

# Tuning the Properties of Iron Nanoparticles: Doping Effects on Reactivity and Aging

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## Abstract

Predicting and controlling the behaviors of nanoparticles in the environment requires understanding the impact of trace elements and impurities (including dopants) on properties, including reactivity and lifetime. The significant impact of many trace elements on the redox activity of iron metal and iron oxide nanoparticles in natural and engineering systems is well established. However, the fundamental mechanisms responsible for specific behaviors and the relationship of the mechanisms to the structural characteristics of the particles and dopants are not as well understood. In addition, the role of trace elements on particle aging and the overall reaction lifetime has not yet received much attention. Here we report the impact of three different processing methods on the reactivity of iron metal-core oxide-shell nanoparticles with carbon tetrachloride.

## Introduction

Iron and iron bimetallic nanoparticles (NPs) have been shown to have favorable reaction kinetics towards a variety of environmentally important solute species, including chlorinated hydrocarbons, oxyanions, and metal cations. They have also been observed to produce different, and sometimes more benign, reaction products than microscale iron particles. In recently completed work, we have found that nanoparticulate iron is highly dynamic and that NP aging in solution can have significant impacts on reaction processes <sup>(1)</sup>. Although such changes complicate full understanding of the behavior and lifecycle of NPs, to the degree that these aging processes can be understood and influenced by NP coatings, size, and composition, they also provide an opportunity to predict and control NP behavior.

The general objective of our research is to understand how the environmental fate and chemical

behavior of iron/iron oxide NPs (including transformations of NPs by aging and transformations by NPs of solutes such as chlorinated hydrocarbons or other environmental contaminants) are controlled by reactions within the NPs (i.e., between the core, shell, and coatings), and interactions between the NPs and the geochemical milieu consisting of water, major solutes (inorganic anions), and minor solutes (contaminants). A particular focus is on understanding the factors that influence contaminant reaction pathways with the secondary objective of using the understanding to “design” NPs for desired lifetime behavior (lifecycle) by altering aspects of the NP including size and composition (dopants and coatings).

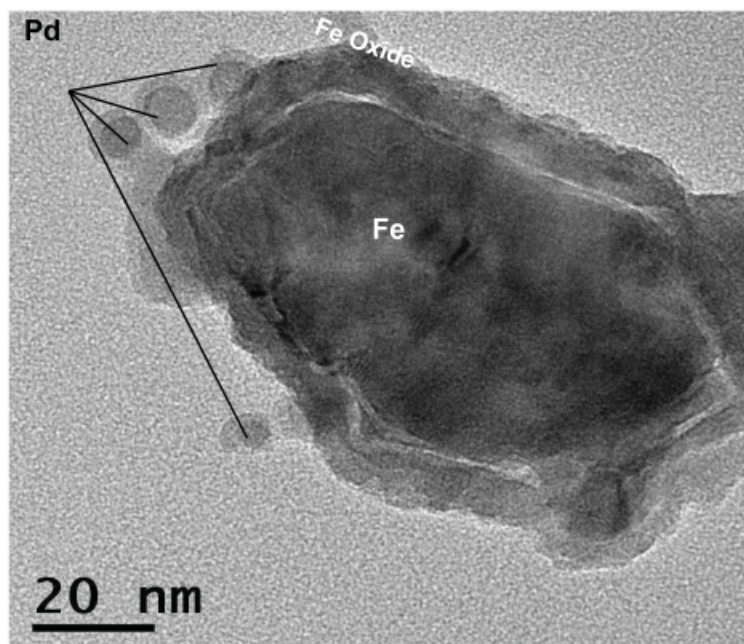
In earlier work examining the interactions of iron metal-core oxide-shell nanoparticles with carbon tetrachloride (CT) in aqueous solution, we have found that many nanoparticles show the similar reaction rates but some particles have a more environmentally friendly reaction pathway.<sup>(2)</sup> Follow up work demonstrated that both the reaction rate and the reaction pathways vary as function of time in solution<sup>(1)</sup>. Understanding and controlling the reaction properties of NPs requires knowledge of how particles evolve in time, how that evolution alters particle reactivity, and the role of impurities, coatings and trace elements on that time evolution.

The impact of metal doping of NPs has received increased research attention. Although iron metal-core oxide-shell NPs have been observed to enhance both reactivity and modify reaction pathways<sup>(3,4)</sup>, other workers note that the process is really not well understood and that some of the observed enhancements are readily observed in deionized water but not simulated groundwater<sup>(5)</sup>. To understand how iron metal-core oxide-shell NPs that are doped with catalyst metals actually function, it is important to have knowledge both of reaction behaviors (as a function of time if possible) and the structure and distribution of the doping material.

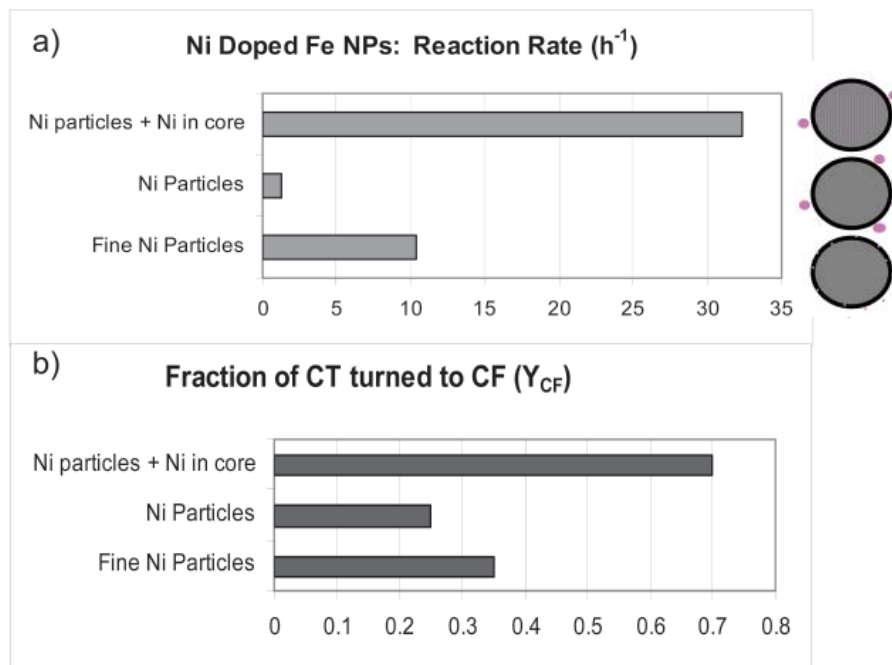
## Materials and Tests

We have examined the impact of Cu, Ni, and Pd on the reactivity and aging behaviors of iron metal-core oxide-shell NPs with the objectives of understanding their reaction pathways and engineering/designing particles with desired reaction pathways and lifetimes. Metal dopants were added to Fe metal-core oxide-shell particles in three slightly different ways. Solution deposition was conducted by adding a metal sulfate salt solution to nano-sized core-shell particles (RNIP-10DS) obtained from Toda Kyoto Corporation (Schaumburg, IL). These metal core particles were made by reducing goethite or hematite and in hydrogen<sup>(6)</sup>. We have also synthesized similar particles by a hydrogen reduction process starting with ferrihydrite, but adding the metal dopants as the ferrihydrite was forming in solution or to the formed particles before hydrogen reduction<sup>(7)</sup>. In addition, high purity iron metal-core oxide-shell nanoparticles were prepared by a sputter aggregation process<sup>(8)</sup>.

The materials were characterized by a variety of methods, including inductively coupled plasma mass spectrometry (ICP-MS)[for trace elemental analysis], transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) [with a particular focus on locating the trace elements], X-ray diffraction (XRD) [to determine the phases and amounts of phases present], and X-ray photoelectron spectroscopy (XPS)[to determine surface compositions and chemical states]<sup>(9)</sup>. Reaction studies were conducted to quantify reactivity and branching ratio of products for the reductive degradation of CT<sup>(1,2,7)</sup>.



**Figure 1.** TEM image of iron metal-core oxide-shell NP doped with Pd before the hydrogen reduction process. Individual Pd nanoparticles are readily observed mostly on the outside of the iron NP shell.



**Figure 2.** The reactivity of Fe metal-core oxide shell nanoparticles doped with ~1 mole% Ni through the three processes producing different distributions of Ni. a) Particle reaction rates with CT; b) Fraction of CT transformed to CF ( $Y_{CF}$ ). Schematic representations of the particles demonstrate the different Ni distributions in the particles.

## Results and Discussion

The combined results of XRD, TEM with EDS, XPS and ICP-MS indicate that the three different metal doping processes produce particles with different distributions of the metal. The solution deposition process produces very small metal dopants distributed within and on the iron oxide shell. These particles are not easily directly observed. Particles produced by the hydrogen reduction process produce larger nanoparticles (2-3 nm) of the catalytic metal on the surface of the oxide (as shown in Fig 1). If the oxide was co-precipitated with the formation of the ferrihydrite, dopant metal is contained within the iron metal core as well as occurring in the identifiable particles. An example of the types of metal NPs formed during the hydrogen reduction process for Pd doping is shown in Fig 1. The effects of different types of doping are shown schematically along with reactivity data for one particle type in Fig. 2.

As one example of the results, we compare the impact of approximately 1 mole % Ni added to the nanoparticles on the reactivity with CT. Even though the amount of Ni added to these particles is nearly identical, the rates of CT loss are significantly different indicating that the distribution of the metal can have significant impact on the particle reactivity. In Figure 2a, the reaction rates for the reduction of CT are shown. The rate differs by about an order of magnitude. In figure 2b, the chloroform (CF) yield ( $Y_{CF}$ ) is shown for each of the particle types.  $Y_{CF}$  is unity for complete conversion of CT to CF and zero for complete conversion of CT to the more benign products of reduction. In this context a lower value is better and significant differences among the three types of doped particles are observed. In particular, the material containing Ni within the iron core and distributed as nanoparticles on the oxide surface is the most reactive but also has the poorest  $Y_{CF}$ . In contrast, the material containing Ni only as nanoparticles on the surface of the oxide shell is the least reactive but has the best (lowest)  $Y_{CF}$ .

The above comparisons are the result of experiments performed at a single time point, for freshly synthesized or doped materials. However, reactivity can vary with time; thus it is important to quantify changes as particles age in solution. Measurements of reaction rates every twenty four hours for several days show that the reaction rates for Ni doped materials increase with time a four day period, ultimately having a low  $Y_{CF}$  and relatively high reaction rates<sup>(7)</sup>.

We have found the in some circumstances the reactivity of NPs with CT mirrors general corrosion behavior<sup>(1)</sup>. Measurements of the corrosion behavior of the commercial RNIP particles and ultra pure nanoparticles shows that the corrosion rates of the pure particles may be more than four times slower than the commercially available material<sup>(10)</sup>. Our work and the work of others<sup>(11)</sup> have demonstrated that the reactivity of some NPs nanoparticles can vary significantly on examining fresh wet or dried particles. It is therefore clear that particle processing and handling, the presence of coatings or contaminants, as well as the distribution of dopants can significantly alter particle reaction behavior.

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## Conference Questions and Answers

***Question:***

Doesn't the reduction of nickel and cadmium used in doping of nanoscale iron particles impact the results you observed?

***Answer:***

Probably, but we do not fully understand how yet. We do know that doping changes not only the particles' reactivity with carbon tetrachloride, but also the overall reactivity and nature of the shell on the nanoparticles. Therefore, a lot of possible effects must be considered.

***Question:***

How much effect does the oxide shell around the iron core have on electron tunneling, the rates of processes, etc?

***Answer:***

We are starting some experiments to measure the effects of the shell. We have conducted AC-XDS to look at charging and line shifts, which show differences in the conducting properties of shells. We saw differences in the properties of aged and fresh shells. We are now doing experiments to see if we can change the property and answer questions such as: Should we dope the particles? If sulfur is present, does it change the property? How much does aging change the property?

***Question:***

Would the degree of aggregation versus crystallinity also be important?

***Answer:***

Yes. When we start with a highly crystalline material and the outside changes, it looks aggregated, somewhat porous, and not at all crystalline. If we start with a really active material, it repassivates, and the repassivated state has different properties.