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Bimetallic nickel–iron nanoparticles for groundwater decontamination: Effect of groundwater constituents on surface deactivation

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ABSTRACT

The incorporation of catalytic metals on iron nanoparticles to form bimetallic nanoparticles (BNPs) generates a class of highly reactive materials for degrading chlorinated hydrocarbons (*e.g.*, trichloroethylene, TCE) in groundwater. Successful implementation of BNPs to groundwater decontamination relies critically on the stability of surface reactive sites of BNPs in groundwater matrices. This study investigated the effect of common groundwater solutes on TCE reduction with Ni–Fe (with Ni at 2 wt.%) bimetallic nanoparticles (herein denoted as Ni–Fe BNPs). Batch experiments involving pre-exposing the nanoparticles to various groundwater solutions for 24 h followed by reactions with TCE solutions were conducted. The results suggest that the deactivation behavior of Ni–Fe BNPs differs significantly from that of the well-studied Pd–Fe BNPs. Specifically, Ni–Fe BNPs were chemically stable in pure water. Mild reduction in TCE reaction rates were observed for Ni–Fe BNPs pre-exposed to chloride (Cl^-), bicarbonate (HCO_3^-), sulfite (SO_3^{2-}) and humic acid solutions. Nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (HPO_4^{2-}) may cause moderate to severe deactivation at elevated concentrations (>1 mM). Product analysis and surface chemistry investigations using high-resolution X-ray photoelectron spectroscopy (HR-XPS) reveal that NO_3^- decreased particle reactivity mainly due to progressive formation of passivating oxides, whereas SO_4^{2-} and phosphate elicited rapid deactivation as a result of specific poisoning of the surface nickel sites. At similar levels, phosphate is the most potent deactivation agent among the solutes examined in this study. While our findings point out the desirable quality of Ni–Fe nanoparticles, particularly their greater electrochemical stability compared to Pd–Fe BNPs, its susceptibility to chemical poisoning at high levels of complexing ligands is also noted. Groundwater chemistry is therefore an important factor to consider when choosing appropriate material(s) for decontaminating the complex environmental media.

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1. Introduction

The applications of bimetallic iron nanoparticles (BNPs) to groundwater and soil remediation are prominent examples of recent advancements in environmental nanotechnology (Karn et al., 2009). The BNPs are typically comprised of zerovalent iron (Fe(0)) as the base metal and electron source and a small amount of a second metal (*e.g.* palladium and nickel) as catalyst additives (Schrick et al., 2002; He and Zhao, 2005; Lien and Zhang, 2007; Tee et al., 2009; Chun et al., 2010). Compared to iron alone, the presence of a second metal often brings about enhancement in reaction rates towards organohalides including chlorinated ethenes, chlorobenzenes, and polychlorinated biphenyls (PCBs) (Zhang et al., 1998; Schrick et al., 2002; Zhu and Lim, 2007; Choi et al., 2008). Another notable advantage of BNPs is their propensity to form more completely dehalogenated hydrocarbons (Lowry and Reinhard, 1999; Urbano and Marinas, 2001; Schrick et al., 2002; Cwiertny et al., 2006), which greatly circumvents the accumulation of toxic intermediates (*e.g.*, vinyl chloride). It is conceived that these beneficial effects are resulted from a combination of factors, including higher rates of Fe(0) oxidation and release of electrons (Xu and Zhang, 2000), the ability of the metal additives to generate and store active hydrogen species (Cwiertny et al., 2006; Lien and Zhang, 2007), and strong interactions between catalyst sites and contaminants to form surface complexes for more facile dehalogenation transformations (Cheng et al., 1997; Fennelly and Roberts, 1998; Chaplin et al., 2012).

Many structural characteristics of BNPs, including size and morphology of the base metal particles, mass loadings of the catalyst additives, and their chemical states and physical distribution in the particle volume are known to influence the reactivity of BNP particles. Heterogeneous distribution of catalyst metals on BNP surface has been observed in various bimetallic systems (McGuire et al., 2003; Tee et al., 2005; Cwiertny et al., 2006; Yan et al., 2010). This is particularly the case for particles prepared via aqueous reductive deposition on pre-formed iron nanoparticles (*i.e.*, the common approach for preparing Pd–Fe particles) as the reduced metal catalyst may serve as additional cathode sites catalyzing rapid reduction of the catalyst precursors, leading to island-like formations of additive metals instead of a uniform surface layer (Lien and Zhang, 2007; Chun et al., 2010; Yan et al., 2010). Another common approach to produce BNPs is through simultaneous reduction (co-reduction) of iron and additive metal precursors by sodium borohydride in one reaction pot, which can result in different intra-particle distribution and dispersion of the catalysts from those prepared with the solution deposition method. Curiously, majority of the Ni–Fe materials studied in the past were produced using the co-reduction method (Schrick et al., 2002; Tee et al., 2009). The hydrodechlorination reactivity and material susceptibility to common solutes in groundwater for Ni–Fe prepared by different methods have not been compared explicitly.

The chemical stability of BNPs in complex groundwater media is a crucial consideration in assessing the feasibility of this remediation technology in actual field applications. While most of the prior studies employed freshly synthesized Ni–Fe nanoparticles, a clear understanding of the effect of background constituents in groundwater on particle reactivity is not available thus far. An interesting contrast among different iron-based BNPs is that the deactivation behavior of Pd-amended iron nanoparticles (Pd–Fe BNPs) is expected to differ significantly from that of Ni–Fe BNPs due to the intrinsic differences in their electrochemical properties and in the chemical speciation of the additive metals in the presence of the iron material. Previous studies have observed rapid deactivation of Pd-amended BNPs in simple aqueous media without salt amendment (Zhu and Lim, 2007; Yan et al., 2010). With aberration-corrected analytical electron microscopic characterizations, it was reported that the Pd–Fe particles experienced pronounced oxidation of the zerovalent iron and the Pd(0) sites originally present on the outer surface of the nanoparticles were engulfed by an extensive matrix of iron oxide after 24 h of immersion in an aqueous solution (Yan et al., 2010). In comparison, monometallic iron nanoparticles were able to retain a significant fraction of the Fe(0) component for over a month in deoxygenated waters (Sarathy et al., 2008; Reardon et al., 2008). The excessively fast corrosion occurred in the case of Pd–Fe can cause loss of Fe(0) to unproductive reaction with water, leaving no stable form of reductant in the soil media for sustained contaminant reduction. Pd metal is also known to be strongly deactivated by groundwater constituents such as dissolved organic matter and reduced sulfur ligands (Hildebrand et al., 2009). Although the rapid deactivation of Pd–Fe BNPs observed in simple laboratory reaction media may be alleviated to some degrees in real groundwater media owing to background solutes serving as corrosion inhibitors (*e.g.* dissolved silica), the intrinsic material instability in Pd–Fe will remain a significant barrier when promulgating the technology to large-scale field applications. Compared to palladium ($E^{o}_{H,\ Pd(II)/Pd(0)} = 0.92$ V), the standard reduction potential of nickel ($E^{o}_{H,\ Ni(II)/Ni(0)} = -0.28$ V) is close to that of iron ($E^{o}_{H,\ Fe(II)/Fe(0)} = -0.44$ V) (Bard et al., 1985), and one would expect that galvanic effect would play a less important role in the deactivation of Ni–Fe BNPs. Furthermore, in solutions where a strongly reducing environment cannot be established (*e.g.* when Fe(0) is limiting or in the presence of background oxidants), a sizable fraction of nickel may present as Ni(II) on the particle surface. This suggests that the chemical stability of surface nickel sites would be markedly different from those of Pd material. Prior studies have noted that Ni–Fe BNPs endured repeated cycles of reactions without significant loss of reactivity (Schrick et al., 2002; Chun et al., 2010). However, as these studies were conducted in simple solutions without electrolytes, a detailed investigation to look at the effect of common background solutes on the deactivation of Ni–Fe nanoparticles is warranted.

In this study, we prepared Ni–Fe BNPs via two widely adopted synthesis approaches, namely, (i) co-reduction of Ni(II) and Fe(III) in borohydride solutions, and (ii) deposition of nickel on pre-formed Fe(0) nanoparticles. Three different nickel salts were used in these methods to evaluate their effects on the reactivity of the resultant particles. The as-synthesized particles were immersed in solutions amended with groundwater anions and/or dissolved organic matter for