

Cleaner water using bimetallic nanoparticle catalysts

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Abstract

Groundwater contaminated by hazardous chlorinated compounds, especially chlorinated ethenes, continues to be a significant environmental problem in industrialized nations. The conventional treatment methods of activated carbon adsorption and air-stripping successfully remove these compounds by way of transferring them from the water phase into the solid or gas phase. Catalysis is a promising approach to remove chlorinated compounds completely from the environment, by converting them into safer, non-chlorinated compounds. Palladium-based materials have been shown to be very effective as hydrodechlorination catalysts for the removal of chlorinated ethenes and other related compounds. However, relatively low catalytic activity and a propensity for deactivation are significant issues that prevent their widespread use in groundwater remediation. Palladium-on-gold bimetallic nanoparticles, in contrast, were recently discovered to exhibit superior catalyst activity and improved deactivation resistance. This new type of material is a significant next-step in the development of a viable hydrodechlorination catalysis technology.

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THE ENVIRONMENTAL PROBLEM

Trichloroethene (TCE) and tetrachloroethene (or perchloroethene, PCE) are two of the most prevalent organic contaminants in groundwater (the source of most drinking water) in the USA and other industrialized parts of the world.^{1–3} Valued for their chemical stability and 'safety-solvent' properties (because they are resistant to combustion and explosion), these chlorinated compounds have been used in a number of industries since the early 1900s – TCE for degreasing metals, and PCE as a dry cleaning fluid. The combination of extensive use and chemical stability has led to widespread contamination of groundwater by these ubiquitous and recalcitrant pollutants, through leakage from storage drums, accidental spills, and direct discharge. There are an estimated 5000 US government and Superfund sites contaminated with these and other chlorinated solvents, and an estimated 27 000 contaminated dry cleaning sites, with the cost of remediation on the order of billions of dollars.^{4–6}

These simple-looking molecules are associated with adverse human health effects, such as liver and kidney cancer and reproductive toxicity (Fig. 1). The US Environmental Protection Agency (EPA) set a maximum contaminant level (MCL) of 5 ppb (0.005 mg L⁻¹) for both compounds, which is readily exceeded at contaminated sites by orders of magnitude.⁷ (For comparison, the World Health Organization recommended concentration limits of 20 and 40 ppb, respectively, for TCE and PCE in drinking water, in its 2003 edition of *Guidelines for Drinking-water Quality*). The concerns about their presence in the environment continue to grow, as more is known about their toxicity to animals and humans. In 2006, the US National Research Council released a comprehensive report on TCE health effects, which could lead to a tightening of TCE

MCL. California announced in 2007 that it will be the first state to eliminate PCE from dry cleaning use by 2023.

The physical properties make these and other chlorinated compounds quite problematic to remove from groundwater. They are heavier than water (specific gravity >1), sinking into ground as dense non-aqueous-phase liquid (DNAPL) deposits that dissolve slowly and serve as a source for sustained groundwater contamination (Fig. 2). With viscosities less than water, these subsurface deposits can migrate with groundwater flow. More perniciously, they can dissolve into water up to their particular ppm-level water solubility limits (for example, the solubility limits of PCE and TCE in water at 20 °C are 150 ppm and 1000 ppm, respectively), leading to the formation of aqueous-

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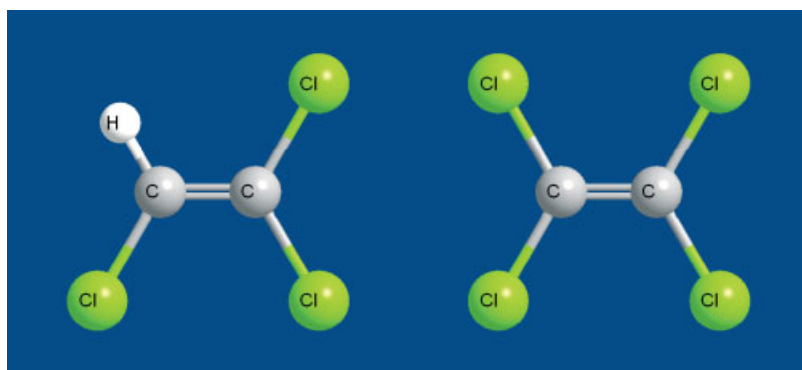


Figure 1. Molecular structures of TCE and PCE.

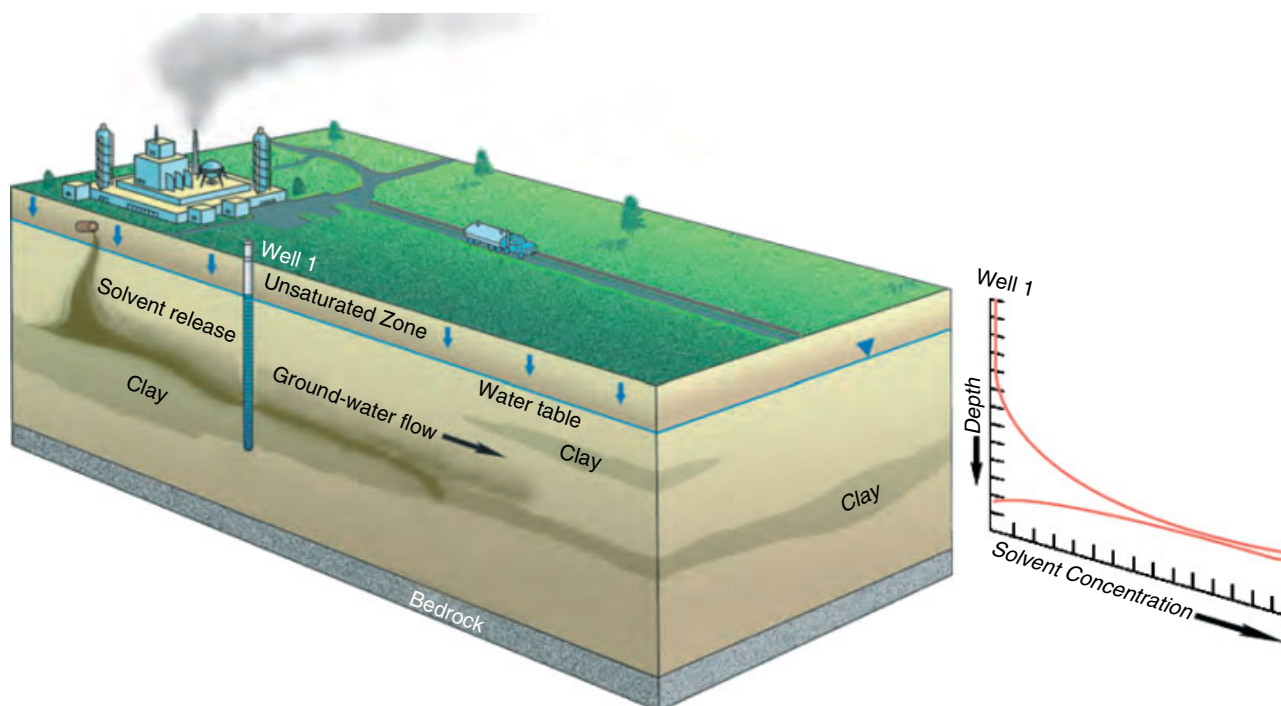


Figure 2. Illustration of a DNAPL deposit and resulting contaminant plume.²

phase contaminant plumes.⁸ The solvent molecules would rather remain in water than be adsorbed onto soil (characterized by low soil organic carbon–water partition coefficient K_{OC} values) and are relatively resistant to microbial degradation, and so plumes can stretch far beyond the DNAPL source. This also means that underground concentrations in groundwater can be highly variable, pointing to the difficulties in control, mitigation, and removal.

CURRENT SOLUTIONS

The commonly used plume containment and groundwater treatment technologies for chlorinated solvents are the *ex situ* (above-ground) pump-and-treat methods of carbon adsorption and air stripping.^{5,9} In carbon adsorption, contaminated groundwater is pumped and sent through a granular activated carbon-containing unit. The organics adsorb onto the pore walls of the high-surface-area carbon material, and the treated water is returned to the aquifer, discharged to a surface water body, or sent to a drinking

water treatment plant. Once saturated, the carbon is replaced with fresh material. It is not generally regenerated for re-use due to cost; rather, it is disposed in landfills or (to a lesser extent) incinerated. In air-stripping, the pumped contaminated groundwater is contacted with air, to volatilize the dissolved organics into the gas phase. The contaminated air stream is then vented into the atmosphere, or treated via carbon adsorption before venting.

These are mature technologies which are best suited for containing the contaminant plume from migrating further underground. In recent years, they have been found inappropriate for site restoration if DNAPL is present, due to the high operating costs associated with the decades-long time scale required to achieve complete removal of the chlorinated solvent. Nevertheless, the pump-and-treat methods remain the most commonly used for Superfund site remediation, especially at sites where the preferred *in situ* (underground) methods may be comparatively more expensive or ineffective.⁶ Thus, improvements in their effectiveness are still needed.¹⁰

WHAT ABOUT CATALYSIS?

The catalytic conversion of chlorinated solvents into safer compounds is a very attractive approach over carbon adsorption and air stripping, both of which merely move the contaminant into a different part of the environment and thus do not eliminate potential liability. In catalysis (here, 'catalysis' refers to heterogeneous catalysis, which involves the use of a solid material as the catalyst. Homogeneous catalysis, which involves the use of a liquid-phase catalyst, is also not well developed for water treatment, and is not discussed here) the target molecule momentarily sticks to a site on the catalytic material's surface and reacts into a different molecule. The product molecule leaves, and the surface site is vacant again for another target molecule. The reaction repeats itself numerous times, such that only a small amount of the catalyst solid is needed to speed up the chemical reaction. As a chemical method, catalysis is well-established in air pollution control, such as in automobile catalytic converters and in NO_x (nitrogen oxides) selective catalytic reduction units at electric power plants. It is currently much less developed for water pollution control.^{11,12}

PALLADIUM MATERIALS AS HYDRODECHLORINATION CATALYSTS

Used in conjunction with a reducing agent, palladium (Pd) and other Group VIII metals are well-known catalytic materials for the hydrodehalogenation of halogenated organic compounds in organic synthesis applications,¹³ in which hydrogen atoms replace the halogen atoms. In the last 15 years, interest in their effectiveness for gas-phase and water-phase environmental remediation has increased significantly (see recent reviews^{14–17}).

Related to Pd catalysts are Pd-coated zero-valent iron (Pd-coated ZVI or Pd/Fe) materials, which are being studied for groundwater treatment.^{18–20} By itself, iron behaves as a reducing agent through its corrosion reaction, releasing electrons that reductively dechlorinate TCE, PCE, and other chlorinated compounds.^{21,22} The primary mechanistic pathway is called β -elimination, in which a chlorinated ethene is converted into an ethyne group through the removal of Cl₂. The chlorinated ethene can go through secondary pathways of hydrogenolysis (C–Cl cleavage and C–H formation) and hydrogenation (formation of ethane from ethene). The Pd coating increases the overall dechlorination reaction through a reaction mechanism that remains to be determined.²³

Research emerged in the early 1990s that indicated that Pd was very effective in catalyzing the hydrodechlorination (HDC, hydrodechlorination refers to the process of converting chlorinated molecules into non-chlorinated ones, mechanistically through hydrogenolysis and possibly hydrogenation) of chlorinated compounds dissolved in water. Kovenklioglu *et al.* found that Pd (supported on carbon or alumina) catalyzed the HDC of various chlorinated solvents in water at room temperature with H₂ gas.²⁴ Reinhard and co-workers verified this for the HDC of PCE²⁵ and other solvent compounds.²⁶ Subsequent work by them^{27–29} and other research groups^{30–32} furthered the development of Pd-supported catalysts for groundwater remediation. While it is not known how HDC proceeds on a catalyst surface, it can be hypothesized through a Langmuir–Hinshelwood mechanism to be a series of chlorine removal and hydrogen addition steps after TCE and H₂ molecules bind to the surface (Fig. 3). The TCE adsorbs to the Pd metal surface at particular locations presumptively called active sites, and H₂ dissociatively adsorbs in the form of surface

H atoms. These surface species then react with one another via hydrogenolysis surface reaction steps to form increasingly dechlorinated surface species (dichloroethene (DCE) isomers and vinyl chloride) until surface-bound ethene is formed. Ethene is then hydrogenated to form ethane, which desorbs into the aqueous phase.

McNab *et al.* designed a catalytic HDC reactor based on Pd/alumina (containing 1 wt% Pd) and H₂ gas, and demonstrated a successful year-long pilot-scale testing at a US Superfund site.³⁰ At a pumped water flow rate of ~ 4 L min⁻¹, the reactor reduced TCE concentrations from ~ 3700 ppb to as low as <1 ppb. The total amount and cost of the Pd catalyst used were very high (52 kg, at the 2000 price of \$270/kg-catalyst or \$27/g-Pd), pointing to the issue of cost-effectiveness as a potential barrier to commercialization. Still, additional catalytic flow reactors have been installed,³³ and Schüth *et al.* recently reported the successful full-scale installation of a catalytic HDC reactor using Pd/zeolite (containing 0.4 wt% Pd) and H₂ gas, at a contaminated site in Germany.³² At both sites, the hydrogeochemistry was such that periodic exposure to an oxidant (air or H₂O₂) was necessary to maintain catalyst durability. Pd catalysts deactivate with time due to poisoning by sulfides (generated by anaerobic, sulfate-reducing bacteria) and fouling by minerals precipitation.

Is there a material that is more active and deactivation-resistant than Pd catalysts for HDC of groundwater? Alternatively, is there a way to improve the activity and deactivation resistance of Pd catalysts? An improved catalyst would lead to reactors that require less material; to smaller reactors; and to fewer operational interruptions due to catalyst regeneration or catalyst replacement. The authors' research group began thinking about this problem several years ago, and formulated a possible solution via the use of carefully constructed *bimetallic* Pd catalysts (Pd-on-Au nanoparticles are not to be confused with Pd-coated zero-valent iron materials, as the HDC mechanisms and modes of use are distinct from one another).

PALLADIUM-ON-GOLD BIMETALLIC NANOPARTICLE CATALYSTS

Bimetallic catalysts can have considerably more favorable activities, selectivity, and/or deactivation properties than monometallic catalysts,³⁴ and the combination of gold (Au) and Pd is no exception. Gold is traditionally considered to be a catalytically inert material,^{35,36} but it is known to enhance the catalytic properties of Pd for various chemical reactions, such as gas-phase HDC of chlorofluorocarbons,³⁷ hydrodesulfurization,³⁸ and vinyl acetate monomer production (an industrial-scale reaction).³⁹ How Au promotes Pd catalysis is not exactly known for most chemical reactions, and it remains a subject of considerable academic and industrial interest. What type of promotional effects, if any, would Au have on Pd for water-phase HDC catalysis?

One difficulty in bimetallic catalysis research is the lack of control of the metallic nanostructure at the synthesis level. Pd-Au bimetallic catalysts are conventionally prepared by depositing onto a support material (e.g. alumina, silica, and carbon) Au and Pd salt species, which are then converted into nanometer-sized metallic domains through gas-phase heat treatment. These domains can have size variations, but more problematically, they can have compositional variations. The presence of monometallic domains alongside the bimetallic ones cannot be ruled out. Furthermore, while Au and Pd can form bulk alloys of any composition, they do not necessarily form alloys at the nanoscale.

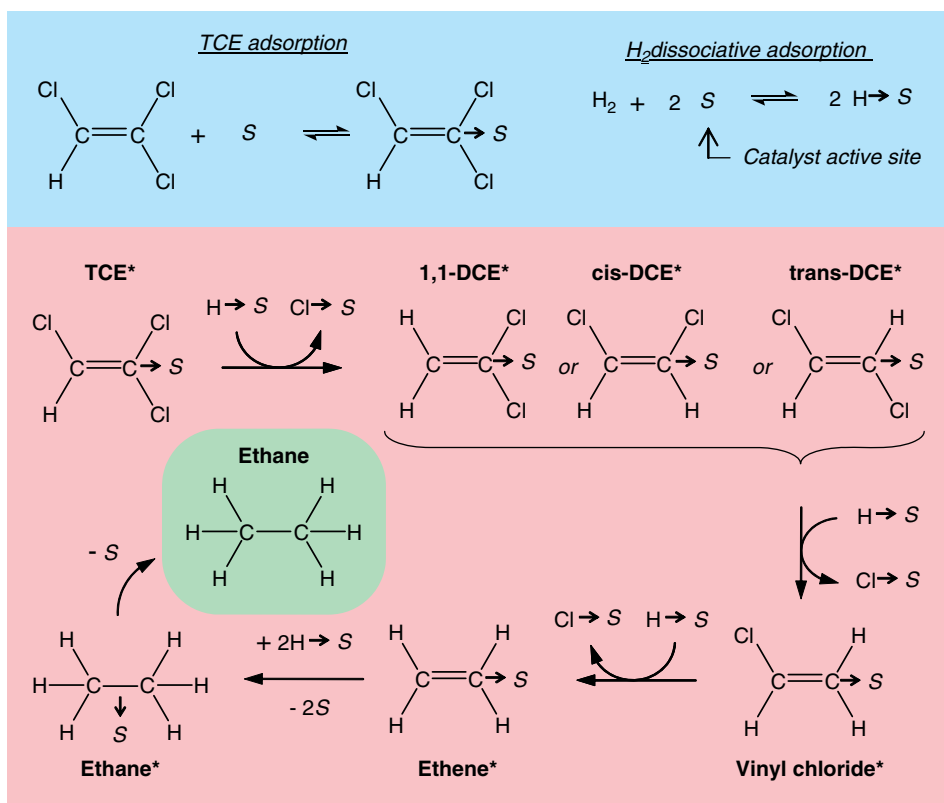


Figure 3. Proposed reaction mechanism for TCE HDC occurring over a Pd (and Pd-on-Au) surface. The 'S' represents an active site somewhere on the metal surface.

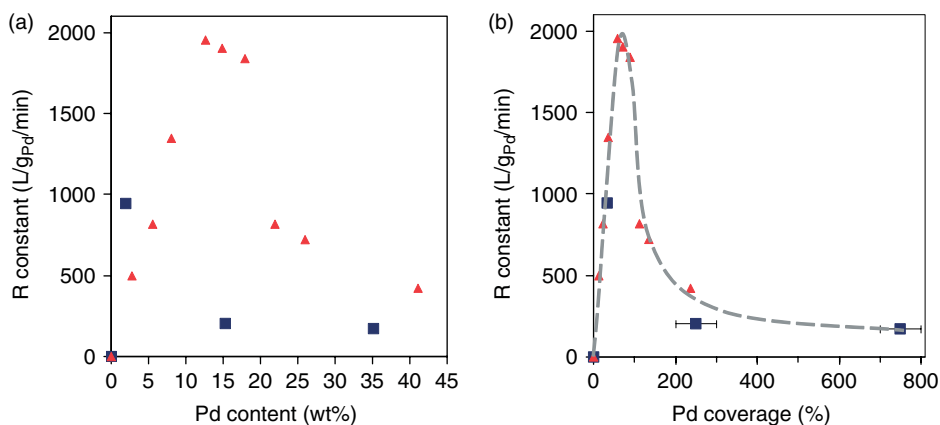


Figure 4. Room-temperature pseudo-first-order reaction constants for Pd-on-Au NPs prepared with 20 nm (blue squares) and 4-nm (red triangles) Au NPs, plotted as a function of (a) Pd weight content and (b) Pd surface coverage. The error bars signify the uncertainty in Pd surface coverage calculations. Dashed line is drawn to guide the eyes.^{40,41}

Metal segregation can occur, leading to domains with metal distributional variations.

These problems were bypassed by synthesizing Pd–Au bimetallic nanoparticles (NPs) *without* the support. Recognizing that Au was inactive for TCE HDC and that Pd was catalytically active, the NPs were designed to have a Au core covered with a variable amount of Pd atoms (referred to as Pd-on-Au NPs).

Pd-on-Au NPs, 'Version 1.0'

In 2005, the successful synthesis and catalyst testing of Pd-on-Au NPs was reported.⁴⁰ Au NPs with a diameter of roughly 20 nm

were synthesized through the Turkevich–Frens (citrate reduction) method, and Pd metal was deposited using Pd chloride salt and ascorbic acid reducing agent. The NPs had astonishingly high reaction rate constants for TCE HDC (Fig. 4); the most active composition exhibited a first-order rate constant (943 L g⁻¹_{Pd} min⁻¹) that was >10, >70, and >2000 times higher than monometallic Pd NPs, Pd/Al₂O₃, and Pd black, respectively. TCE was hydrodechlorinated completely, with ethane as the main product. Stoichiometrically, the TCE HDC reaction could be represented as



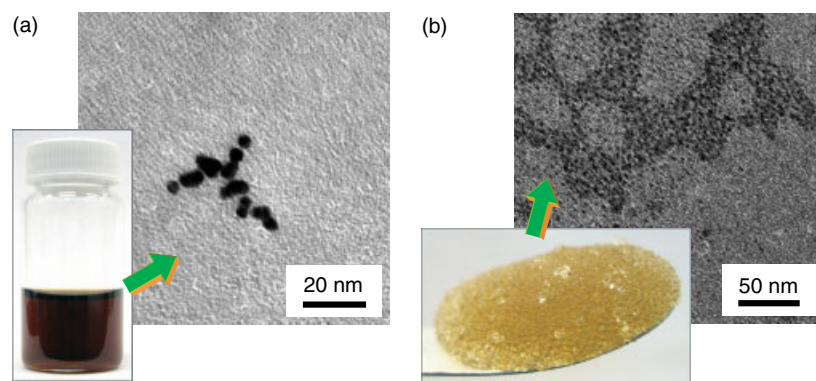


Figure 5. (a) Transmission electron microscope (TEM) image of Pd-on-Au NPs with 60% Pd surface coverage, also shown as a suspension in the vial. (b) TEM image of the same NPs immobilized within ion-exchange resin spheres (Mitsubishi Diaion TSA1200 type). The spheres were microtomed into thin cross-sections for imaging. The NPs appeared highly agglomerated, which is attributed to the drying and contraction of the microtomed spheres.

These exciting results were the first evidence that Au enhances the catalysis of Pd metal in water at room temperature, leading to the prospects of bimetallic NPs for catalytic groundwater remediation. From a nanotechnology point of view, the results suggested that the very active catalysts had a bimetallic nanostructure in which the Pd metal only partially covered the Au surface. Is $\sim 33\%$ Pd surface coverage the most favorable for highest catalytic activity?

Pd-on-Au NPs, 'Version 2.0'

The 20 nm Au NPs were too large for practical applications (i.e. wasted gold metal, even at this particle size), and so we sought to synthesize smaller Au NPs. Au NPs with a diameter of about 4 nm were synthesized through the Slot-Geuze (citrate/tannic acid reduction) method, and Pd metal was deposited using Pd chloride salt and H_2 gas reducing agent (Fig. 5(a)). Using H_2 gas was a more robust metal reduction step than using ascorbic acid, with the latter occasionally leading to colloidal unstable NP suspensions. The resultant smaller NPs were more catalytically active, with the most active composition (~ 13 wt% Pd) twice as active as the 20 nm NPs with 1.9 wt% Pd (Fig. 4(a)).⁴¹

The two reaction rate–Pd content 'volcano' curves indicated that the 4 nm and 20 nm NPs had two different optimum Pd metal contents leading to maximum activity. The curves could be re-plotted by changing the x-axis to Pd surface coverage. Figure 4(b) shows that the data points fall on a common curve, leading to several conclusions. One, catalytic activity is very sensitive to a quantifiable characteristic of the bimetal structure, specifically the Pd surface coverage. Two, the most active catalyst is 4 nm Au NPs with 70% Pd coverage. And three, 70% Pd coverage may be the optimum for TCE HDC activity, at least for Au particle sizes between 4 and 20 nm.

It was concluded that Au NPs could be promoting Pd catalysis through a geometric effect (formation of Pd clusters or ensembles on the Au surface), a mixed metal site effect (formation of Pd–Au surface species as a new population of active sites), or an electronic effect (donation of electron density from the Au to the Pd atoms, according to X-ray photoelectron spectroscopy (XPS) measurements). The initial turnover frequency ('TOF,' calculated as TCE molecules converted per Pd atom per second, after accounting for mass transfer effects) increased with increasing Pd surface coverage, or in other words, the per-Pd-atom activity increased with increasing amounts of deposited Pd atoms, which is evidence for geometric and mixed metal site effects. The TOF decreased

above $\sim 70\%$ Pd coverage, suggesting that the hypothesized Pd–Au active sites were reduced in number with additional Pd atoms deposited. This activity decrease also suggested that the additional Pd atoms were depositing on top of the surface Pd ensembles and thereby reducing the accessibility of all Pd atoms for reaction. This trend was quite apparent above 100% Pd coverage, where Pd atoms necessarily deposit on top of the surface Pd layer.⁴¹

We are certain that the Pd metal is located on the Au NP surface, to the extent of the limitations of the characterization methods. Pd is on the order of one atom thick, and was too thin to image through TEM. XPS data showed a systematic change in Pd d-orbital binding energy states with surface coverage, indicative of the intimate contact between the Pd and Au metals.⁴¹ It is not likely that pure Pd NPs are formed during the Pd deposition step, as the former process (homogeneous nucleation) is energetically less favored than the latter (heterogeneous nucleation). No evidence has been found for such Pd NPs in co-suspension with Pd-on-Au NPs. If they do exist, they would be contributing negligibly to the observed catalytic activity of the NP suspensions.

X-ray absorption spectroscopy (XAS) is a powerful materials characterization technique that provides detailed information about atomic coordination numbers and interatomic distances. To ascertain the state of the Pd-on-Au nanostructure, XAS was performed on Pd-on-Au NPs (with $\sim 70\%$ Pd coverage) and Au NPs at the Argonne National Laboratory (Advanced Photon Source).⁴² The NPs were synthesized and dispersed on a carbon powder, and analyzed in a flow reactor cell that allowed the supported NPs to be treated at different temperatures and gas compositions before spectral measurements. Some significant conclusions could be made from preliminary analysis of the collected extended X-ray absorption fine structure (EXAFS) data.⁴³ It was found that the Pd-on-Au NPs had a larger particle diameter than Au NPs, supporting the idea that the Pd precursor reduction step leads to the deposition of Pd metal on Au NPs. It was also found that the detected Pd atoms were located on the Au surface (likely as a Pd–Au surface alloy), and not located in the Au NP interior. The Pd-on-Au NPs were thus confirmed to have an Au-rich core and a Pd-rich surface.

Pd-on-Au NPs, 'Version 3.0'

By themselves, the Pd-on-Au NPs cannot be used directly for groundwater remediation because they exist as a water suspension

of freely floating particles. The NPs need to be in a supported form, such that they are surface-bound to a solid matrix. Contaminated water would be brought into contact with the supported NPs through pumped flow. The NPs can be immobilized onto a porous solid, such as ceramic oxides or polymeric resins, through charge or covalent interactions after they are synthesized. Figure 5(b) shows negatively charged Pd-on-Au NPs with 70% Pd coverage adsorbed electrostatically onto positively charged polymeric spheres known as ion-exchange resins (particle diameter = 0.65 mm, pore diameter = 1–30 nm).

This resin-supported Pd-on-Au NP material proved useful in demonstrating HDC performance characteristics under flow conditions (Fig. 6). With water flowing continuously at 4.4 mL min⁻¹ and containing 15 ± 5 ppm TCE (pH 7–8) and ~1.5 ppm H₂,

the resin-supported NPs were highly active for TCE HDC and remained active over the course of almost 4 days of operation. The resin by itself did not reduce TCE concentration, indicating that the NPs were solely responsible for TCE reduction. In comparison, commercial Pd/Al₂O₃ (with 1 wt% Pd loading, similar to that used by McNab and co-workers³⁰) was overall less active over the same period of time, even though more Pd metal was used. The average reaction rate constant of the supported NP catalyst was significantly larger than that of the Pd/Al₂O₃ (Table 1).

The catalyst cost can be estimated by considering the HDC remediation of 1000 L (or ~1 ton) water from 100 ppm TCE to the EPA limit of 5 ppb in 2 days. The amount of Pd metal needed for the Pd/Al₂O₃ was calculated to be three orders of magnitude more than that needed for the NP/resin catalyst. Considering that

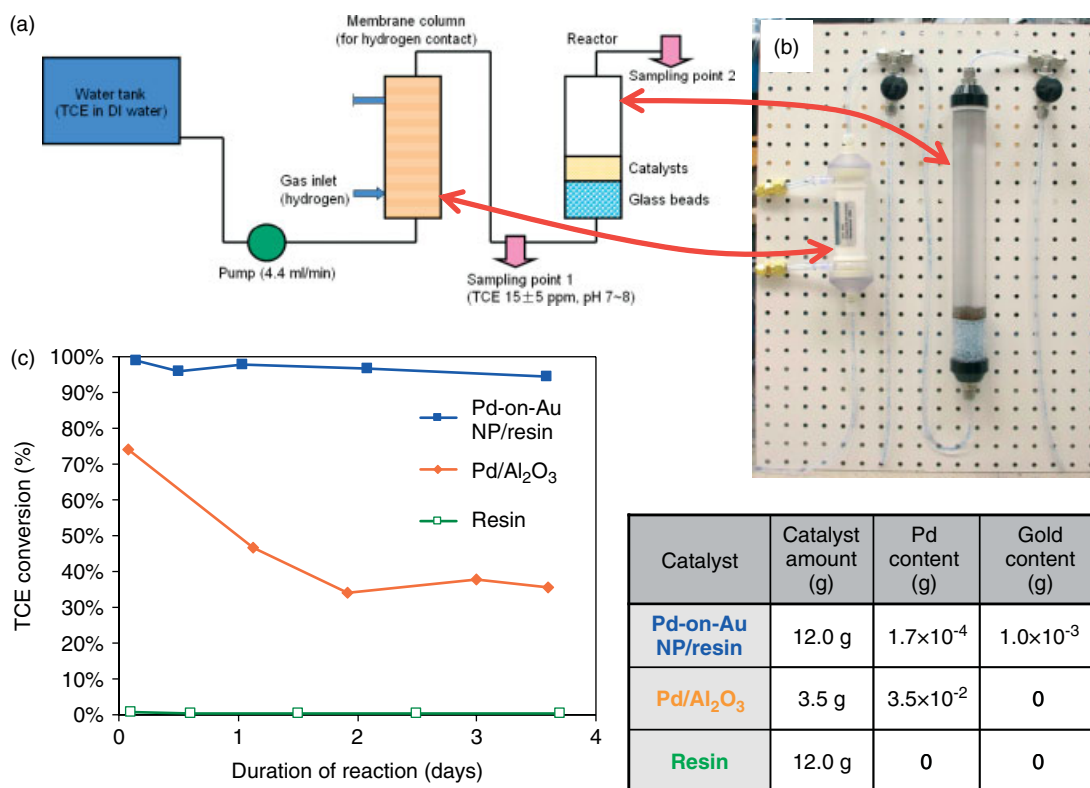


Figure 6. (a) Schematic flow diagram and (b) the continuous-flow reactor constructed for TCE HDC testing. (c) Time-on-stream activity data for resin-supported Pd-on-Au NPs (70% Pd coverage), Pd/Al₂O₃ pellets, and the resin support.

Table 1. Cost comparison of resin-supported Pd-on-Au NPs and Pd/Al₂O₃ pellets

Catalyst	Pd-on-Au NP/resin	Pd/Al ₂ O ₃
Average reaction rate constant (L kg ⁻¹ Pd day ⁻¹)	8.4 × 10 ⁷	7.8 × 10 ^{4a}
To treat 1000 L of water from 100 ppm TCE to 5 ppb TCE in 2 days (at a flow rate of 0.35 L min ⁻¹), the following catalyst amounts are needed		
Total Pd (g)	0.0589	94.2
Total Au amount (g)	0.343	0.0
Total ion-exchange resin support (g)	9404	n/a
Total commercial Pd/Al ₂ O ₃ catalyst (g)	n/a	9417
Materials cost		
Total cost of catalyst	\$142 ^b	\$2543 ^c

^a Close to the 5.3 × 10⁴ value reported by McNab *et al.*³⁰

^b Based on estimated cost of ion-exchange resin (0.014 US\$/g) and spot prices (28 April 2008) of palladium (437 US\$ oz⁻¹) and gold (893 US\$ oz⁻¹).

^c Based on estimated cost of commercial Pd/Al₂O₃ (\$0.27 US\$ g⁻¹).³⁰

Au and Pd prices have increased by ~200% and 100% respectively in the last 5 years, the Pd-on-Au NP/resin catalyst still costs ~20 times less than Pd/Al₂O₃ (Table 1).

ADDITIONAL CATALYTIC PROPERTIES

The Pd-on-Au NPs catalyzed the HDC of other chlorinated compounds into ethane very efficiently (Table 2). The ethenes reacted faster the less chlorinated they were (similar to observations found for Pd/Al₂O₃ catalysts³¹) in the following order: DCEs > TCE > PCE. The observed trends currently cannot be explained by C–Cl bond strength alone, as the cis and trans forms of DCE did not follow. Interestingly, for the DCE isomers, higher reaction rates appear to correlate with increased distance between the two Cl atoms.

An important implication is that PCE and TCE become progressively easier to react the more it loses its chlorines, which would explain why no build-up of partially dechlorinated compounds is seen at the end of the reaction. The formation of partially dechlorinated compounds is a problem for biologically mediated HDC and zero-valent iron HDC.⁴⁶ The reaction rates for the HDC of chlorinated methanes, like carbon tetrachloride and chloroform, are much lower than those for chlorinated ethenes using Pd/Al₂O₃.^{27,31} This trend appears to hold true for Pd-on-Au NPs also; studies to quantify these reaction rates are currently ongoing.

As mentioned earlier, groundwater contains a number of possible catalyst poisons, the most concerning of which are chloride and sulfide ions, which are known to lower Pd-based catalytic activity.^{47–49} It was found that Pd-on-Au NPs has an

unusually high tolerance to sulfide and chloride ions relative to Pd-only catalysts (Fig. 7).

Early results indicate that Pd-on-Au NPs deactivate half as rapidly as Pd NPs in the presence of sodium sulfide.^{43,44} At a sulfide/Pd-surface-atom ratio of 0.5, Pd NPs lost all catalytic activity for TCE HDC, whereas Pd-on-Au NPs (30% Pd coverage) retained activity at ~30% of its original TOF value and remained active up to a sulfide/Pd-surface-atom ratio of 1 (Fig. 7(a)). Curiously, Pd/Al₂O₃ was relatively unaffected by sulfide until a ratio of 1, suggesting that the alumina support could further enhance the sulfide tolerance of Pd-on-Au NPs. With regard to chloride (groundwater has chloride concentrations up to ~0.02 mol L⁻¹), Pd-on-Au NP activity was not affected by sodium chloride (Fig. 7(b)). In contrast, TCE HDC activity for Pd NPs and Pd/Al₂O₃ decreased by ~50% at 0.02 mol L⁻¹ chloride concentration.

FUTURE PROSPECTS

The advantages of Pd-on-Au NP catalysts over single-metal Pd catalysts are clear: significantly increased catalytic activity, and greater durability against deactivation from sulfide and chloride agents. Many exciting questions have followed, stimulating new directions in basic science and engineering research:

1. Supported Pd-on-Au NP catalyst scale-up is challenging. The process of synthesizing of Pd-on-Au NPs and subsequent immobilizing on a porous solid support is impractical to scale-up, because the amount of NPs produced per batch (~10¹⁴ NP mL⁻¹) is very low. Alternatively, synthesizing the NPs directly on a support surface is a viable process, as this is already being done for commercial supported bimetallic catalysts. Traditional supported bimetallic catalysis preparation methods are known, but techniques that lead to controlled bimetallic distribution (i.e. Pd-on-Au metal nanostructure) remains to be developed, as discussed earlier.
2. Field testing will be needed for the catalyst reactor containing the supported Pd-on-Au NPs. Long-term remediation performance that shows the durability of the catalyst and ease of regeneration will be important information to collect, so that cost comparisons with current pump-and-treat systems can be made. Further, with attention being paid to DNAPL now, and with many DNAPL remediation methods (based on biological, thermal, solvent flushing, and other processes) being

Table 2. HDC rate constants for selected chlorinated ethenes, using 4 nm Pd-on-Au NPs (with 25% Pd coverage). Reaction conditions are the same as above.⁴⁴

Compound		Rate constant (L g ⁻¹ _{Pd} min ⁻¹)	C–Cl bond strength (kJ mol ⁻¹) ^{31,45}
PCE	Cl ₂ C=CCl ₂	270	381
TCE	ClHC=CCl ₂	858	391
1,1-DCE	H ₂ C=CCl ₂	1519	393
cis-DCE	ClHC=CHCl	1813	370
trans-DCE	ClHC=CClH	2303	371

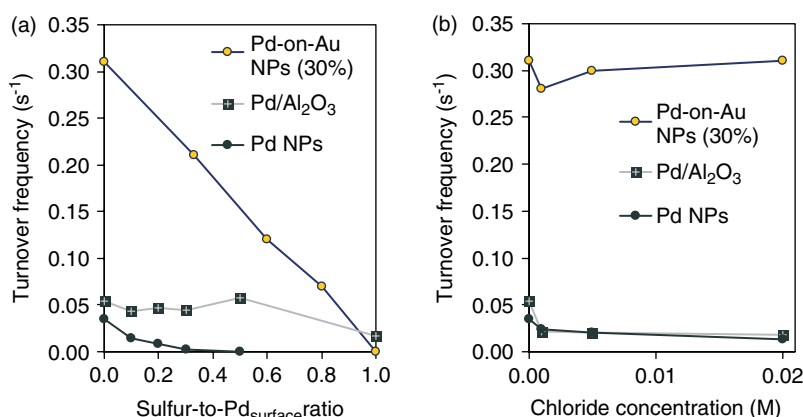


Figure 7. Turnover frequency values (calculated as molecules of TCE converted per surface Pd atom per second) for Pd-on-Au NPs (30% Pd coverage), Pd/Al₂O₃ (1 wt%), and Pd NPs, as a function of (a) sulfide:surface Pd atom ratio and (b) chloride concentration.

- studied at pilot-scale.^{5,50} the catalytic treatment of DNAPL is an exciting future possibility.
- Nowadays, the concern for any nanomaterial that can enter the environment is its potential for causing harm to the ecosystem and ultimately to humans. For a groundwater treatment technology based on highly efficient NP catalysts, it is possible that the NPs become dislodged from the reactor and released with the treated groundwater. Though it seems very unlikely that Au and Pd released in nanoparticulate form will be harmful to the environment, a rigorous assessment of Pd-on-Au NPs should be performed to confirm this hypothesis. One such analysis can be carried out by following the Nano Risk Framework guidelines, as developed and released to the public by Environmental Defense and DuPont in June 2007.
 - What is(are) the mechanism(s) by which Au promotes Pd catalytic activity and deactivation resistance? A thorough understanding would be highly beneficial for improved catalytic performance. Also, NPs smaller than the current 4 nm particles would be better for more efficient use of the precious metals, but it is not clear at all if particle size effects come into play. Interestingly, it is now well known that below 4 nm, Au NPs begin to show catalytic properties that bulk Au does not have. Perhaps other (less precious) metals can serve a similar role to Au.
 - What is the actual reaction pathway for TCE HDC over the Pd-on-Au NP surface? It has been hypothesized by the authors (and others for Pd/Al₂O₃) that TCE sequentially loses its chloride atoms after the molecule binds to the metal surface, while it gains hydrogen atoms before finally desorbing as a fully hydrogenated ethane molecule (Fig. 3). The Pd-on-Au NPs introduce the additional complication that the exposed Au surface and Pd–Au metal sites (in addition to Pd metal) could participate in TCE HDC at some point during the reaction. The range of reaction rates for the different DCE isomers suggests that TCE HDC proceeds through a trans-DCE intermediate preferentially, as an example of catalysis sensitivity to reactant molecular structure (Table 2). A mechanistic understanding of TCE HDC would allow us to predict and control the efficacy of Pd-on-Au NPs for other halogenated compounds.

SUMMARY

Contamination of groundwater by hazardous compounds is a significant problem in the USA and throughout the rest of the world.^{51,52} Nanotechnology – in the form of catalytic NPs – provides an exciting means to address this problem. Gold nanoparticles partially covered by palladium atoms are extremely effective for catalyzing TCE HDC, an important chemical pathway to treating solvent-contaminated groundwater. These NPs are also very resistant to the deactivation effects of chloride and sulfide ions, significantly lowering a technology implementation barrier. These NPs are illustrative of a new way to manipulate the catalytic properties of Pd metal for water-phase catalysis, towards a safe and effective water treatment nanotechnology.

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REFERENCES

- Moran MJ, Zogorski JS and Squillace PJ, Chlorinated solvents in groundwater of the United States. *Environ Sci Technol* **41**:74–81 (2007).
- Zogorski JS, Carter JM, Ivahnenko T, Lapham WW, Moran MJ, Rowe BL, *et al*, The quality of our nation's waters: volatile organic compounds in the nation's ground water and drinking-water supply wells. Circular 1292. US Geological Survey, Reston, VA (2006).
- Kueper BH, Wealthall GP, Smith JWN, Leharne SA and Lerner DN, *An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface*. R&D Publication 133. Environment Agency, Almondsbury, Bristol (2003).
- Linn W, Appel L, Davis G, DeZeeuw R, Dukes C, Eriksen P, *et al*, Conducting contamination assessment work at drycleaning sites. State Coalition for Remediation of Drycleaners; <http://www.drycleancoalition.org/download/assessment.pdf> (2004).
- Committee on Source Removal of Contaminants in the Subsurface, *Contaminants in the Subsurface: Source Zone Assessment and Remediation*. The National Academies Press, Washington, DC (2005).
- U.S. Government Accountability Office, Groundwater contamination: DOD uses and develops a range of remediation technologies to clean up military sites : report to congressional committees; GAO-05-666. US Government Accountability Office, <http://purl.access.gpo.gov/GPO/LPS61609>, Washington, DC (2005).
- Scott CS and Cogliano VJ, Trichloroethylene health risks: State of the science. *Environ Health Perspect* **108**:159–160 (2000).
- Liu DHF and Lipták BG, *Groundwater and Surface Water Pollution*. Lewis Publishers, Boca Raton, FL (2000).
- Crittenden JC, Trussell RR, Hand DW, Howe KJ and Tchobanoglous G, *Water Treatment Principles and Design*, 2nd edn. John Wiley & Sons, Hoboken, NJ (2005).
- U.S. Environmental Protection Agency, Improving nationwide effectiveness of pump-and-treat remedies requires sustained and focused action to realize benefits, Report No. 2003-P-000 006. U.S. Environmental Protection Agency, Washington, DC (2003).
- Pirkanniemi K and Sillanpää M, Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere* **48**:1047–1060 (2002).
- Matatov-Meytal YI and Sheintuch M, Catalytic abatement of water pollutants. *Ind Eng Chem Res* **37**:309–326 (1998).
- Alonso F, Beletskaya IP and Yus M, Metal-mediated reductive hydrodehalogenation of organic halides. *Chem Rev* **102**:4009–4092 (2002).
- Urbano FJ and Marinas JM, Hydrogenolysis of organohalogen compounds over palladium supported catalysts. *J Mol Catal A – Chem* **173**:329–345 (2001).
- Kovalchuk VI and d'Itri JL, Catalytic chemistry of chloro- and chlorofluorocarbon dehalogenation: from macroscopic observations to molecular level understanding. *Appl Catal A – Gen* **271**:13–25 (2004).
- Yu H, Kennedy EM, Adesina AA and Dlugogorski BZ, A review of CFC and halon treatment technologies – the nature and role of catalysts. *Catal Surv Asia* **10**:40–54 (2006).
- Keane MA, A review of catalytic approaches to waste minimization: case study – liquid-phase catalytic treatment of chlorophenols. *J Chem Technol Biotechnol* **80**:1211–1222 (2005).
- Muftikian R, Fernando Q and Korte N, A method for the rapid dechlorination of low-molecular-weight chlorinated hydrocarbons in water. *Water Res* **29**:2434–2439 (1995).
- Zhang WX, Wang CB and Lien HL, Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. *Catal Today* **40**:387–395 (1998).
- Gavaskar A, Tatar L and Condit W, Cost and performance report for nanoscale zero-valent iron technologies for source

- remediation. Battelle/Naval Facilities Engineering Service Center, CR-05-007-ENV, Columbus, OH (2005).
- 21 Matheson LJ and Tratnyek PG, Reductive dehalogenation of chlorinated methanes by iron metal. *Environ Sci Technol* **28**:2045–2053 (1994).
- 22 Arnold WA and Roberts AL, Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environ Sci Technol* **34**:1794–1805 (2000).
- 23 Lien HL and Zhang WX, Hydrodechlorination of chlorinated ethanes by nanoscale Pd/Fe bimetallic particles. *J Environ Eng – ASCE* **131**:4–10 (2005).
- 24 Kovenkloglu S, Cao ZH, Shah D, Farrauto RJ and Balko EN, Direct catalytic hydrodechlorination of toxic organics in wastewater. *AIChE J* **38**:1003–1012 (1992).
- 25 Schreier CG and Reinhard M, Catalytic hydrodehalogenation of chlorinated ethylenes using palladium and hydrogen for the treatment of contaminated water. *Chemosphere* **31**:3475–3487 (1995).
- 26 Schüth C and Reinhard M, Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water. *Appl Catal B – Environ* **18**:215–221 (1998).
- 27 Lowry GV and Reinhard M, Hydrodehalogenation of 1-to 3-carbon halogenated organic compounds in water using a palladium catalyst and hydrogen gas. *Environ Sci Technol* **33**:1905–1910 (1999).
- 28 Lowry GV and Reinhard M, Pd-catalyzed TCE dechlorination in water: Effect of [H₂](aq) and H₂-utilizing competitive solutes on the TCE dechlorination rate and product distribution. *Environ Sci Technol* **35**:696–702 (2001).
- 29 Lowry GV and Reinhard M, Pd-catalyzed TCE dechlorination in groundwater: Solute effects, biological control, and oxidative catalyst regeneration. *Environ Sci Technol* **34**:3217–3223 (2000).
- 30 McNab WW, Ruiz R and Reinhard M, In-situ destruction of chlorinated hydrocarbons in groundwater using catalytic reductive dehalogenation in a reactive well: testing and operational experiences. *Environ Sci Technol* **34**:149–153 (2000).
- 31 Mackenzie K, Frenzel H and Kopinke FD, Hydrodehalogenation of halogenated hydrocarbons in water with Pd catalysts: Reaction rates and surface competition. *Appl Catal B – Environ* **63**:161–167 (2006).
- 32 Schüth C, Kummer NA, Weidenthaler C and Schad H, Field application of a tailored catalyst for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater. *Appl Catal B – Environ* **52**:197–203 (2004).
- 33 Reinhard M (personal communication).
- 34 Sinfelt JH, *Bimetallic Catalysis: Discoveries, Concepts and Applications*. Wiley, New York (1983).
- 35 Bond GC, Louis C and Thompson DT, *Catalysis by Gold*, in *Catalytic Science Series*, ed by Hutchings GJ. Imperial College Press, London (2006).
- 36 Thompson DT, Using gold nanoparticles for catalysis. *Nano Today* **2**:40–43 (2007).
- 37 Bonarowska M, Malinowski A, Juszczak W and Karpinski Z, Hydrodechlorination of CCl₂F₂ (CFC-12) over silica-supported palladium–gold catalysts. *Appl Catal B – Environ* **30**:187–193 (2001).
- 38 Venezia AM, La Parola V, Deganello G, Pawelec B and Fierro JLG, Synergetic effect of gold in Au/Pd catalysts during hydrodesulfurization reactions of model compounds. *J Catal* **215**:317–325 (2003).
- 39 Chen MS, Kumar D, Yi CW and Goodman DW, The promotional effect of gold in catalysis by palladium–gold. *Science* **310**:291–293 (2005).
- 40 Nutt MO, Hughes JB and Wong MS, Designing Pd-on-Au bimetallic nanoparticle catalysts for trichloroethene hydrodechlorination. *Environ Sci Technol* **39**:1346–1353 (2005).
- 41 Nutt MO, Heck KN, Alvarez P and Wong MS, Improved Pd-on-Au bimetallic nanoparticle catalysts for aqueous-phase trichloroethene hydrodechlorination. *Appl Catal B Environ* **69**:115–125 (2006).
- 42 Miller JT, Kropf AJ, Zha Y, Regalbuto JR, Delannoy L, Louis C, *et al*, The effect of gold particle size on Au–Au bond length and reactivity toward oxygen in supported catalysts. *J Catal* **240**:222–234 (2006).
- 43 Fang Y-L, Miller JT, Heck KN, Alvarez P and Wong MS, (in preparation).
- 44 Nutt MO, Engineering palladium-on-gold bimetallic nanoparticles as groundwater remediation catalysts. Chemical and Biomolecular Engineering Department. Rice University, Houston, TX USA (2006).
- 45 D’sa ED, Wentworth WE and Chen ECM, Thermal electron attachment to chloroethylenes and bromoethylenes. The demonstration of a new electron capture detector mechanism. *J Phys Chem* **92**:285–290 (1988).
- 46 Helland BR, Alvarez PJJ and Schnoor JL, Reductive dechlorination of carbon tetrachloride with elemental iron. *J Hazard Mater* **41**:205–216 (1995).
- 47 Chen N, Rioux RM and Ribeiro FH, Investigation of reaction steps for the hydrodechlorination of chlorine-containing organic compounds on Pd catalysts. *J Catal* **211**:192–197 (2002).
- 48 Munakata N and Reinhard M, Palladium-catalyzed aqueous hydrodehalogenation in column reactors: modeling of deactivation kinetics with sulfide and comparison of regenerants. *Appl Catal B – Environ* **75**:1–10 (2007).
- 49 Chaplin BP, Shapley JR and Werth CJ, Regeneration of sulfur-fouled bimetallic Pd-based catalysts. *Environ Sci Technol* **41**:5491–5497 (2007).
- 50 <http://www.clu-in.org/>, Hazardous Waste Clean-Up Information (CLU-IN) Web Site. US Environmental Protection Agency.
- 51 Hillie T and Hlophe M, Nanotechnology and the challenge of clean water. *Nature Nanotechnology* **2**:663–664 (2007).
- 52 Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Marinas BJ and Mayes AM, Science and technology for water purification in the coming decades. *Nature* **452**:301–310 (2008).