

Research Article

Dechlorination of Environmental Contaminants Using a Hybrid Nanocatalyst: Palladium Nanoparticles Supported on Hierarchical Carbon Nanostructures

Hema Vijwani,¹ Abinash Agrawal,² and Sharmila M. Mukhopadhyay¹

¹Center for Nanoscale Multifunctional Materials, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA

²Department of Earth and Environmental Sciences, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA

Correspondence should be addressed to Hema Vijwani, vijwani.2@wright.edu

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This paper demonstrates the effectiveness of a new type of hybrid nanocatalyst material that combines the high surface area of nanoparticles and nanotubes with the structural robustness and ease of handling larger supports. The hybrid material is made by fabricating palladium nanoparticles on two types of carbon supports: as-received microcellular foam (Foam) and foam with carbon nanotubes anchored on the pore walls (CNT/Foam). Catalytic reductive dechlorination of carbon tetrachloride with these materials has been investigated using gas chromatography. It is seen that while both palladium-functionalized carbon supports are highly effective in the degradation of carbon tetrachloride, the rate of degradation is significantly increased with palladium on CNT/Foam. However, there is scope to increase this rate further if the wettability of these structures can be enhanced in the future. Microstructural and spectroscopic analyses of the fresh and used catalysts have been compared which indicates that there is no change in density or surface chemical states of the catalyst after prolonged use in dechlorination test. This implies that these materials can be used repeatedly and hence provide a simple, powerful, and cost-effective approach for dechlorination of water.

1. Introduction

Chlorinated hydrocarbons (CHCs) are common organic contaminants in soil and groundwater across the globe that includes chlorinated alkanes, alkenes, and aromatic hydrocarbons. The presence of CHCs in drinking water sources is of great concern worldwide, as they are highly toxic and have adverse effects on human health and environment. Various CHC compounds have been widely manufactured and used in industrial applications, and they were intentionally or accidentally released into the environment. Due to their chronic toxicity, use of such chemicals was either banned or regulated in United States by US Environmental Protection Agency (US-EPA) and colloquially in most other developed countries [1, 2]. Mandatory groundwater monitoring has reported the presence of CHCs at a large number of sites. In spite of stringent regulations they are present in soil and groundwater even today due to their resistance to natural attenuation by microbiological degradation. Carbon

tetrachloride (CT), also known as tetrachloromethane, is among the widespread CHCs reported in impacted soil and ground water. CT was largely used in fire extinguishers, as cleaning and metal degreasing agents (solvents) and also as a chemical precursor compound for refrigerants like chloro-fluoro carbons [3]. CT can have adverse effects on the nervous system, liver, and kidneys. The US-EPA guidelines recognized it as a potential carcinogenic agent and regulated its maximum contaminant level (MCL) in drinking water at 5 µg/L. However, levels of CT reported in groundwater at many locations across the United States still exceed its MCL (safe drinking water limit) [4–6].

In recent years, there has been a growing emphasis on developing techniques for pollutant removal in groundwater by converting the highly toxic CHCs to less toxic nonchlorinated product. Catalytic reductive dechlorination technique employs transition metals as catalysts for treating CHCs in contaminated groundwater. The dechlorination reaction involves reduction/breaking of carbon-chlorine bonds by

molecular H_2 facilitated by a catalyst, where hydrogen replaces the chlorine in the compound, leading to a reduced chlorine compound. Common catalysts used for such applications include isolated or supported nanoparticles of metals such as Pd, Ni, or bimetals such as Pd/Fe, Ni/Fe [7, 8]. In this study, supported palladium nanoparticles (Pd-NPs) [9] are investigated, as Pd is well known to catalyze reductive dechlorination reactions.

Heterogeneous catalysis is a surface specific phenomenon; therefore attributes of support materials that provide attachment to catalyst particles may influence catalytic reactions. Support materials with a high specific surface area such as activated carbon, free-standing carbon nanotubes (CNTs), and carbon nanofibers (CNF) have been extensively used for anchoring metal nanocatalysts [10, 11]. In heterogeneous catalysis, the reactants are in liquid phase and the catalyst materials, although in solid phase, are mostly in suspended form (isolated or supported on free-standing nanotubes) [11]. However, for water treatment applications, supported nanoparticles in suspended form can pose a significant challenge, because successful recovery of nanoparticles from the treated water can be tedious. Nanoparticles, especially of precious metals, if not recovered completely from the treated water and reused, can be uneconomical, and presence of nanoparticles in drinking water may also pose safety hazards [12, 13], requiring further purification of the treated water thereby increasing the cost of treatment.

A new class of hybrid, microporous graphitic support designed for anchoring metal nanoparticles [9] can address the previous limitations and make it cost effective as they can prevent the loss due to dispersal and inefficient recovery of suspended nano catalysts. The microporous graphitic carbon supports (called "graphite foam," henceforth), investigated in this study, exhibit a robust yet porous structure that offers high surface area, while its surface area can be further enhanced by grafting carbon nanotube (CNT) on the microporous graphitic foam. Therefore, catalyst nanoparticles supported on such hierarchical structures can be easily loaded and unloaded into the liquid environment providing simple economical catalysis on an as-needed basis. The robustness, ease of handling, and structural integrity along with the high surface area stipulated by carbon nanotubes that are strongly attached to the microporous graphitic foam supports surpass other types of porous catalysts currently available.

The present study focuses on the bench-scale batch investigation of reductive dechlorination of carbon tetrachloride (CT) in the aqueous phase using two kinds of hybrid catalyst structures: Pd-NPs fabricated on graphitic foam support (Pd/Foam) and Pd-NPs on CNT-attached graphitic foam support (Pd/CNT/Foam). Batch experiments were performed to characterize the catalytic transformation of CT and formation of degradation products with Pd/Foam and Pd/CNT/Foam. Durability of these structures for structural integrity and chemical stability was also investigated by monitoring the chemical and physical state of fresh and used catalyst materials after repeated cycles of use. Reusability of the Pd/Foam and Pd/CNT/Foam was also examined in repeated batch experiments at similar conditions. Various

experimental parameters examined in the investigation include (i) the effect of varying amount of supported catalysts and (ii) the effect of varying H_2 concentration, on CT degradation kinetics and daughter product formation.

2. Materials and Methods

2.1. Chemicals. The reagents used in this study were of analytical grade and used without further purification including carbon tetrachloride (CCl_4 , Fisher Scientific), chloroform ($CHCl_3$, Fisher Scientific), sodium hydroxide (solid, 97.0% NaOH, EMD Chemicals Inc.), and TAPSO buffer (99%, $C_7H_{17}NO_7S$, Sigma-Aldrich Inc.). Other materials are MilliQ DI water, high purity gases (zero grade) that include pure nitrogen, and hydrogen-nitrogen gas mixes (5% H_2 with balance N_2 and 50% H_2 with balance N_2). The CT stock solution was prepared by adding 20 μ L of the CT compound to a 160 mL borosilicate glass serum bottle containing organic-free Milli-Q water that was sealed with a Teflon-lined rubber stopper and aluminum crimp without headspace. The bottle was then placed on a rotary shaker for 72 hours to allow the CT compound to dissolve completely.

2.2. Hybrid Catalysts Preparation. Two types of hybrid catalyst structures are investigated: Pd nanoparticles supported on graphitic foam (Pd/Foam) and palladium nanoparticles supported on carbon nanotubes that are strongly attached to graphitic foams (Pd/CNT/foam). The microcellular graphitic foam used in this study was L1a grade foam provided by Koppers Inc. The linear dimensions (lbh) of each hybrid catalyst structure were $10 \times 5 \times 2$ mm³, weighing 55 mg approximately.

CNTs were grafted on the microcellular graphitic foam by chemical vapor deposition technique using iron as floating catalyst, details of which are published earlier [14–16]. Pd-NPs on graphitic foam and CNT-attached graphitic foam were synthesized by liquid-phase synthesis technique combined with thermal reduction process in inert atmosphere (Ar), using tetra-amine palladium nitrate as a precursor solution and hydrogen gas as a reducing agent. The details of one-coating cycle of supported Pd nanoparticle synthesis procedure used in this study are described elsewhere [9]. Figure 1 shows the scanning electron microscopy (SEM) images of supported Pd-NPs fabricated on foam (Pd/Foam) and on CNT-grafted foam (Pd/CNT/Foam).

2.3. Batch Degradation Studies. The bench-scale investigation of CT dechlorination was carried out in batch reactors consisting of 160 mL glass serum bottles containing supported catalyst. The supported catalysts having $10 \times 5 \times 2$ mm³ size (Pd/Foam or Pd/CNT/Foam) were attached to the inside wall of the serum bottle using a double-sided carbon tape. TAPSO buffer (1 mM) adjusted to pH 7.5 was prepared in Milli-Q water, and 96 mL of this buffer was added to the reactors, maintaining the solution to headspace ratio of 60:40. The pH was monitored using a pH meter AP10 (Denver Instruments). The reactors were sealed with Teflon-lined butyl rubber stopper and sealed with aluminum

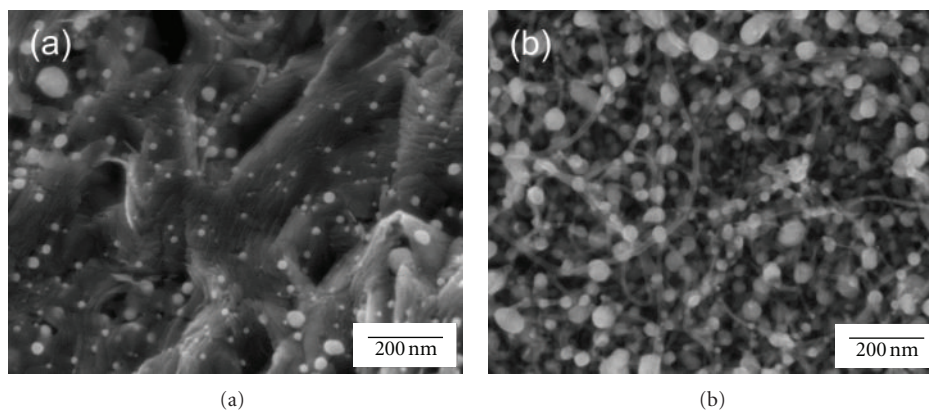


FIGURE 1: SEM micrographs of Pd-NPs supported on (a) carbon foam support (Pd/Foam) and (b) CNT-grafted foam support (Pd/CNT/Foam).

crimp. The reactors were then purged for 30 min with a high purity H_2-N_2 gas mixture (generally with 5% H_2 and balance N_2 , $[pH_2] = 0.05$ atm). An aqueous CT stock solution was injected into each reactor (initial CT conc. = $200 \mu\text{g L}^{-1}$; initial CT amount = $0.125 \mu\text{moles}$) using a gas-tight syringe using established laboratory procedure [17]. The reactors were then placed on an end-over-end rotary shaker at room temperature (32 rpm, 45° inclination), so as to minimize the liquid-gas mass transfer effects. The bottles were rotated at an inclination for the solid samples to remain in contact with the solution at all times so that the reactions take place continuously.

2.4. Chemical Analysis. Carbon tetrachloride and its degradation products such as chloroform, dichloromethane, and methane were analyzed by gas chromatography (GC) and quantified using established laboratory procedure [17]. Headspace samples from the reactors set were analyzed to estimate their aqueous phase concentration and total amount present at each sampling time. Headspace samples were analyzed by an HP 7890 gas chromatographic system, equipped with an electron capture detector (ECD) and a flame ionization detector (FID). The peak area values of analytes from gas chromatography were transformed into their respective amount at equilibrium using laboratory calibration curves, based on a published method [18], and their dimensionless Henry's constants: K'_H at 25°C [19]. The pH measurements were made using a handheld meter (model AP10 pH/mV/temp; Denver Instrument, Bohemia, NY) by collecting small liquid samples from the reactors at the beginning and end of each experiment.

2.5. Materials Characterization. Surface morphology of palladium nanoparticles fabricated on such hierarchical architectures (Pd/Foam and Pd/CNT/Foam) was characterized by scanning electron microscopy technique using JEOL 7401F FE-SEM. The chemical characterization was accomplished by X-ray Photoelectron Spectroscopy (XPS) using Kratos (Axis Ultra) XPS system. XPS was performed with a monochromatized Al- $K\alpha$ (1486.6 eV) source in ultrahigh

vacuum environment (UHV $\sim 10^{-9}$ Torr). The survey scans (BE: 1000–0 eV) and high-resolution fine scans of respective elements were collected. Any static charge in the samples was corrected by assigning a value of 284.4 eV to C 1s spectrum, a well-known binding energy value of carbon in graphite [20].

The chemical and physical state of fresh and used carbon supported Pd-NPs samples was investigated by repeatedly using the samples for up to three batch experiments. The conditions of each batch test include vigorous rotation of reactors at 32 rpm for 1–2 days. The samples were analyzed before and after these tests for microstructural and spectroscopic elemental data using SEM and XPS. The reusability and efficiency of Pd catalyst were also tested for its ability to degrade CT by repeatedly using the samples for up to 6–7 times.

2.6. Data Treatment. For each experiment, CT degradation rate constants were calculated based on an assumption of pseudo-first-order kinetics. All degradation experiment data were fit with a pseudo-first-order rate model, given by (1),

$$-\frac{dC}{dt} = k_{\text{obs}}[M], \quad (1)$$

where k_{obs} (hr^{-1}) is the observed degradation rate constant and M (μmoles) is the CT amount in the reactor at time, t (hr). The CT degradation rate can also be expressed in terms of half-life, $t_{0.5}$ (hr), time required for CT amount in the reactor to reach half of the initial CT amount (where $M_0 = 0.125 \mu\text{moles}$), and obtained from the following equation:

$$t_{0.5} = (k_{\text{obs}})^{-1} \ln 2. \quad (2)$$

3. Results and Discussions

3.1. Reductive Dechlorination of CT

3.1.1. Comparison of Catalytic Activities of Different Materials. Batch experiments were performed using the following materials: (A) control (blank, no material), (B) foam without Pd, (C) CNT/Foam without Pd, (D) foam with Pd

TABLE 1: Estimated surface area of Palladium nanoparticles on different supports and values of rate constants for reduction and half-life of CT (k_{obs} , $t_{0.5}$) at $[\text{pH}_2]$ 0.05 atm.

S. No.	Type of support	*Estimated surface area Pd area per mL of water (each support—100 mm ³), 10 ⁻² mm ² /mL	CT transformation rates	
			k_{obs} (Hr ⁻¹)	$t_{0.5}$ (Hr)
1	Pd/Foam	8.3	0.109	6.35
2	Pd/CNT/Foam	25×10^3	0.376	1.84
3	2x Pd/Foam	16.6	0.181	3.82
4	2x Pd/CNT/Foam	50×10^3	0.711	0.97

*Obtained from the data published earlier [9].

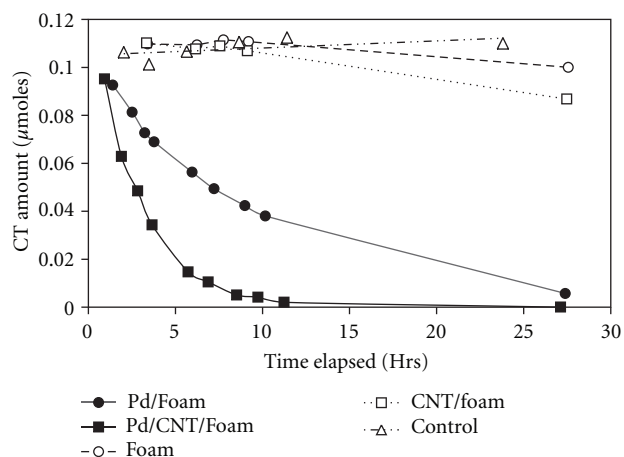


FIGURE 2: Carbon tetrachloride (CT) transformation curves obtained with various types of catalyst supports.

nanoparticles (Pd/Foam), and (E) CNT/Foam with Pd nanoparticles (Pd/CNT/Foam). Figure 2 shows the plot of carbon tetrachloride concentration versus time for these different materials (A–E). The control experiments as well as the two carbon samples without Pd catalyst (set-up A–C) showed very little or no reduction in CT amount (Figure 2). However, the reactors containing supported Pd nanoparticles (set-up D and E) showed complete degradation of CT.

Figure 3 shows the pseudo-first-order rate constant, k_{obs} of CT degradation obtained using Pd catalysts. It is obvious that the rate of CT dechlorination with Pd/CNT/Foam catalyst is significantly greater than that with Pd/Foam. This was expected since the CNT grafted on the microporous graphitic foam with hierarchical structure provides greater surface area for metal nanoparticles attachment per unit volume of the support and hence a greater catalytic response (Table 1). In fact, this has scope for much higher increase of CT degradation rate (k_{obs}) in future as discussed in the next section.

3.1.2. Influence of Catalyst/Support Size. These experiments were repeated using twice the amount of Pd nanoparticle catalysts (two pieces of Pd/Foam and Pd/CNT/Foam, each $10 \times 5 \times 2$ mm³ in size) for the same volume of liquid in each reactor. In other words, the catalyst to liquid volume was doubled. The transformation kinetics of CT with twice

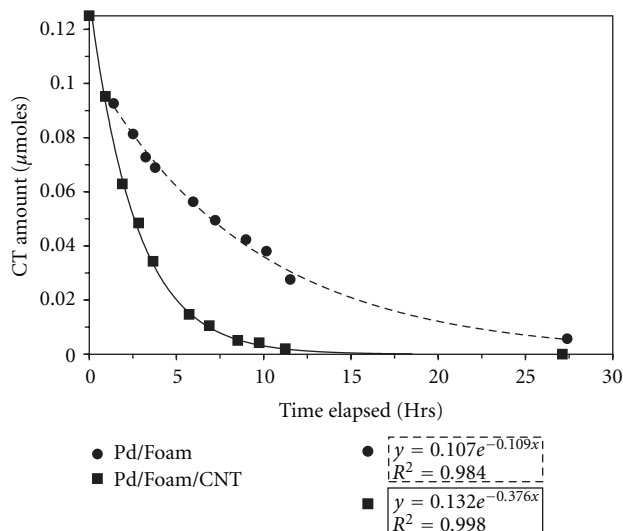


FIGURE 3: Carbon tetrachloride (CT) degradation curves with exponential curve fitting obtained for Pd/Foam and Pd/CNT/Foam samples.

the amount of Pd nanoparticle catalysts showed a twofold increase in its degradation rate constant, k_{obs} for both types of supports (Figure 4). These results indicate that increase in the number/size of the supports (which would increase the available area of catalyst) is expected to systematically increase the catalytic activity. The rate constants and half-life of all these catalysts are tabulated in Table 1 and discussed more in the next sections.

3.1.3. Role of Hydrogen Gas Concentration. Batch experiments were performed with variations in partial pressures of H₂ gas at 0, 0.05 and 0.5 atm (0%, 5%, and 50% H₂ balance N₂, resp.) in the reactors with Pd/Foam and Pd/CNT/Foam. Figure 5 shows significant degradation of CT in the presence of H₂. While the reactor with no added H₂ showed very little or no degradation of CT, the reactors with gaseous H₂ present at 0.05 and 0.5 atm showed rapid and near complete CT degradation, suggesting that CT degradation was dependent on the availability of gaseous H₂ as a reductant. However, the CT degradation rate constants (Table 2) were quite similar at 0.05 and 0.5 atm $[\text{pH}_2]$ and did not show significant increase at higher $[\text{pH}_2]$ both with Pd/Foam and Pd/CNT/Foam. Similar catalytic activity

TABLE 2: Values of rate constants for reduction and half-life of CT (k_{obs} , $t_{0.5}$) with Pd hybrid catalyst and varying hydrogen gas concentrations, [pH₂].

S. no.	Type of support	H ₂ gas [pH ₂] atm	CT transformation rates	
			k_{obs} (Hr ⁻¹)	$t_{0.5}$ (Hr)
1	Pd/Foam	0.5	0.101	6.86
		0.05	0.109	6.35
		0	0.003	231.0
2	Pd/CNT/Foam	0.5	0.404	1.71
		0.05	0.376	1.84
		0	0.015	46.2

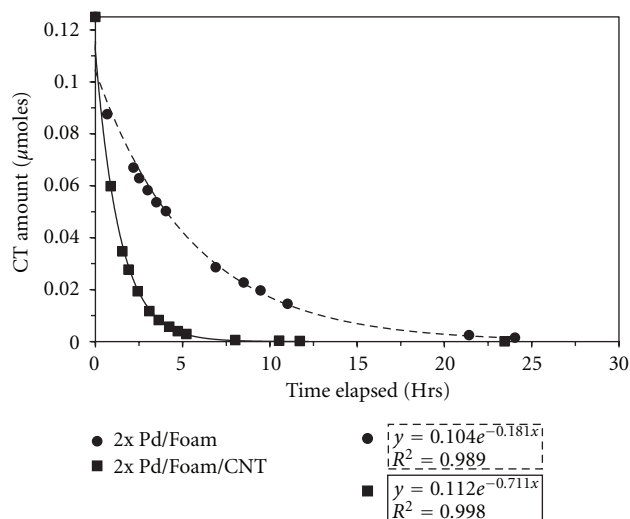


FIGURE 4: Carbon tetrachloride (CT) degradation curves with exponential curve fitting obtained for twice the amount of Pd nanoparticle catalysts (two pieces of Pd/Foam and Pd/CNT/Foam), 2x Pd/Foam and 2x Pd/CNT/Foam samples.

(Table 2) at 0.05 and 0.5 atm [pH₂] may imply other factors affecting degradation, such as rate-limited mass transfer of aqueous intermediate species to/from Pd catalyst surface. The study implies that whereas the presence of H₂ is required for sustained and complete degradation of CT and other similar CHCs by catalytic reductive dechlorination, excessive hydrogen enrichment may not have any additional effect. In-depth study on influence of H₂ concentration is beyond the scope of this paper.

3.1.4. Formation of Daughter Products. The dechlorination of CT with supported Pd nanoparticle catalysts yielded chloroform (CF) as the major product of the reaction in all cases as shown in Figure 6. Decrease in CT concentration correlates well with increase in CF concentration until all CT is reduced. Trace amounts of formation of dichloromethane (DCM) were also produced, which may be attributed to the further reduction of CF, as after 100% reduction of CT, the CF level begins to drop indicating degradation of CF to DCM (Figures 6(b) and 6(d)).

The mechanism of catalytic reductive dechlorination of CT to CF in the presence of Pd and H₂ has been discussed previously [21–23], which may proceed through numerous intermediate steps. The overall reaction may include adsorption of reactant species (H₂ and CCl₄) on the active sites of Pd metal, their dissociation into intermediate species followed by reaction between intermediate species to form reduced products (CHCl₃ and HCl), and desorption of final products from Pd surface. Further sequential reduction of the adsorbed intermediate species to daughter products may also similarly happen before desorption from Pd surface, such as chloroform (CHCl₃) transformation to dichloromethane (CH₂Cl₂). However, it is distinct that in the presence of these hybrid Pd structures and H₂, the concentration of CT decreases with time, and CF is formed as the first by-product.

3.2. Influence of Catalyst Surface Area and Geometry. A correlation between reaction kinetics and the available surface area of the Pd component will be important for extending the application of this concept to other geometries. Table 1 plots the measured rate kinetic parameters along with palladium surface area available to unit volume of liquid. While the detailed surface morphologies of the carbon foam, as well as CNT-attached foam used in this study, have been obtained using geometrical model, the particle size distribution and surface area of Pd-NPs on these materials have also been investigated using microstructural data which is published elsewhere [9, 14]. Based on the structural data, the estimated surface area of Pd per unit volume of the hybrid catalyst structure has been obtained and is included in Table 1.

From Table 1, it is clear that for a given catalyst geometry, CT degradation results show clear scaling effect; that is, doubling the catalyst units will double the transformation rate (k_{obs}). However, when the simpler Pd/Foam structure is replaced with a hierarchical Pd/CNT/Foam architecture, the reaction rate increase of three to four times (300%–400%) is not to the same extent as the increase in available Pd surface of about 3,000% times or 300,000%. This strongly suggests incomplete percolation of water through the CNT forest, which may be attributed to the hydrophobic nature of carbon nanotubes in general. If in the future, the CNT-grafted support can be functionalized to make it hydrophilic in nature, deeper infiltration of water can be achieved. This study indicates that improved wettability may have

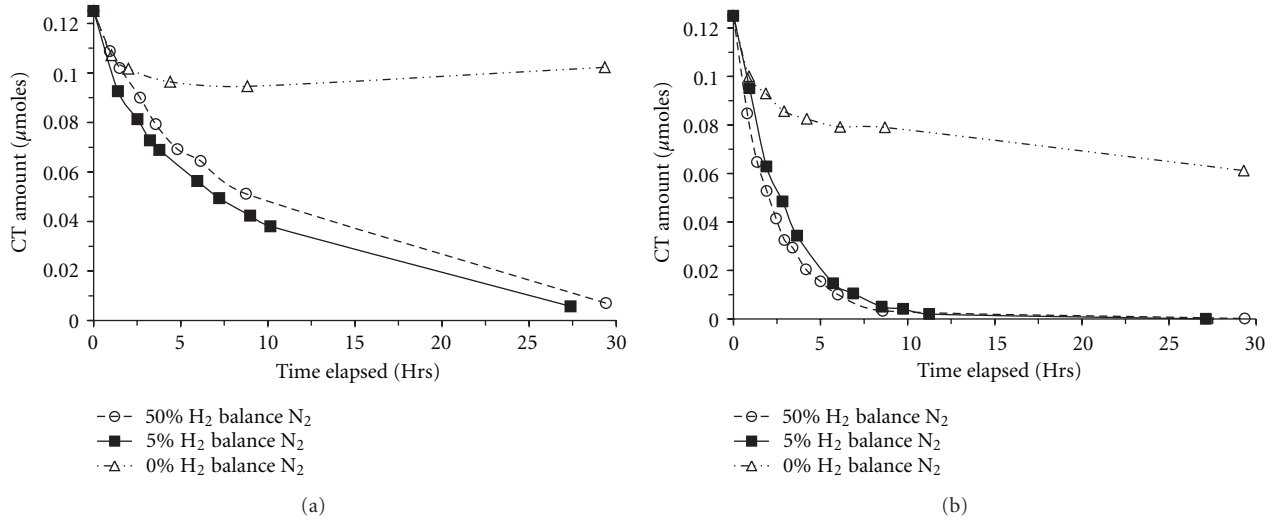


FIGURE 5: Carbon tetrachloride (CT) transformation curves obtained with (a) Pd/Foam and (b) Pd/CNT/Foam catalyst and varying hydrogen concentration.

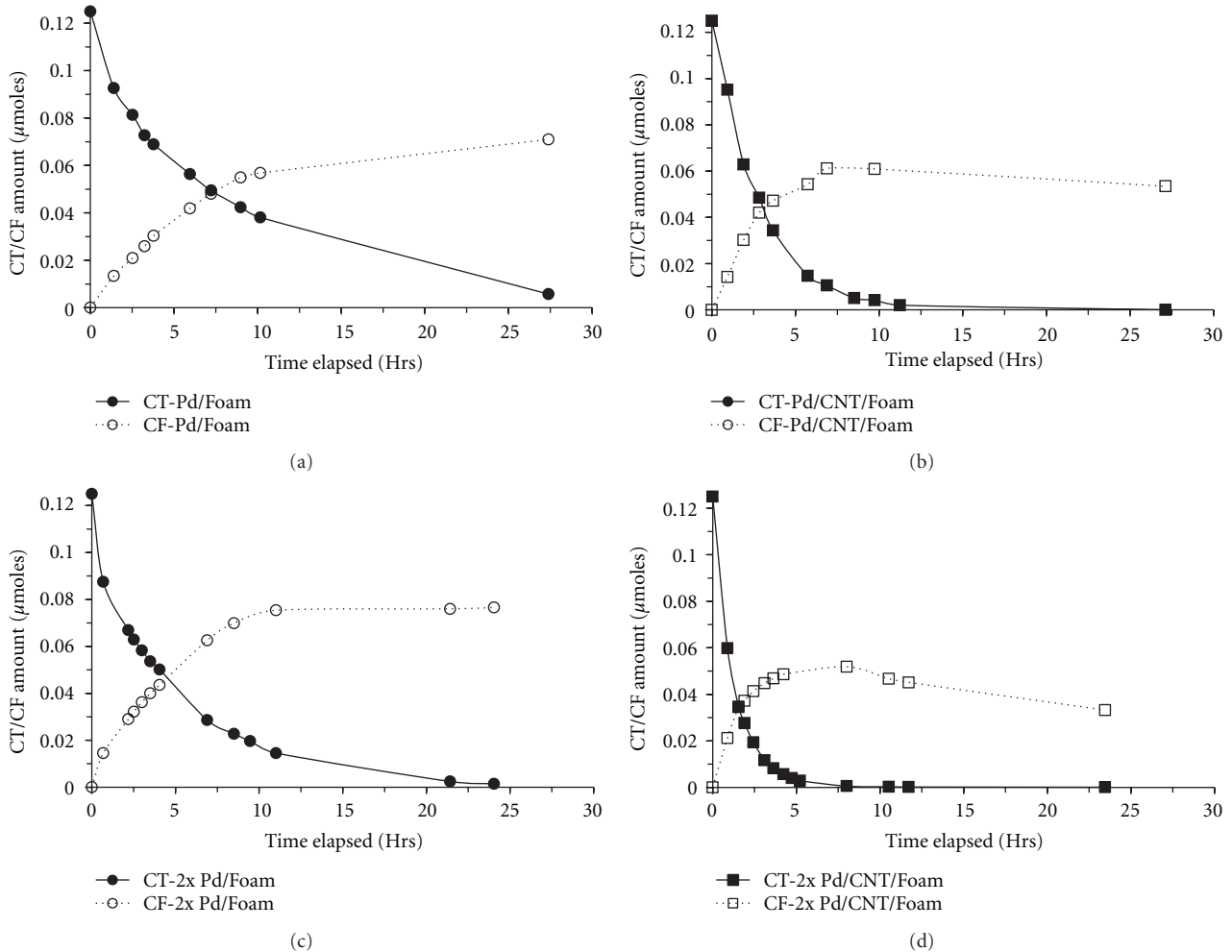


FIGURE 6: Carbon tetrachloride (CT) degradation and chloroform (CF) formation curves with (a) Pd/Foam, (b) Pd/CNT/Foam, (c) 2x Pd/Foam, and (d) 2x Pd/CNT/Foam.

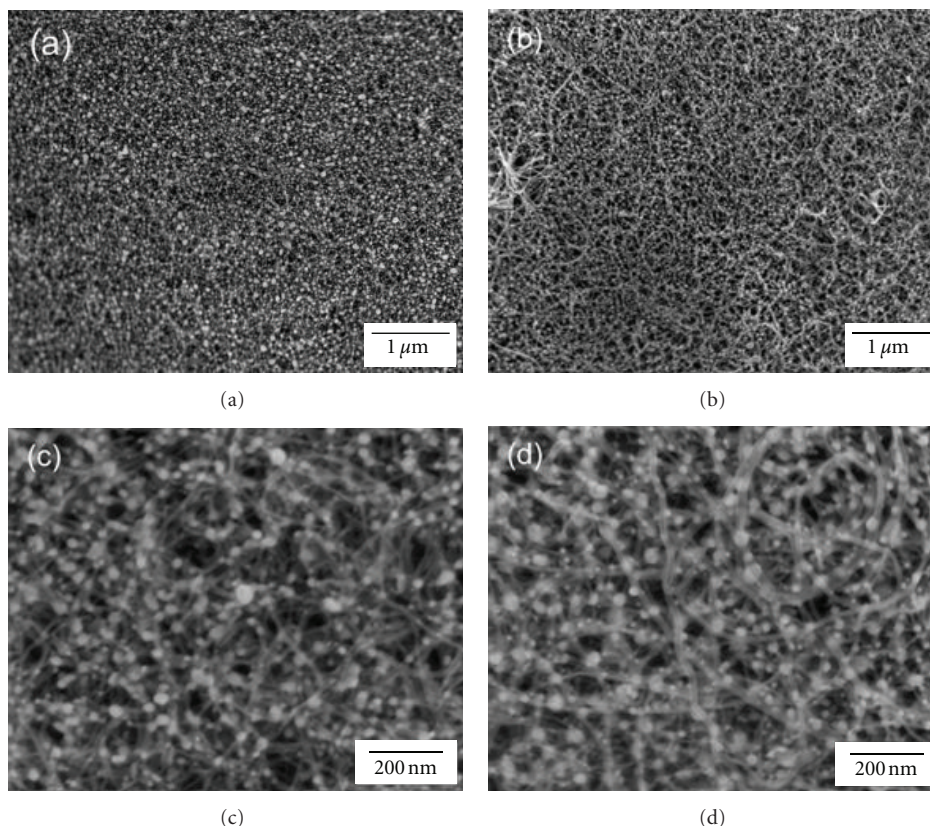


FIGURE 7: SEM micrographs of Pd/CNT/Foam (a, c) before and (b, d) after the carbon tetrachloride (CT) dechlorination test.

the potential to cause an additional 1000 times increase in dechlorination rate in the water-based environments.

3.3. Chemical and Physical Durability Test. The chemical and physical durability of carbon supported Pd-NPs samples was analyzed by characterizing the Pd-NPs of fresh and used samples, that is, before and after dechlorination tests. Figure 7 shows the SEM micrographs of Pd-NPs on CNT/Foam supports before and after three dechlorination cycles, which is a total of approximately 90 hours in the reactor at 32 rpm. It can be seen that Pd-NPs stay intact with the CNT. The physical durability of CNT-foam structures has been tested previously in various loading conditions [9, 14]. This study indicates that not only is the CNT/Foam durable, but also the Pd-NPs on these hybrid foam samples survive the prolonged movement in the rotating reactor.

The chemical state of Pd was studied on the Pd/CNT/Foam catalyst before and after CT dechlorination using XPS. The fine scans of Pd 3d, C 1s, and Cl 2p are shown in Figure 8. Pd 3d_{5/2} peaks for both fresh and used catalyst were observed at 335.18 eV which indicates that the Pd-NPs did not undergo any chemical change (Figure 8(a)). The energy values of Pd 3d peaks correspond to the metallic state of Pd (Pd⁰) [9]. The fine scan of C 1s (Figure 8(b)) shows a prominent peak at 284.4 eV that corresponds to C–C bonding for graphitic form of carbon. The C 1s

peak after CT batch test shows a satellite peak at 286.1 eV, which can be attributed to the contamination on CNT. No detectable chlorine peak (Cl 2p) was observed from the used catalysts (Figure 8(c)). This implies that the contaminations on CNT are chlorine-free carbonaceous impurities that could plausibly be from the hydrocarbons of organic TAPSO buffer.

The batch studies were also performed in duplicate and/or triplicate for each type of sample and reproducible results were observed. The CT dechlorination rate of the catalysts was monitored by reusing the samples in the batch tests. It was observed that the rate constant (k_{obs}) values of CT degradation with these samples were consistent and remained within the error bar for six consecutive tests and total usage time of 200 hours, indicating that these hybrid catalysts are expected to be robust and reusable, at least within the ~200 hours usage time tested. Long-term tests ranging from a period of months to years may be needed in the future for deployment in real purification systems.

4. Concluding Remarks and Future Work

Two types of hybrid catalysts comprising of palladium nanoparticles supported on porous carbon have been successfully tested for reductive dechlorination of carbon tetrachloride. In this study, aqueous phase dechlorination

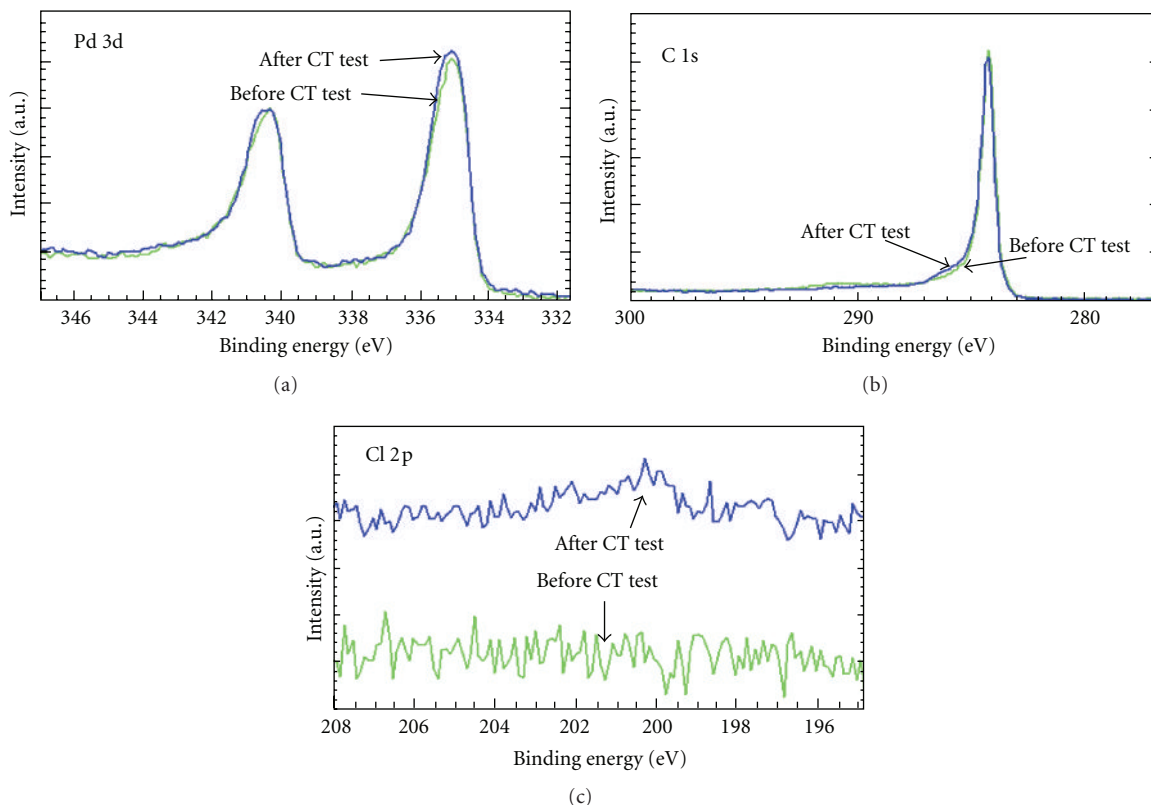


FIGURE 8: X-Ray photoelectron spectrometry (XPS) fine scans of (a) Pd 3d spectra, (b) C 1s spectra, and (c) Cl 2p spectra, obtained from Pd/CNT/Foam sample, before (green line) and after (blue line) the carbon tetrachloride (CT) dechlorination test.

of CT at ambient temperatures was accomplished using a bench-scale batch reactor. In the presence of hydrogen, complete degradation was observed, where CT was initially transformed to less-toxic chloroform. Pd/CNT/Foam catalyst shows 3-4 times higher activity compared to Pd/Foam catalyst. It is expected that the degradation rate can be further increased by orders of magnitude if the wettability of nanotube forests can be improved. XPS analysis of samples after a total of ~96 hours of catalytic degradation shows unchanged surface chemical states of the Pd-NPs. This architecture of Pd-NPs attached to larger hierarchical carbon supports can be recovered easily and reused multiple times. Such structures may therefore provide a nonpolluting, reusable, and cost-effective solution for the removal of organic pollutants such as CT from contaminated water.

Acknowledgments

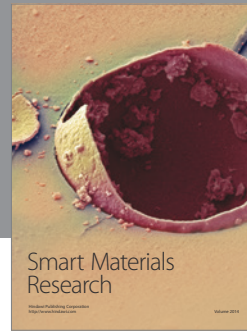
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