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Trichloroethene hydrodechlorination by Pd-Fe bimetallic nanoparticles: Solute-induced catalyst deactivation analyzed by carbon isotope fractionation

Yanlai Han[a], Changjie Liu[b], Juske Horita[b], Weile Yan[a,*]

[a] Department of Civil, Environmental, and Construction Engineering, Texas Tech University, Lubbock, TX 79409, USA
[b] Department of Geosciences, Texas Tech University, Lubbock, TX 79409, USA

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ABSTRACT

Pd-Fe bimetallic nanoparticles (BNPs) have substantially higher reactivity for reductive dehalogenation of chlorinated ethenes (*e.g.*, trichloroethylene, TCE) compared to monometallic zero-valent iron nanoparticles, yet the rapid deactivation of BNPs in groundwater matrices limits their large-scale use in field applications. In spite of this shortcoming, the causes of BNP deactivation have not been clearly delineated. Stable carbon isotope fractionation measurements and product distribution analysis were used in this study to investigate the mechanisms of Pd-Fe deactivation in the presence of common groundwater solutes. Based on the apparent TCE degradation rates and at a constant solute concentration of 5 mM (except for humic acid, which was dosed at 20 mg/L), Pd-Fe BNPs exposed to SO_4^{2-}, HPO_4^{2-}, and humic acid solutions showed moderate declines in TCE dechlorination rates. Aging the bimetallic particles in Cl^-, SO_3^{2-}, HCO_3^-, and NO_3^- solutions, however, resulted in excessive or complete loss of TCE dechlorination reactivity. Analyses of the isotope fractionation associated with TCE hydrodechlorination (ε_{TCEHDC}) as well as the yield of ethane over other dechlorination products suggest at least four distinctive causes of deactivation: (i) aging the BNPs in deionized water and humic acid induces surface passivation due to buildup of mineral or organic carbon deposits; (ii) SO_3^{2-} and Cl^- ions interact specifically with Pd sites and disable the catalyst functions; (iii) NO_3^- and HCO_3^- inhibits iron corrosion, thereby limiting the production of H_2 as the precursor of reactive hydrogen species, and (iv) selective deactivation of surface sites involved in ethene hydrogenation was observed for BNPs aged in SO_4^{2-} and HPO_4^{2-} solutions. The findings suggest the Pd-on-Fe configuration of the bimetallic particles is susceptible to deactivation in a broader range of groundwater chemistry than previously expected.

1. Introduction

Catalytic hydrodechlorination (HDC) is an efficient and sustainable approach for the treatment of industrial wastewater or groundwater contaminated with chlorinated contaminants. Among many catalysts evaluated for this application, palladium is considered one of the most active metal for HDC reactions [1,2]. The prominent role of Pd stems from its ability in activating molecular hydrogen (H_2) to form reactive hydrogen species (*e.g.*, atomic hydrogen or hydride) [1,3] and efficient dissociation of carbon-chlorine bonds [4,5]. An important class of materials exemplifying Pd-catalyzed HDC is palladium-iron (Pd-Fe) bimetallic particles, in which a small amount of Pd is deposited onto zero-valent iron particles through a facile aqueous replacement reaction [6–8]. When colloidal or nanoscale iron is used, the resultant bimetallic nanoparticles (BNPs) can be directly injected into underground environment for *in situ* remediation of aquifers contaminated with chlorinated hydrocarbons [9,10].

Among many groundwater contaminants amenable to dehalogenation with Pd catalysts, chlorinated ethenes including trichloroethene (TCE) and tetrachloroethene (PCE) have received great attention because of their widespread occurrence at many U.S. superfund sites and their rapid transformation in the presence of Pd to completely dechlorinated products [2,11]. In contrast to chlorinated methanes or ethanes which undergo reduction via direct electron transfer, TCE or PCE reduction on metal surfaces involves an indirect reduction mechanism via reactive hydrogen species [12,13]. To enable *in situ* degradation of subsurface contaminants, a local source of H_2 is needed in the vicinity of Pd. As corrosion of iron in anoxic water produces

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[*] Corresponding author.
E-mail address: weile.yan@ttu.edu (W. Yan).

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hydrogen, a favorable synergy exists for Pd-Fe bimetallic material, where iron serves as the hydrogen source and catalyst support, and Pd acts as a catalyst for both hydrogen activation and HDC reactions. Indeed, rapid decomposition of chlorinated ethenes at rates thousand times that of the uncatalyzed iron have been documented in many laboratory investigations without forming the harmful chlorinated intermediates (*e.g.*, dichloroethenes or vinyl chloride) that are commonly observed in biological dehalogenation systems [14–16].

As with other metal catalysts, a serious impediment associated with the use of Pd is catalyst deactivation in the reaction media. Deactivation is particularly relevant to *in situ* groundwater remediation, as the aqueous phase typically contains substantial amounts of background electrolytes as well as dissolved organic carbon originated from natural decay processes. Typical inorganic solutes include chloride (Cl^-), sulfate ($SO_4{}^{2-}$), bicarbonate ($HCO_3{}^-$), nitrate ($NO_3{}^-$), and sulfide (HS^-), and their concentrations vary considerably with the site location, depth, and biogeochemical conditions. Among them, many are known to be potent deactivators of Fe [17,18] or Pd [19–21]. Not surprisingly, the Pd-Fe bimetallic nanoparticles have shown large susceptibility to solute-induced loss of reactivity [22,23]. In previous studies, particle deactivation was assessed by the rates of TCE degradation in batch experiments. Although bulk reaction rate is a useful indicator of the apparent effect of aqueous aging on particle reactivity, it offers limited insights into deactivation mechanisms caused by different groundwater solutes and the resultant impact on TCE degradation pathways.

Compound-specific isotope analysis (CSIA) is a valuable tool for assessing contaminant degradation in natural and laboratory environments [24–27]. The kinetic isotope effect (KIE) is built upon the principle that organic molecules with heavier isotopes generally experience slower bond breakage and thus, the heavier isotope tends to accumulate in the parent compound during the course of a degradation process. Consequently, an important application of CSIA is to assess the extent of contaminant transformation in an open system, since non-destructive loss of contaminants at a field site due to processes such as volatilization, sorption, diffusion, or dilution would contribute little to the isotope fractionation [25,28]. When applied in a controlled environment, isotope fractionation is useful to diagnose contaminant reaction pathways. It has been reported that abiotic dechlorination of PCE and TCE mediated by Fe(II)-containing minerals (*e.g.*, green rust, magnetite, or pyrite) [29] or zerovalent iron [15,30,31] is associated with more negative carbon isotope enrichment factors than biotic dechlorination processes [16]. Liang et al. attributed the suppressed isotope fractionation in biotic degradation to an increasing control of the degradation rates by mass transfer or complexation processes [16], which is analogous to the masking effect encountered in abiotic catalytic conversion reactions [32]. Elsner et al. observed that during abiotic dechlorination of dichloroethanes on Zn(0), the carbon isotope fractionation associated with β-dichloroelimination was much greater than the fractionation incurred during hydrogenolysis or α-elimination [33], thus the isotope data can be used to identify plausible mechanisms of the rate-limiting reactions. In a bimetallic system, iron and palladium need to work cooperatively in order to attain optimal HDC efficiency, thus the cause of particles deactivation is potentially more complex than monometallic iron. It is expected that CSIA combined with bulk kinetic and product speciation analyses would enable us to delineate the different mechanisms of catalyst deactivation in different groundwater matrices.

The objective of this study is to investigate the effects of common groundwater anions or natural organic matter on the reactivity of Pd-BNPs in TCE dechlorination reaction and to identify major factors contributing to the loss of reactivity or change in reaction pathways. Specifically, freshly made and various aged Pd-Fe BNPs (*i.e.*, particles pre-exposed to solutions containing different groundwater anions or natural organic carbon) will be evaluated in batch TCE hydrodechlorination experiments. The carbon isotope fractionations of TCE and daughter products were analyzed simultaneously using gas chromatography with a combustion isotope ratio mass-spectrometer (GC-C-IRMS) to quantify the TCE bulk enrichment factor (ε_{bulk}) and product-specific isotope fractionation values. Interpreting isotope effects together with kinetic data and product distribution allows insights to be gained into specific processes responsible for the declines in catalyst activity in different aqueous environment. This knowledge would serve to better predict and improve the performance of bimetallic material under environmentally relevant conditions.

2. Materials and methods

2.1. Preparation of nanoparticles

Nanoscale zero-valent iron (nZVI) particles were synthesized via borohydride reduction of an aqueous solution of ferric ions. Briefly, 10.8 g of $FeCl_3{\cdot}6H_2O$ (Fisher) were dissolved in a 500-mL solution mixture of distilled de-ionized (DDI) water and ethanol (1:1, v/v). 500 mL of 0.4 M $NaBH_4$ solution (Acros Organics) was introduced to the ferric solution at approximately 17 mL/min under a vigorous mixing condition, during which the ferric solution turned black due to the formation of colloidal-sized iron particles. The particles formed were collected by vacuum filtration and were stored in ethanol for further use. Pd-Fe bimetallic nanoparticles (denoted as Pd-Fe BNPs) were prepared by immersing the freshly prepared nZVI with an ethanol/water (1:1, v/v) solution of palladium chloride (Acros Organics) and ultrasonicating the mixture for 5 min [23]. The mass loading of Pd with respect to iron was fixed at 1.5% for all Pd-Fe BNPs. DDI water used in all procedures, including particle synthesis, aging and TCE experiments, was deoxygenated by purging with N_2 for 30 min.

2.2. Aging experiments

Aging experiments were conducted in 250-mL amber glass vials containing 200 mL of deoxygenated solutions amended with a common groundwater solute at 1–5 mM. Stock solutions of chloride, bicarbonate, nitrate, phosphate, sulfate and sulfite were prepared from their sodium salts, respectively. Stock solution of humic acid (Sigma-Aldrich, used as received) was prepared at 100 mg/L and was ultrasonicated for 10 min prior to use. The initial pH of the solutions was adjusted with dilute NaOH or HCl to between 7.4–8.2 to simulate the typical pH values encountered in groundwater. An appropriate amount of freshly made Pd-Fe BNPs was added into each solution at 2 g/L (dry weight) and the vial was sealed and agitated on a mechanical shaker for 24 h at room temperature ($22 \pm 1\,^{\circ}C$). The aged particles were collected by vacuum filtration and were used immediately in TCE degradation experiments.

2.3. TCE experiments and analytical method

TCE dechlorination experiments were performed to compare the reactivity of fresh and aged Pd-Fe BNPs. All batch experiments were conducted in 250-mL amber glass vials containing 200 mL of aqueous solution and the balance as headspace. Experiments were performed with fresh or aged nanoparticles added at 1–5g/L (dry weight). The vials were capped with Teflon Mininert valves, spiked with a small aliquot of TCE stock solution (in methanol and amended with 2-propanol as an internal standard), and placed on a wrist-action shaker at 250 rpm at room temperature. To monitor the concentrations and carbon isotope ratios of TCE and the reaction