles is a chemical process controlled reaction. (Scherer et al., 1997) The effect of temperature on the bimetallic nanotubes system described here was investigated by conducting two batch dechlorination reactions of PCB 77 at 25 and 40 °C. Values of k_{obs} of 0.8 and 1.4 h^{-1} were calculated from the linear fit line of the dechlorination reactions at 25 and 40 °C, respectively. Subsequently, the apparent activation energy was calculated according to Arrhenius equation to be 29 kJ mol^{-1} . This value indicates that the diffusion of PCB 77 through the solution to the palladium surface is the rate-determining step of the dechlorination reaction with Pd/Fe bimetallic nanotubes.

3.4. Stability and Catalyst Reuse

Long stability of the Pd/Fe nanostructures is very important for in-situ remediation. However, owing to the high reactivity of these nanostructures in aqueous solution, their dechlorination efficiency is diminished as a result of surface oxidation and deposition of iron oxides/hydroxide. (Sarathy et al., 2008; Choi et al., 2009; Yan et al., 2010) To study the long term reactivity of the as-synthesized Pd/Fe bimetallic nanotubes, eight dechlorination cycles of PCB 77 were conducted with the same amount of Pd/Fe bimetallic nanotubes. Complete dechlorination was achieved within the first 12 h of the reaction for the first 4 cycles, while 90% dechlorination was noticed within 24 h for the last 4 cycles (Fig. 3SI Supporting Information). In order to investigate the cause of this deactivation, fresh amount of Fe nanotubes and palladium nanoparticles were individually added to two vials with the Pd/Fe bimetallic nanotubes after eight dechlorination cycles. Subsequently, an amount of 50 mL of $25 \mu\text{M}$ PCB 77 was added to each vial and the batch dechlorination reaction was run as described in the experimental section. The vial with fresh Fe nanotubes showed 75% dechlorination in two days of the reaction. On the other hand, no dechlorination was noticed for the vial with fresh palladium nanoparticles. This indicates that the decline in the dechlorination efficiency is attributed to the deposition of iron oxides/hydroxide on the nanotubes surface that limits further reaction. Further, TEM images were acquired for Pd/Fe nanotubes after dechlorination. We found that some short length nanotubes were still present after being used in eight dechlorination cycles, and most of the nanotubes had opened forming nanosheets (Fig. 5). However, such transformation (nanotube/nanosheet) maintains high exposed surface area, which explains the long lifetime dechlorination reactivity of these nanotubes. HRTEM imaging shows core/shell architecture with different crystalline structures, which are attributed to a core of iron metal covered with a shell of iron oxides/hydroxide. This was further proven by EDS analysis, which showed a broad peak at 0.5 keV. However, quantification of the oxygen percentage could not be achieved from the EDS spectrum because of the overlap between the oxygen peak and the Fe L α peak. Therefore, to

investigate the ensemble of the iron, palladium, and iron oxides/hydroxide in the material after dechlorination, EDS mapping in dark field STEM mode was acquired. In this case, the iron K α peak, which is very distal from the oxygen peaks, was collected along with the Pd L α and oxygen K α while scanning a small area of the material with the 1-nm electron probe. As evident from Fig. 5, the palladium map indicates the presence of Pd in the nanotubes after eight dechlorination cycles, which is consistent with the aforementioned dechlorination experiments. The composed mapping image in Fig. 5 indicates the presence of a surface layer of iron oxide on a core of metallic iron. This layer limits the interaction of the Pd/Fe nanomaterial with the reactants.

4. Conclusions

Pd/Fe bimetallic nanotubes demonstrated high efficiency in dechlorination of the coplanar 3,3',4,4'-tetrachlorobiphenyl (PCB77). This efficiency was reflected on the stepwise mechanism of PCB 77 dechlorination by remarkably high selectivity for *para*-substituted PCBs over *meta*-substituted ones. Pd/Fe bimetallic nanotubes of 100 nm outer diameter showed reduced dechlorination efficiency in comparison with the 200 and 400 nm ones. The hollow interior of the as-synthesized Pd/Fe bimetallic nanotubes also contributes to their reactivity. Increasing the palladium content of the bimetallic nanotubes increases the rate of the dechlorination reaction in a linear fashion up to a content of 3 wt%, while further increasing the Pd ratio had lesser effect. The activation energy of the dechlorination reaction of PCB 77 by Pd/Fe bimetallic nanotubes was found to be 29 kJ mol⁻¹, suggesting that the diffusion of PCB 77 through the solution to the palladium surface is the rate-determining step. The as-synthesized Pd/Fe bimetallic nanotubes displayed extended lifetime reactivity in dechlorination reactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- ▶ Design of novel iron nanotube material decorated with palladium nanoparticles
- ▶ Pd/Fe nanotubes demonstrate high efficiency in dechlorination of PCBs
- ▶ The size of the tube, Pd content, and temperature affect the dechlorination efficiency
- ▶ The Pd/Fe nanotubes are stable for multiple dechlorination cycles

Fig. 1. Electron microscopy images of Fe metallic and Pd/Fe bimetallic nanotubes: (A) SEM image of partially dissolved PC membrane with 200 nm Fe nanotubes, (B) TEM image of 200 nm Fe nanotubes, (C) TEM image of 400 nm Pd/Fe nanotubes, (D) TEM image of 100 nm Fe nanotubes, and (E) high magnification image of 200 nm Pd/Fe nanotube.

Fig. 2.
Dechlorination profile of PCB 77 with Pd/Fe nanotubes. The Z-axis values represent the % of PCB 77 and other dechlorination products relative to the carbon balance.

Fig. 3. Dechlorination of 25 μM PCB 77 using Pd/Fe nanotubes of different outer diameter sizes with 0.25 mg/mL metal loading: (▲) 400 nm Pd/Fe nanotubes, (◆) 200 nm Pd/Fe nanotubes, and (●) 100 nm Pd/Fe nanotubes. Inset: linear fit kinetics of the dechlorination reaction, where C^0 is the initial concentration of PCB 77, and C is the concentration at the corresponding time.

Fig. 4. Dechlorination of 25 μ M PCB 77 using (metal loading of 0.25 mg/mL) Pd/Fe bimetallic nanotubes with 200 nm external diameter and different wt% of palladium: ($\blacktriangle$) 0.9 wt% palladium, ($\blacksquare$) 1.9 wt% palladium, ($\blacklozenge$) 3.2 wt% palladium and ($\bullet$) 5.1 wt% palladium. Inset: Effect of palladium loading on the rate of dechlorination of PCB 77 by Pd/Fe bimetallic nanotubes with 200 nm external diameter.

Fig. 5. TEM images of the Pd/Fe nanotubes after being used for eight dechlorination cycles. The green box denotes the area scanned with the electron beam and the yellow box denotes a reference area to track the spatial drift.