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Degradation of Trichloroethylene and Dichlorobiphenyls by Iron-Based Bimetallic Nanoparticles

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Abstract

Bimetallic nanoparticles of Ni/Fe and Pd/Fe were used to study the degradation of trichloroethylene (TCE) at room temperature. The activity for different iron-based nanoparticles with nickel as the catalytic dopant was analyzed using iron mass-normalized hydrogen generation rate. Degradation kinetics in terms of surface area-normalized rate constant was observed to have a strong correlation with the hydrogen generated by iron oxidation. A sorption study was conducted, and a mathematical model was derived that incorporates the reaction and Langmuirian-type sorption terms to estimate the intrinsic rate constant and rate-limiting step in the degradation process, assuming negligible mass transfer resistance of TCE to the solid particles phase. A longevity study through repeated cycle experiments was conducted to analyze the effect of activity loss on the reaction mechanistic pathway, and the results showed that the attenuation in the nanoparticles activity did not adversely affect the reaction mechanisms in generating gaseous products such as ethylene and ethane.

Keywords

bimetallic nanoparticles; chlorinated organics; intrinsic reaction rate constant; Langmuirian-type sorption isotherm

1. Introduction

Reductive dechlorination of chlorinated organics using zero valent metals such (Fe and Zn) has been well documented in the literature. The advances achieved in nanotechnology have stimulated further research in the synthesis of bimetallic nanoparticles having as a goal the enhancement of reaction kinetics and improvement in metal usage. Bimetallic systems consisting of a base metal, such Fe⁰ as the reductant, and a second dopant metal such as nickel or palladium as the catalytic agent have been synthesized. These bimetallic nanoparticles have reaction rates that are orders of magnitude higher than the corresponding monometallic nanoparticles. It is hypothesized that nanostructured particles with catalytic dopant are able to alter the dechlorination pathways as reported in the literature [1]. Specifically, the dechlorination pathways of chloro-organics by zero valent metals that include the reductive α/β elimination (dihalo-elimination), hydrogenolysis (hydrogen substitution of halogen), or hydrogenation (multiple bonds cleavage) are theorized to be shifted to the catalytic reductive hydrodechlorination mechanism. Our previously reported results and degradation studies by others using bimetallic nanosystems (Ni/Fe, Pd/Fe, etc.) have demonstrated increased surface

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area-normalized rate constants with the formation of less-chlorinated side-products that accounted for less than 5 wt% of the total initial carbon balance [2,3,4,5,6]. This indeed proved that the bimetallic nanoparticles have higher reactivity towards the destruction of chloro-organics than the bulk and monometallic systems.

In many studies, the heterogeneous degradation of chlorinated organics has been modeled using a pseudo first-order reaction mechanism [1,2,3,7,8]. The observed first-order mechanism was used due to its simple and excellent agreement with the kinetic data obtained experimentally. The surface area-normalized reaction rate constant determined by the model assumed that the particle surface has similar sorption energy and reactivity in the degradation reaction. This assumption has neglected the importance of surface heterogeneity that consists of reactive and non-reactive sorption sites. Gotpagar et al. [9] introduced a term called the *fraction active sites parameter* and demonstrated the ability of their model to predict the intrinsic reaction rate by assuming the new parameter to be constant. Another study by Burris et al. has assumed that the sorption of TCE is to non-reactive sites, effectively separating the non-reactive sorption from the reactive sites responsible for the degradation process [10,11]. The authors have also shown that the quasi-equilibrium sorption is non-linear and can be fitted using a generalized Langmuir isotherm.

The synergistic characteristics of bimetallic systems involved the oxidation of iron as the active reactant in generating the electrons and hydrogen necessary for the degradation process. The hydrogen generation reaction is represented by $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$. The electrons and hydrogen generated are then utilized by a second dopant metal to catalyze the reaction through the formation of active surface metal-hydride as a powerful reductant represented as $2\text{M} + \text{H}_2 \rightarrow 2\text{M-H}$, where M can be nickel or palladium. The anaerobic oxidation of bulk iron in the presence of different cosolutes has been studied by Reardon, but the analysis lacks the kinetic data needed to explain the correlation between iron oxidation and the dechlorination process [12]. The oxidative nature of Fe/B nanoparticles was established by Liu et al. in terms of total hydrogen generation [13]. The authors demonstrated the catalytic effect of Fe/B nanoparticles in dechlorinating TCE by its ability to utilize the hydrogen generated in the oxidation process. The reported results showed the importance of active surface sites that are capable of utilizing hydrogen in the dechlorination reaction by comparing the Fe/B nanoparticles with the commercial nanoiron, where the later sample showed inactivity towards hydrogen utilization. Another study by Schrick et al. reported that the enhanced degradation kinetics of Ni/Fe nanoparticles was accompanied by hydrogen generated by anaerobic iron oxidation of the bimetallic system [3]. On the contrary, the nano and bulk iron, which had reaction rates that were two orders of magnitude lower than Ni/Fe, had significantly lower hydrogen generation.

The objectives of this study are (1) to analyze the hydrogen generation rate by the anaerobic oxidation of nanoiron and different iron-based bimetallic nano systems (Ni/Fe) with and without degradation process, (2) to correlate the hydrogen generation rate with the surface area-normalized rate constant of TCE degradation by Ni/Fe nanoparticles, (3) to analyze the surface sorption effect on the degradation kinetics by an extraction study, (4) to derive a mathematical model for the determination of the intrinsic degradation rate, and (5) to determine the effect of deactivation on reaction kinetics and products formation through a cycle study.

2. Reaction Mechanisms and Kinetic Models

2.1. TCE Degradation Mechanism under Batch Study

Similar to the fundamental understanding of heterogeneous catalytic reactions, the batch degradation process of TCE includes (a) the transport of reactants from the bulk solution to the liquid-solid interface followed by adsorption to surface sites, (b) catalytic

hydrodechlorination on the active surface sites, and (c) desorption of the products and transport back to the bulk solution.

(a1): Adsorption of TCE from the solution phase to the particle surface forming a π -bonded adsorbate:

(a2): Formation of a di- σ -bonded species from the π -bonded intermediate:

(b): Reductive hydrodechlorination reactions on the surface by active nickel hydride (Ni-H) with the formation of ethane as the final product.

(c): Desorption of product from the surface and transfer back to the bulk solution phase.

Combining the hypothesized surface-mediated catalytic mechanisms, the overall TCE degradation with iron oxidation is written as follows:

2.2. Model Derivation?

Derivation of the mathematical model for the heterogeneous degradation reaction of TCE in the batch solution study is illustrated in Figure 1. According to the schematic, TCE is sorbed first (physical sorption and/or chemisorption) on the particles surface followed by the degradation reaction. The main equation with reaction coupled with adsorption can be represented as:

$$m_{\text{Ni/Fe}} \frac{dq_{\text{TCE}}}{dt} = -k_{\text{int}} m_{\text{Ni/Fe}} q_{\text{TCE}} - V_{\text{aq}} \frac{dC_{\text{aq}}}{dt} \quad (8)$$

where C_{aq} ($\mu\text{mol/L}$) and q_{TCE} ($\mu\text{mol/g}$) is the TCE aqueous phase concentration and surface-sorbed TCE per mass of metal, respectively; k_{int} (h^{-1}) is the intrinsic reaction rate constant; V_{aq} (L) is the total reaction volume; and $m_{\text{Ni/Fe}}$ (g) is the total metal mass used. In addition to

the sorption on the metal surface according to (1), TCE can also form inactive-sorbed species on nanoparticles according to the following (S_i denotes inactive vacant surface sites on the particles):

The TCE aqueous concentration can then be written as the following:

$$V_{aq} \frac{dC_{aq}}{dt} = -k_{a1} V_{aq} m_{Ni/Fe} C_{aq} C_v - k_{a2} V_{aq} m_{Ni/Fe} C_{aq} C_v + k_{-a1} m_{Ni/Fe} q_{TCE} + k_{-a2} m_{Ni/Fe} q_{Si} \quad (10)$$

The first two terms correspond to the sorption of TCE to the metal surface and, the remaining two terms represent desorption of surface-sorbed TCE back to the solution phase. The definition of the rate constants can be found in nomenclature. Transmigration of the inactive-sorbed TCE in (9) between adjacent reactive sites can occur on the metal surface, and such phenomena have been observed and reported in the literature [14]:

If we assume that the transmigration process of (11) is rapid, we can write:

$$m_{Ni/Fe} \frac{dq_{Si}}{dt} \cong 0 \cong -k_{Si} m_{Ni/Fe} q_{Si} + k_{-Si} m_{Ni/Fe} q_{TCE} \quad (12)$$

and we get:

$$q_{Si} = K_{Si} q_{TCE}, \quad \left(K_{Si} = \frac{k_{-Si}}{k_{Si}} \right) \quad (13)$$

Substituting eq (13) into eq (10) and upon further rearrangements we obtain the following TCE aqueous concentration equation:

$$V_{aq} \frac{dC_{aq}}{dt} = -K_A m_{Ni/Fe} C_{aq} C_v + K_B m_{Ni/Fe} q_{TCE} \quad (14)$$

with:

$$K_A = (k_{a1} + K_{a2}) V_{aq}, \quad K_B = (k_{-a1} + k_{-a2} K_{Si}) \quad (15)$$

Combining eq (8) and eq (14) we obtain the representative equation for degradation of surface-sorbed TCE:

$$m_{Ni/Fe} \frac{dq_{TCE}}{dt} = - (k_{int} + K_B) m_{Ni/Fe} q_{TCE} + K_A m_{Ni/Fe} C_{aq} C_v \quad (16)$$

The surface-sorbed TCE can be characterized by Langmuirian-type quasi-sorption isotherm written as the following (the sorption of aqueous TCE to the surface is termed quasi because of the simultaneous sorption and degradation reactions):

$$q_{TCE}(t) = \frac{KQC_{aq}(t)}{1+KC_{aq}(t)} \quad (17)$$

where K (L/ μ mol) and Q (μ mol/g) are the sorption parameter and maximum sorption concentration, respectively. Equation (16) is transformed into aqueous phase TCE concentration by using eq (17). After some mathematical operations the final equation becomes:

$$\frac{dC_{aq}}{dt} = -(k_{int} + K_B)C_{aq}(1 + KC_{aq}) - \frac{K_A}{K} \frac{C_v}{Q} C_{aq}(1 + KC_{aq})^2 \quad (18)$$

This is the general model derived for batch degradation reaction with surface sorption and rapid transmigration of inactive-sorbed TCE to nearby active sites. We have assumed that the reaction is first-order with respect to the surface-sorbed TCE concentration. The pseudo first-order reaction model is widely used and reported in the literature for TCE studies [1,2,3,7,8]. The assumptions used in deriving the model for the complex heterogeneous surface reactions are summarized as followed:

- a. Mass transfer resistance between the aqueous and solid boundary layer is negligible.
- b. Degradation reactions for TCE and any surface-sorbed intermediates are irreversible.
- c. TCE dechlorination occurs on the surface of the particles before desorption of products to the bulk solution.
- d. Reactions are at isothermal condition.
- e. Absence of inter- and intra-species competitive effects.
- f. Gaseous products such as ethylene and ethane are assumed to accumulate only in headspace because of their low solubility at the aqueous phase.

3. Experimental Section

3.1. Materials

Granular sodium borohydride ($\text{NaBH}_4 = 99.99\%$), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O} = 99.99\%$), ultrapure grade tris(hydroxymethyl)-aminomethane (purity = 99.9+%), and denatured anhydrous reagent grade ethanol (water < 0.0003%) were purchased from Aldrich Chemical Company. Ferrous chloride (assay as $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} = 102.0$), trichloroethylene ($\text{C}_2\text{HCl}_3 = 99.99\%$), sodium hydroxide solution (certified as 0.2490–0.2510 N), hydrochloric acid solution (certified as 0.2 N), nitric acid (trace metal grade), hexane (GC-MS grade), and deionized ultra-filtered water (DIUF) were from Fischer Scientific. All chemicals were used as purchased. Deoxygenated DIUF was prepared by heating at $\sim 60^\circ\text{C}$ and bubbling with N_2 gas overnight.

3.2. Bimetallic Nanoparticle Synthesis

The synthesis procedure for the bimetallic Ni/Fe nanoparticles was similar to that reported in the literature [2]. In brief, Ni/Fe nanoparticles with different nickel content were synthesized using sodium borohydride as the reducing agent from an aqueous mixture of Fe^{2+} and Ni^{2+} . The final dark colloidal particles were washed with ethanol and deoxygenated DIUF water

followed by filtration. The nanoparticles were vacuum-dried at room temperature overnight and used immediately for the TCE study. BET surface area analysis for the prepared Ni/Fe nanoparticles was conducted using Micromeritics ASAP 2000 model.

3.3. Batch Degradation Study

A 120-mL EPA certified vial with Mininert® septum valve was used for the TCE and DCB batch degradation studies. Two initial aqueous TCE concentrations (10 mg/L and 500 mg/L) occupying a total volume of 40 mL with 80 mL headspace were used in the TCE study. In the study of the effect of pH on the hydrogen generation rate, the initial solution pH of 6.50 was adjusted to 5.0 and 8.0 using HCl or NaOH and tris(hydroxymethyl)-aminomethane (TRIS) as buffer. This organic buffer was chosen because of its reported weak interaction with ferrous ions in solution [1,13]. Bimetallic Ni/Fe nanoparticles of 0.10 g were added to the TCE solution under nitrogen purging, and the container was immediately sealed with the Mininert® valve. For the TCE cycle study, a new set of seven batches of TCE solutions were used for each of the cycle analysis. A volume of 4 mL of reacted sample from each of the TCE solutions at the end of the first cycle (120 min) was withdrawn, and another 4 mL of stock TCE solution (100 mg/L) was added back into the vial for a fresh TCE initial concentration of 10 mg/L. A new septum vial was used at the beginning of each cycle study. The same procedure was used at the end of second cycle (140 min) for the third cycle analysis.

3.4. TCE Analysis

For the determination of the aqueous phase TCE concentration, a known amount of sample solution from the reaction vial was injected into another 42-mL total volume septum-sealed glass vial filled with 40 mL DIUF water at specific reaction time intervals. The instrumentation technique and equipment were similar to those reported in a previous TCE study.¹⁰ To determine the total TCE concentration (aqueous phase plus solid phase), a specific sample volume was withdrawn from the same reaction vial until 20 mL of solution was left in the container. A volume of 20 mL of hexane was added into the vial containing both the TCE solution and nanoparticles. The extraction process was allowed to run overnight. The total TCE concentration was determined using the hexane phase solution and analyzed by GC-ECD using Varian CP3800 equipped with an RTX-624 capillary column from Restek coupled with a CP8300 autosampler. A standard curve for chloride ranging from 1.00 to 50.00 mg/L was constructed from Ultra Scientific's TCE standard (100.40 ± 0.50 mg/L in methanol). Periodic curve-check was conducted at 15 and 25 mg/L Cl prepared from dilution of the same standard.

3.5. Hydrogen Gas Analysis

Quantification of hydrogen evolved due to the oxidation of nanoiron and bimetallic nanoparticles (Ni/Fe) was conducted by GC-TCD analysis using Agilent 6890N Network GC System interfaced with ChemStations software and equipped with a Carboxen 1004 micropacked column from Supelco. A Hamilton airtight lock syringe was used to withdraw 1 mL of headspace volume from the vials and injected directly to the manual injection port. The total moles of H₂ generated was correlated with a five-point calibration curve constructed using standard gas of 1% H₂ in nitrogen (analytical accuracy = $\pm 0.02\%$) from Scott Specialty Gasses. To check the accuracy of the calibration curve, a known mass of Fisher electrolytic iron was digested in a 120 mL-vial with 40 mL of 1.0 M nitric acid. A volume of 1 mL of the headspace sample was analyzed, and the total H₂ generated was determined using the standard curve. The theoretical value and calculated results using the standard curve were within $96.50 \pm 0.50\%$ accuracy. Imbalance may be due to the formation of surface impurities such as oxides upon exposure of Fisher Fe in the air. Leakage through the Mininert® septum vial was checked by injecting a known volume of H₂ standard gas into the vial filled with 40 mL of deoxygenated water and 80 mL headspace. The headspace H₂ gas was re-drawn from the headspace at

different time intervals (5 h and 10 h), and its concentration was analyzed using the H₂ standard curve. Neglecting the solubility of hydrogen in water, percent errors between the initial and time-lapsed value were determined to be less than 5%. For the TCE cycle study, gaseous degradation products, such as ethylene and ethane, were analyzed using another calibration curve constructed using standard gas (1% of acetylene, carbon monoxide, carbon dioxide, ethane, ethylene, methane, and the balance nitrogen) from Scott Specialty Gases.

4. Results and Discussion

4.1. Hydrogen Generation by Ni/Fe Nanoparticles

Figure 2 shows the total amount of hydrogen generated by Ni/Fe nanoparticles with different nickel content normalized with iron mass under anaerobic condition. The results represent the sum of the gas phase and aqueous phase hydrogen gas produced:

$$H_2 = H_2(g) + H_2(aq) \quad (19)$$

where the gas phase hydrogen, H₂ (g), is determined directly from the headspace GC-TCD analysis, and the aqueous phase hydrogen, H₂ (aq), is obtained as follows:

$$H_2(aq) = (7.515 \times 10^{-6}) H_2(g) R T M_{H_2O} / V_{HS} \quad (20)$$

where $7.515 \times 10^{-6} \text{ mol kg}^{-1} \text{ kPa}^{-1}$ is the solubility of hydrogen in water at 100 kPa at 25 °C; R is the gas constant; T is the room temperature; and M_{H_2O} and V_{HS} are the mass of the total solution and headspace volume, respectively. Solid phase hydrogen due to the diffusion and entrapment of H₂ by the nanoparticles is assumed to be negligible in short-term analysis (2-h duration). This assumption is justifiable since the solubility of H₂ in metal particles is relatively low ($< 10^{-5} \text{ cm}^3 \text{ kg}^{-1}$ at 100 kPa H₂ for pure iron and $< 10^{-2} \text{ cm}^3 \text{ kg}^{-1}$ at 100 kPa H₂ for nickel).

Initial hydrogen generated by the anaerobic iron oxidation increased linearly with time within the first two hours for four of the bimetallic systems (20 wt%, 25 wt%, 50 wt%, and 75 wt% nickel), with the 20 wt% and 25 wt% Ni nanoparticles being two of the highest hydrogen generating systems. Lower hydrogen generation with increase in nickel content can be explained by the enriched nickel concentration at the edge of the particles that acts as a protective layer to minimize the oxidation of iron. This observation is expected since the simultaneous reduction of a Ni²⁺ and Fe²⁺ mixture will generate nanoparticles with nickel predominantly concentrated at the outer layer as reported in the literature [2]. It is interesting to observe that in Figure 2 the total hydrogen generation for Ni = 20 wt%, 25 wt%, and 50 wt % falls on a relatively linear trend line ($r^2 = 0.905$) when normalized by the iron mass. The obtained iron-normalized hydrogen generation rate, k_{H_2} , based on the regression line is $63.2 \text{ } \mu\text{mol H}_2 / \text{g Fe h}$. This showed that the bimetallic system with up to 50 wt% nickel content still provides satisfactory iron surface concentration in producing hydrogen under anaerobic condition. In contrast, the 75 wt% Ni nanoparticles had significantly lower iron-normalized H₂ generation ($k_{H_2} = 6.70 \text{ } \mu\text{mol H}_2 / \text{g Fe hr}$). This observation confirmed that particles with higher nickel content had surfaces enriched in nickel leading to a decrease in the surface iron concentration.

The hydrogen analysis of pure iron nanoparticles in Figure 3 shows that H₂ production rate for the acid-treated sample is close to two-fold higher than the non-treated nanoparticles. As anticipated, the acid treatment removes any passive surface material that might affect the corrosion of iron and effectively increases the hydrogen generation rate from $25.1 \text{ } \mu\text{mol H}_2 / \text{g}$

Fe h to $44.6 \mu\text{mol H}_2/\text{g Fe h}$. The passive surface species may include boron/boride due to the borohydride synthesis method and surface oxides by the oxidation of iron exposed to air. The iron-normalized hydrogen generation rate for the acid-treated nanoiron in Figure 3 and 20 wt % Ni nanoparticles in Figure 2 is $44.6 \mu\text{mol H}_2/\text{g Fe h}$ and $64.3 \mu\text{mol H}_2/\text{g Fe h}$, respectively. However, the five-fold lower surface-area normalized TCE degradation rate, obtained by using the nanoparticle's BET surface area, ($k_{SA} = 0.72 \times 10^{-2} \text{ L}/\text{m}^2 \text{ h}$) for the acid-treated nanoiron as compared to $3.50 \times 10^{-2} \text{ L}/\text{m}^2 \text{ h}$ for the bimetallic nanoparticles (20 wt% Ni) indicated that the hydrogen generated from the corrosion process cannot be utilized effectively in the absence of a second catalytic metal dopant for the degradation of chlorinated organics. It is hypothesized that the hydrogen molecule disproportionates into atomic H on the nickel forming nickel hydride that reduces and hydrogenates the chlorinated organics adsorbed on the metal surface simultaneously [14–17].

4.2. TCE Degradation and Its Effect on Hydrogen Generation

Figure 4 shows that degradation of TCE by Ni/Fe (20 wt% Ni) under anaerobic conditions increases the hydrogen generation and results in a lower final pH as compared to the TCE-free solution. This observation can be attributed to the complex heterogeneous reactions occurring in the aqueous solution. As the reaction proceeds, breaking of the carbon chlorine bond occurs on the metal surface generating Cl^- according to reaction (7). Chloride ion is well known for its corrosive nature being capable of inducing pitting corrosion and increasing iron reactivity [18,19]. Under the experimental conditions used in this study, approximately $7.75 \mu\text{mol}$ and $382 \mu\text{mol}$ of H_2 are needed for the complete degradation of 10 mg/L and 500 mg/L TCE, respectively. Hydrogen collected in the headspace was in excess ($30 \mu\text{mol H}_2$) compared to what is needed for the complete degradation of 10 mg/L TCE. On the other hand, the significantly lower amount of hydrogen collected ($180 \mu\text{mol H}_2$) at 500 mg/L TCE for longer period of time (10 h) indicates that the pitting corrosion induced by Cl^- is not sustainable in the long run.

The pH of the solution in which iron undergoes oxidation is expected to increase due to the formation of OH^- . It is interesting to observe that the increase in pH for the TCE-degradation study is lower than the pure aqueous hydrogen analysis of Ni/Fe nanoparticles as shown in Figure 4. In the absence of any cosolutes in the reaction solution, this observation can only be attributed to the complex heterogeneous reactions of TCE, such as the reaction caused by Cl^- generated during the degradation of TCE and the formation of metal-hydride that acts as a catalytic reducing agent. The detail mechanisms responsible for the lower pH observed in the TCE study were not determined in this study.

Analysis of the hydrogen generated by the 20 wt% Ni nanoparticles and nanoiron under TCE-free anaerobic conditions at different solution pH (<1.0, 5.0, 6.5, and 8.0) was conducted. Figure 5 shows that the total H_2 generation is not a strong function of the solution pH in the pH range from 5.0 to 8.0. This observation is similar to the reported literature where iron corrosion at room temperature is independent of pH in the range from 4.0 to 10.0 [20].

It is expected that the iron corrosion rate will increase in the presence of a catalytic metal such as nickel based on the galvanic cell hypothesis, where iron is the sacrificial metal protecting the nickel. Figure 5 indeed shows that higher hydrogen generation was observed for the bimetallic Ni/Fe as compared to the nanoiron. In addition, the consistency in the total hydrogen generated by the 20 wt% Ni nanoparticles irrespective of the solution pH (5.0 to 8.0) supports the hypothesis that the higher H_2 generation in Figure 4 is indeed due to the chloride-induced pitting corrosion.

Figure 5 also shows that the acid treatment improved the total amount of hydrogen generation by more than two-fold compared with the non-treated nanoiron at different pH conditions. This

observation compliments the results shown in Figure 3 where the iron-normalized H_2 rate is higher for the acid-treated sample. Table 1 shows the complete digestion study at $pH < 1.0$ for different iron-based nano systems. Because the experimentally produced hydrogen from the complete oxidation of zero valent nanoiron is less than the value predicted theoretically, it can be assumed that the method used in the nanoiron synthesis cannot totally prevent the formation of surface oxide impurities upon exposure to air. On the other hand, the bimetallic Ni/Fe nanoparticles (20 wt% and 50 wt% Ni) synthesized using the same method possess higher oxidation resistance when exposed to air, as indicated by the similar level of hydrogen generation to the one corresponding to the acid-washed nanoiron as shown in Table 1. The digestion study indicated that enhanced air-stability of the nanoparticles can be achieved with the presence of nickel, which is an additional advantage to the catalytic effect that Ni has on the degradation kinetics and reaction pathways.

Table 2 shows that a strong correlation exists between the surface area-normalized TCE reaction rate (k_{SA} , L/m² h) and hydrogen generation ($k_{H_2}^*$, $\mu\text{mol } H_2/\text{m}^2 \text{ h}$) for the Ni/Fe nanoparticles with different nickel content. Reported literature results of k_{SA} and $k_{H_2}^*$ for iron, nanoiron and Ni/Fe systems are also listed in Table 2. As anticipated, nanoparticles with higher surface area have higher hydrogen generation rate. It should be noted that the nano Fe/B synthesized by Liu et al. is able to utilize the H_2 generated by iron oxidation during TCE degradation leading to enhanced reaction kinetics [13]. This observation was hypothesized to be the catalyzing effect of the highly disordered Fe/B solid phase. Current analysis and previously reported results of TCE degradation by iron nanoparticles, as shown in Table 2, demonstrate that the hydrogen generation rate is similar to those reported by Liu et al., but with reaction kinetics that is an order of magnitude slower [2,13]. This observation can be explained by the lack of catalyzing effect of the synthesized nanoparticles that are able to utilize the H_2 produced by iron oxidation. This is attributed to the method used in the nanoparticles synthesis, as different k_{SA} values were reported by authors that have employed dissimilar synthesis procedures. As expected, the acid-treated nanoiron showed great improvement in both of the $k_{H_2}^*$ and k_{SA} values as compared to the fresh nanoiron. However, the observed low k_{SA} value, even after the acid treatment, as compared to the results reported by Liu et al. is another indication of the presence of structural and surface compositional differences between the nanoiron systems [13]. The presence of nickel as the catalyzing agent was clearly demonstrated by the observed results between the acid-treated nanoiron and 50 wt% Ni nanoparticles. Both of these nanoparticles showed relatively similar $k_{H_2}^*$ values, but the bimetallic Ni/Fe system demonstrated reaction kinetics that are an order of magnitude higher than for the nanoiron. The TCE degradation study using bimetallic Ni/Fe reported by Schrick et al. demonstrated fast reaction kinetics, but has significantly lower $k_{H_2}^*$ that is similar in magnitude to the one corresponding to bulk Fisher iron powder [3]. In this case, other explanations and analysis have to be used to clarify the observed results besides using the reported $k_{H_2}^*$.

Figure 6 shows that both the surface area-normalized degradation and hydrogen generation rates demonstrate ‘volcano’-like characteristics with respect to the nickel content in the nanoparticles. Based on this observation, derivation of a functional representation that incorporates relevant parameters, such as the hydrogen generation rate and bimetallic composition, was attempted in this study. With the previous assumptions that the hydrogen generation is solely a result of the oxidation of zero valent iron, and that an undetermined fraction of the H_2 produced undergoes diatomic dissociation on the nickel surface forming active metal hydride for the degradation reaction:

the first-order surface area-normalized reaction constant, k_{SA} , is hypothesized to be a function of the aforementioned experimental parameters expressed as follows:

$$k_{\text{SA}} = N_{\text{Ni}} V_{\text{aq}} k_{\text{H}_2}^* (F_s \eta) + k_{\text{SA}}|_{\text{Fe}}, (N_{\text{Ni}} < 1.00) \quad (23)$$

where $k_{\text{H}_2}^*$ ($\mu\text{mol H}_2/\text{m}^2 \text{ h}$) is the surface area-normalized hydrogen generation rate obtained experimentally; V_{aq} (L) is the total reaction volume; N_{Ni} is the weight fraction of nickel in the bimetallic particles; the product F_s and η ($1/\mu\text{mol H}_2$) is a constant with each of the parameters defined as follows:

$$F_s = \frac{\text{H}_2 \text{ adsorbed on metal surface}}{\text{non-adsorbed H}_2} \quad (24)$$

$$\eta = \frac{1}{\text{adsorbed H}_2 \text{ undergoing diatomic dissociation on nickel and being used in the degradation reaction}} \quad (25)$$

and the last term in eq (23) is the surface area-normalized reaction rate constant for the iron nanoparticles:

$$k_{\text{SA}} = k_{\text{SA}}|_{\text{Fe}} \quad (26)$$

It should be noted that nickel nanoparticles ($N_{\text{Ni}} = 1.00$) should not be considered in the correlation as shown in eq (23) because of the inability of nickel to produce H_2 at near neutral pH condition for the degradation reaction. The inset in Figure 6 shows a linear relation with a correlation coefficient of 0.98; the constant ($F_s \eta$) obtained is $8.40 (\mu\text{mol H}_2)^{-1}$. The parameters of F_s and η are dynamic in nature, depend on nickel composition, and may account for the geometric and electronic effects of the bimetallic nanosized nature of the particles. We can approximate the maximum hydrogen adsorption capacity by estimating the surface nickel atoms of the bimetallic nanoparticles. Using the reported molar volume for nickel (6.59 cm^3), the Avogadro's number ($6.02 \times 10^{23} \text{ atom/mol}$), the surface area of the nanoparticles ($30 \text{ m}^2/\text{g}$), and assuming that the surface area coverage of nickel atoms is similar in magnitude to its weight fraction (N_{Ni}), the calculated surface nickel atoms for nanoparticles with 20 wt% Ni is 2.10×10^{18} ($3.48 \mu\text{mol Ni}$). Based on the reported analysis of nickel-adsorbed surface hydrogen atoms that is close to one monolayer and assuming that hydrogen adsorbed dissociatively on nickel forms Ni-H, the maximum number of hydrogen molecules adsorbed on 20 wt% Ni nanoparticles is $1.72 \mu\text{mol H}_2$ [21]. Based on the reaction mechanism of eq (5), about $7.75 \mu\text{mol H}_2$ is needed in order to completely degrade $3.1 \mu\text{mol TCE}$. This indicates that the formation of nickel-hydride of eq (3) is rapid as compared to other surface reactions.

4.3. TCE Batch Degradation Modeling

Figure 7 shows the quantitative analysis of the sorption study obtained experimentally through extraction of the nanoparticles in organic solvent. TCE sorption per metal mass, q_{TCE} ($\mu\text{mol/}$

g), is determined by the difference between the total, C_{TCE} , and aqueous concentration, C_{aq} , according to the following expression:

$$q_{TCE} = \frac{C_{TCE} - (C_{aq} V_{aq})}{m_{Ni/Fe}} \quad (27)$$

The results demonstrated a Langmuirian-type quasi-sorption isotherm. The coefficients of K and Q in eq (17) were determined by linear regression, and the values obtained is 0.014 L/ μ mol and 135.1 μ mol/g, respectively. In addition, nonlinear regression analysis was also conducted (*nlinfit* function in Matlab 7.0 based on the Gauss-Newton and Levenberg-Marquardt algorithm) for comparison purpose, and the values obtained for K and C_T with 95% confidence limit were 0.0015 L/ μ mol and 140.2 μ mol/g, respectively. The sorption isotherm plateau of the Ni/Fe nanoparticles was about 120 μ mol/g. The cross-section area of a TCE molecule laying flat on a surface was estimated to be 40 $\text{\AA}^2$ /molecule [22]. Ni/Fe has a surface area of about 30 m²/g. Assuming monolayer coverage and the particles having similar energy of interaction with the adsorbent, the surface area coverage of TCE based on the sorption plateau is estimated to be around 90%. This indicates that the surface of the Ni/Fe nanoparticles is closely packed with TCE molecules at high concentration, which includes sorption at both the non-reactive and reactive sites on the nanoparticle surface. Based on the reported study of TCE sorption to iron surface by Farrell et al., the fractional surface coverage of TCE may be lower due to the shortening of the carbon-carbon bond after the formation of sigma bonding, which is similar in magnitude to the conversion of a double to triple bond [23].

Degradation of TCE at low and high initial concentrations was investigated, and mathematical modeling was conducted to study the reaction kinetics and sorption effect. At high initial concentration (TCE = 500 mg/L, 0.16 mmol), the total surface coverage of the nanoparticles approached the monolayer saturation limit, and no more vacant sites should be available for TCE sorption. Using eq (18) with C_V equal to zero, we obtain the expression for degradation with surface sites saturated with TCE:

$$\frac{dC_{aq}}{dt} = - (k_{int} + K_B) C_{aq} (1 + K C_{aq}) \quad (28)$$

Another realistic assumption is that desorption is negligible when the particle surface is saturated with TCE, where k_{-a1} and k_{-a2} are approximately zero. Then, eq (28) is further simplified to eq (29):

$$\frac{dC_{aq}}{dt} = - k_{int} C_{aq} (1 + K C_{aq}) \quad (29)$$

Experimental results were correlated with eq (29) by numerical integration using Matlab 7.0 (ODE15s solver) to estimate the reaction rate constant. Figure 8 shows that agreement between the experimental and calculated results was obtained with k_{int} of about 0.10 h⁻¹. At low initial concentration (TCE = 10 mg/L, 3.10 μ mol), less than 10% of the total surface area was covered by TCE molecules. Equation (18) is further simplified to eq (30) with the following assumptions:

$$(1 + K C_{aq}) \approx 1, K_{si} = \frac{k_{-si}}{k_{si}} \approx 0 (k_{si} \geq k_{-si})$$

$$\frac{dC_{aq}}{dt} = -k' C_{aq} \quad (30)$$

with

$$(k' = k_{int} + k_{-a1} + \frac{K_A C_V}{K Q}) \quad (31)$$

The modeling results in Figure 9 show that excellent agreement between the calculated results and experimental data was obtained with the lumped parameter k' value of 3.60 h^{-1} . Based on the previously obtained estimated k_{int} value (0.10 h^{-1}), K parameter ($0.0015 \text{ L}/\mu\text{mol}$), and fraction of occupied sites ($C_V / Q \approx 0.90$), the magnitude of the sorption effect between the bulk solution and the particles surface can be estimated using eq (31). After substitution of all the appropriate parameters into eq (31) and assuming that k_{-a1} is negligible, the sorption rate of TCE is $0.15 \mu\text{mol h}^{-1}$, which is on the same order of magnitude as the reaction rate observed under the experimental conditions used in this study. This implies that the degradation reaction by the nanoparticles is not truly a rate-limiting step because TCE will undergo transformation once it is surface-bound at the same rate as it is sorbed onto the surface.

The insets in Figure 8 and Figure 9 showing the time-dependent plot of the ratio of ethane/ethylene formation with respect to the TCE degradation also provide some insight regarding the reaction mechanism. Complete TCE degradation was achieved in 2-hour period with the formation of ethane that accounted for more than 92% of the total carbon balance at low TCE aqueous concentration. However, at high concentration where the surface of the nanoparticles was saturated with TCE molecules, complete TCE degradation was only achieved after 10 h of reaction time with shift in product formation. Ethylene and ethane are the main products formed within the first four hours of reaction time that accounted for about 70% of the degraded TCE balance. As the reaction progressed, ethylene and ethane were produced in relation to the degraded TCE. However, chlorinated intermediates were not detected in the aqueous phase for the entire degradation duration. The main hypothesis from this observation is that saturation of the surface sites does not strongly affect the reaction mechanism. As the surface becomes occupied with TCE molecules, no vacant sites would be available for further sorption and transmigration. Degraded intermediates will continue to be strongly adsorbed on the same sites where its parent TCE molecule was first sorbed. This undergoes further reductive hydrogenation reaction forming gaseous products of ethylene and ethane.

It should be noted that the derived model does not account for the formation of any intermediates and was used to characterize the concentration of TCE degraded in aqueous phase with respect to time. However, based on the absence of any chlorinated by-products in the aqueous phase together with the quantitative analysis of ethylene and ethane formation, we can hypothesize that TCE degradation follows reaction pathways involving the rapid elimination and hydrogenation reactions that form chloroacetylene, acetylene, and finally ethylene/ethane. The observed formation of dichlorinated intermediates and acetylene as well as lower reaction rates by bulk iron suggest that TCE undergoes different reaction mechanisms (non-acetylene pathway) as compared to the bimetallic nanoparticles.

4.4. Effect of Deactivation on Reaction Mechanism

A batch TCE cycle study was conducted to assess the effect of activity loss on the reaction mechanism. Using the hydrogen data in Figure 4 ($k_{H_2} = 184.60 \mu\text{mol H}_2 / \text{g Fe h}$) and the amount of TCE degraded forming ethane/ethylene at different time intervals in each cycle,

Figure 10 shows the degradation kinetics corrected with the loss in iron mass due to the consumption of iron as electron donor and reductant in the aqueous phase degradation and oxidation reactions. Interpretation of kinetic data without correcting for the loss of iron will overestimate the effect of deactivation as demonstrated by the inset in Figure 10. As expected, gradual decrease in reaction kinetics with successive degradation cycles was observed indicating the occurrence of progressive deactivation by the precipitated by-products on the metal surface. Precipitation of different iron subspecies in long-term degradation studies with different solution chemistry has been documented and was found to have a profound impact on the reaction kinetics [24,25]. Some of the cosolutes have been found to be able to enhance the degradation. However most of them lower the reactivity by forming a mixed surface layer of precipitate, which mostly consists of ferrous or ferric related compounds [24,25]. With the absence of any inorganic or organic cosolutes in this study, the attenuation in reactivity is mainly caused by the precipitation of corrosion products of insoluble hydroxides that passivated the metal surface. This indicates that the chloride-corrosion promoting effect, as mentioned earlier, that enhanced the hydrogen generation is relatively short-lived (decreasing $k_{H_2}^*$ as shown in Table 3) and does not prevent the formation of a passivating layer in the long run. This observation is also reported by others where initial increase in the degradation kinetics was achieved in chloride-containing solution, but such rate-enhancing effect cannot be sustained in the long-term study [25,29]. In addition, the gradual increase in pH from 6.50 to the final pH of 8.20 at the end of the third cycle as the reaction progresses may also contribute to the decrease in reactivity as the generation of more OH^- accelerated the formation of hydroxides species.

It is interesting to observe that even though the reactivity gradually decreased over time, no chlorinated intermediates were detected in the aqueous phase by GC analysis for each of the three cycles, and ethane remained as the major product with respect to the TCE degraded at different time intervals. This implies that passivation of the bimetallic nanoparticles does not adversely modify the reaction mechanism of the TCE degradation process where ethane remained as the major product. This is indeed indicated in Figure 11, which shows the time-independent plot of TCE conversion and ethane yield as well as the ratio of ethane formation and TCE degradation with respect to time. In addition to the decrease in reactivity, the shift in product formation with increasing reaction times is also being mentioned by authors studying the longevity of zero-valent iron for dechlorination reactions [24,25]. This has also been observed in our studies (shown as an inset in Figure 11) where the formation of ethylene accounted for most of the product balance in the gas phase for the second and third cycles. The absence of less completely reduced compounds in the aqueous solution coupled with the gas phase products balance analysis is hypothesized to be due to the rapid transmigration of the surface-sorbed intermediates from the surface-passivated site to another reactive site before they can be desorbed and transferred to the bulk solution phase.

A surprising observation in the cycle study is the increase of particles surface area (N_2 -BET analysis) as the reaction progresses. This observation is counter to the anticipated decrease in surface area as a result of the expected occurrence of processes such as the deposition of inactive layers on the particles surface, reduced porosity due to pore clogging, and dissolution of metal in the deactivation study of heterogeneous catalysis as reported in the literature [30–32]. A possible explanation for this observation is that the insoluble iron (hydr)oxide layer formed in the corrosion is highly porous. The porous nature of the corroded precipitates has been recently confirmed in the literature [33]. Precipitation of porous corroded oxides that increased the BET surface area and enhanced the conduction and interfacial polarization of zero valent iron was also reported by Wu et al [34]. Additionally, chloride may induce nickel corrosion forming a porous nickel oxide layer as well as cracked surfaces [35,36]. The SEM images in Figure 12 clearly reveal the corrosion of the nanoparticles and precipitation reactions. This figure shows that the bimetallic Ni/Fe nanoparticles underwent morphological changes from the initial

spherical nanosized particles to the indistinguishable agglomerates of colloidal clusters. Changes in metal surface morphology resulting from corrosion and precipitation are expected and reported in the literature as well [36,37,38].

5. Conclusion

The compositional distribution of bimetallic Ni/Fe nanoparticles was established through iron oxidation analysis where increase in the overall nickel content led to surface nickel saturation that diminished the hydrogen generation and subsequently lowered the TCE degradation rate. The reactivity of bimetallic Ni/Fe nanoparticles expressed in terms of surface area-normalized rate constant based on a pseudo first-order model was correlated with the iron-normalized hydrogen generation rate. The presence of chloride-induced pitting corrosion that leads to higher iron oxidation was observed in this study, but this effect was not sustainable in the long run. Modeling analysis using the derived equation of reaction coupled with sorption term indicated that the surface reaction is not the rate-limiting step. Surface saturation where TCE approaches the monolayer limit does not affect the reaction mechanistic pathways. The less completely reduced intermediates continued to be surface-sorbed and underwent further transformation into ethane/ethylene. TCE cycle analysis shows minimum loss of reactivity where ethane remained as the major product formed at the end.

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Nomenclature

C_{aq}	aqueous phase TCE concentration ($\mu\text{mol/L}$)
C_V	vacant surface concentration ($\mu\text{mol/g}$)
k_{a1}	active surface sorption rate ($1/\mu\text{mol h}$)
k_{-a1}	active surface desorption rate ($1/\text{h}$)
k_{a2}	inactive surface sorption rate ($1/\mu\text{mol h}$)
k_{-a2}	inactive surface desorption rate ($1/\text{h}$)
k_{H_2}	iron mass-normalized hydrogen generation rate ($\mu\text{mol} / \text{g Fe h}$)
$k_{\text{H}_2}^*$	surface area-normalized hydrogen generation rate ($\mu\text{mol} / \text{m}^2 \text{ h}$)
k_{int}	intrinsic TCE degradation rate constant ($1/\text{h}$)
k_{SA}	surface area-normalized reaction rate constant ($\text{L}/\text{m}^2 \text{ h}$)
k_{Si}	forward transmigration rate ($1/\text{h}$)
$k_{-\text{Si}}$	reverse transmigration rate ($1/\text{h}$)
K	Langmuirian-type sorption coefficient ($\text{L}/\mu\text{mol}$)
K_B	parameter defined in eq 28 ($1/\text{h}$)
K_{Si}	equilibrium transmigration sorption constant ($k_{-\text{Si}} / k_{\text{Si}}$)
$m_{\text{Ni/Fe}}$	mass of Ni/Fe nanoparticles for degradation study (g)
q_{TCE}	surface-sorbed TCE concentration ($\mu\text{mol/g}$)
q_{Si}	surface-sorbed inactive TCE concentration ($\mu\text{mol/g}$)
Q	maximum sorption capacity for surface-sorbed concentration ($\mu\text{mol/g}$)
S	active vacant surface as designated in reaction (1)
S_i	inactive vacant surface due to iron hydr(oxides) precipitation as designated in reaction (9)
V_{aq}	total solution volume (L)

Figure 1. Schematic for batch TCE sorption and degradation reaction by the Ni/Fe (Ni = 20 wt%) nanoparticles.

Figure 2.

Total hydrogen generation normalized with iron for different bimetallic Ni/Fe nanoparticles versus time under anaerobic aqueous solution. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.

Figure 3.

Iron-normalized hydrogen generation of iron nanoparticles with (open diamond symbols) and without acid treatment (solid diamond symbols) under anaerobic condition. Nanoiron = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.

Figure 4.

Total hydrogen produced normalized by iron versus time for Ni/Fe (Ni = 20 wt%) nanoparticles with TCE degradation reaction (open diamond symbols) and TCE-free aqueous solution (solid diamond symbols). Insert shows the hydrogen produced in degradation of high initial TCE concentration (open square symbols) and TCE-free aqueous solution (solid square symbols). Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.

Figure 5.

Effect of pH on hydrogen generation for Ni/Fe nanoparticles (Ni = 20 wt%) and iron nanoparticles (acid-treated and non-treated) under anaerobic aqueous solution. Analysis time is 2 hours. Nanoiron and Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.

Figure 6.

Volcanic profile of surface area-normalized TCE reaction rate and hydrogen generation rate with respect to Ni wt% of the Ni/Fe nanoparticles. Insert is the linear correlation between k_{SA} and $(k_{H_2} N_{Ni})$.

Figure 7.

Langmuirian-type quasi sorption isotherm for TCE batch experiment study by Ni/Fe nanoparticles (Ni = 20 wt%) at high initial concentration. Inset shows the close ups of the low initial TCE concentration region. The solid line is the isotherm fit obtained by linear regression ($r^2 = 0.9904$). Ni/Fe = 0.1 g, volume = 40 ml, initial pH = 6.5.

Figure 8.

TCE degradation and modeling by Ni/Fe (Ni = 20 wt%) nanoparticles at high initial TCE concentration (Initial TCE = 500 mg/L) with eq (31). Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Inset shows the ratio of gaseous products formation and TCE degraded with respect to time. Solid line in insert is only “guide to the eye”.

Figure 9.

Modeling for TCE degradation by Ni/Fe (Ni = 20 wt%) nanoparticles at low TCE concentration (initial TCE = 10 mg/L) with eq (32). Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Inset shows the ratio of gaseous products formation and TCE degraded with respect to time. Solid line in inset is only “guide to the eye”.

Figure 10.

Batch cycle study for TCE degradation by Ni/Fe (Ni = 20 wt%) nanoparticles corrected by consumption of iron content. Ni/Fe (Ni = 20 wt%) = 0.10 g, initial TCE = 10 mg/L, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Inset shows the raw data for TCE degradation.

Figure 11.

Time-independent plot of TCE degradation by Ni/Fe nanoparticles (Ni= 20 wt%): ethane yield and TCE conversion. Inset shows the time-dependent plot of ethane formation with respect to TCE degraded. Solid line corresponds maximum possible ethane yield.

Figure 12.

SEM images of TCE degradation by Ni/Fe nanoparticles (Ni = 20 wt%) at 1st (reaction time = 120 min), 2nd (reaction time = 140 min), and 3rd (reaction time = 140 min) cycle for a total reaction time of approximately 7 hours.

Table 1

Hydrogen generation for nanoiron and Ni/Fe nanoparticles at acidic conditions using 0.1 g of nanoparticles

Sample	Hydrogen generation after complete digestion* ($\mu\text{mol H}_2$)	% of maximum**
Fe nanoparticles	1.55×10^3	86.4%
Acid-treated Fe nanoparticles	1.74×10^3	96.8%
Ni/Fe nanoparticles (Ni = 20 wt%)	1.72×10^3	95.6%
Ni/Fe nanoparticles (Ni = 50 wt%)	1.71×10^3	94.7%

* trace metal grade concentrated nitric acid was used for pH < 1 solution

** Assuming Fe and Ni are in zero-valent state, hydrogen generated at complete digestion = $1.80 \times 10^3 \mu\text{mol H}_2$

Table 2

Surface area-normalized reaction rate and hydrogen generation rate constant for Fe and Ni/Fe nanoparticles

Iron – based Nanoparticles	Surface area-normalized hydrogen generation rate ^{**} k_{H_2} ($\mu\text{mol H}_2/\text{m}^2 \text{ h}$)	Surface area-normalized TCE degradation rate k_{SA} ($\text{L}/\text{m}^2 \text{ h}$)
Acid-washed Fe from Fisher ¹	0.01	0.03×10^{-2}
Fe/B nanoparticles ²	0.85	1.40×10^{-2}
Fe nanoparticles ³	1.03	0.05×10^{-2}
Acid-treated Fe nanoparticles	1.78	0.72×10^{-2}
Ni/Fe nanoparticles ⁴ (Ni = 25 wt%)	0.20	9.80×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 20 wt%)	2.23	3.50×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 25 wt%)	2.57	5.75×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 50 wt%)	1.90	2.35×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 75 wt%)	0.25	1.25×10^{-2}
Ni/Fe nanoparticles ³ (Ni = 80 wt%)	0.04	0.09×10^{-2}

^{**} initial H_2 generation rates were determined from measurements obtained up to 120 min where linear increase with time was observed. Initial pH 6.5

¹ k_{SA} from Su et al. *Environ. Sci. Technol.* 1999, 33, 163.

² k_{SA} and k_{H_2} from Liu et al. *Environ. Sci. Technol.* 2005, 39, 1338.

³ k_{SA} from Tee et al. *Ind. Eng. Chem. Res.* 2005, 44, 7062.

⁴ k_{SA} and k_{H_2} from Schrick et al. *Chem. Mater.* 2002, 14, 5140.

Table 3

Cycle studies for TCE degradation on Ni/Fe (Ni = 20 wt%) nanoparticles and associated physical properties and chemical reactivity

	Initial pH	BET (m ² /g)	$k_{H_2}^*$ ($\mu\text{mol} / \text{m}^2 \text{ h}$)	$\frac{[\text{TCE}]}{[\text{TCE}]_0}$	$\frac{[\text{C}_2\text{H}_6]}{[\text{TCE}]_0}$	$\frac{[\text{C}_2\text{H}_4]}{[\text{TCE}]_0}$
Cycle 1	6.50	28.28	6.65	Complete degradation after 120 min	0.92	NA
Cycle 2	6.90	60.66	3.18	> 99% degradation after 140 min	0.87	0.04
Cycle 3	7.60	90.80	1.32	70% degradation after 140 min	0.56	0.10