

Reductive dechlorination of tetrachloroethylene by bimetallic catalysts on hematite in the presence of hydrogen gas

Kyunghoon Choi^{1a}, Nara Lee² and Woojin Lee^{*2}

¹ Department of Environmental Engineering, Chungnam National University,
99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea

² Department of Civil and Environmental Engineering, Korea Advanced Institute for Science and Technology,
291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

(Received November 02, 2013, Revised February 10, 2014, Accepted March 07, 2014)

Abstract. Among the combination of 4 different second metals and 3 different noble metals, Ni 10%-Pd 1%/hematite (Ni(10)-Pd(1)/H) showed best tetrachloroethylene (PCE) removal (75.8%) and production of non-toxic products (39.8%) in closed batch reactors under an anaerobic condition. The effect of environmental factors (pH, contents of Ni and Pd in catalyst, and hydrogen gas concentration) on the reductive dechlorination of PCE by Pd-Ni/hematite catalysts was investigated. PCE was degraded less at the condition of Ni(5)/H (13.7%) than at the same condition with Ni(10)/H (20.6%). Removals of PCE were rarely influenced by the experimental condition of different Pd amounts (Pd(1)/H and Pd(3)/H). Acidic to neutral pH conditions were favorable to the degradation of PCE, compared to the alkaline condition (pH 10). Increasing Ni contents from 1 to 10% increased the PCE removal to 89.8% in 6 hr. However, the removal decreased to 74.2% at Ni content of 20%. Meanwhile, increasing Pd contents to 6% showed no difference in PCE removal at Pd content of more than 1%. Increasing H₂ concentration increased the removal of PCE until 4% H₂ which was maximumly applied in this study. Chlorinated products such as trichloroethylene, 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and vinyl chloride were not observed while PCE was transformed to acetylene (24%), ethylene (5%), and ethane (11%) by Ni(10)-Pd(1)/H catalyst in 6 hr.

Keywords: tetrachloroethylene; Pd; Ni; hematite; bimetallic catalyst

1. Introduction

Chlorinated organic compounds (COCs) are widely used as industrial purposes and common contaminants in soil and groundwater. Most of the COCs are persistent and ubiquitous in the environment due to their intensive use and release during industrial activities and the leakage from non-point sources (Lee and Doong 2008). Tetrachloroethene (PCE) is one of the most frequently found COCs in contaminated soil and groundwater systems, widely known to be toxic, likely to be carcinogenic, and mutagenic to humans and animals (US EPA 2014). Moreover, PCE has been reported to cause cancer of the blood, lymphoma, and brain disease, and the United States

*Corresponding author, Professor, E-mail: woojin_lee@kaist.ac.kr

^a Ph.D., E-mail: choikhooon@gmail.com

Environmental Protection Agency has issued its maximum contaminant level at $5 \mu\text{g L}^{-1}$ by the Safe Drinking Water Act (US EPA 2012). Therefore, continuous efforts to remediate soil and groundwater contaminated with PCE have been made at many contaminated sites.

PCE has been treated by iron-bearing soil minerals (ISBMs) such as magnetite, green rust, and mackinawite (Kenneke and Weber 2003, Lee and Batchelor 2003, Borch *et al.* 2010), anaerobic microorganisms able to dechlorinate COCs (Gander *et al.* 2002, Dong *et al.* 2009), and interactions between ISBMs and bacteria in natural and engineered environments (Gander *et al.* 2002, Bae and Lee 2010). However, most of the technologies have taken relatively long time to clean up PCE and the biogeochemical factors such as an anaerobic condition determining the existence and reductive capacity (Lee *et al.* 2000) of ISBMs has significantly limited the transformation rate and degradation pathway of COCs (Elsner *et al.* 2004, Jeong and Hayes 2007, Dong *et al.* 2009, Borch *et al.* 2010, Van der Zee and Cervantes 2009). In addition, PCE can be transformed to more toxic products such as cis-dichloroethene and vinyl chloride via hydrogenolysis pathway (Maymó-Gatell *et al.* 2001) by FeS, pyrite, and magnetite, and even by iron nanoparticle (Amir and Lee 2011). To cope with the limitations, bimetallic catalysts composed of second metal (e.g., Co, Ni, Cu, and Zn) and noble metal (e.g., Pd, Pt, and Au) have attracted attention to date. Synthesized bimetallic catalyst using Au and Pd has shown the remarkable degradation of PCE in a short reaction time (Zhao *et al.* 2013), however still there might be several issues such as necessity on using very expensive metals. Therefore, bimetallic catalyst supported on soil mineral was applied in this study. No significant studies on the degradation of PCE by bimetallic catalysts on soil mineral supporter have been conducted to date.

The objectives of this research were (1) to identify the characteristics of PCE degradation by Pd-Ni catalyst on hematite in the presence of H_2 gas, (2) to investigate the effects of pH, contents of Pd and Ni, and H_2 concentrations on the reductive dechlorination kinetics of PCE for the application to ex-situ remediation technology, and (3) to elucidate reaction mechanism during the reaction. H_2 gas was added to promote the reductive dechlorination of PCE by bimetallic catalysts. We selected PCE as a representative COC because it is one of major pollutants found in groundwater and has been known to be hazardous to humans and persistent in diverse environments. Various bimetallic combinations of noble metals (Pd, Pt, and Au) and second metals (Co, Ni, Cu, and Zn) were tested to select an optimum bimetallic catalyst on hematite as well.

2. Materials and methods

2.1 Chemicals

Noble metals (palladium(II) chloride (PdCl_2 , 99%, Sigma-Aldrich), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 37.5%, Sigma-Aldrich), and gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 49%, Sigma-Aldrich)) and second metals (cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 97%, Samchun Pure Chemical), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 97%, Samchun Pure Chemical), copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 97.5%, Samchun Pure Chemical), and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Sigma-Aldrich)) were used for preparation of each metal precursor solution. Hydrochloric acid (HCl, 37%, Sigma-Aldrich) was used to dissolve noble metals. Sodium borohydride (NaBH_4 , 98%, Samchun Pure Chemical) was used to reduce the bimetallic catalysts. Hematite (α - $\text{Fe}^{\text{III}}_2\text{O}_3$, Bayferrox 105 M) was purchased

from LANXESS Corp. PCE (99.9%, Sigma) was used to prepare stock and standard solutions. Methanol (99.9%, Merck) for the preparation of PCE stock solution, n-hexane (99.9%, Merck) for preparation of extractant, and 1,2-dibromopropane (1,2-DBP, 97%, Sigma) as an internal standard were all HPLC grade. Trichloroethylene (TCE, 99.5%, Sigma-Aldrich), 1,1-dichloroethylene (1,1-DCE, 99%, Aldrich), cis-1,2-dichloroethylene (cis-DCE, > 99%, Tokyo Chemical Industry), trans-1,2-dichloroethylene (trans-DCE, >98%, Tokyo Chemical Industry), and vinyl chloride (VC, > 99%, Supelco) were used for the identification of chlorinated products during PCE degradation. Scotty mixed gas (1% CO, CO₂, methane, ethane, ethylene, and acetylene in nitrogen, respectively, Supelco) was used as a standard for the analysis of non-chlorinated transformation products. Sodium acetate trihydrate (> 99%, Sigma-Aldrich) and acetic acid (> 99.7%, Sigma-Aldrich), MOPS (99.5%, Sigma-Aldrich, pK_a = 7.20), and CAPS (> 98%, Sigma, pK_a = 10.4) were used to keep the pH constant at 4, 7, and 10, respectively, during the reductive degradation of PCE. All of the chemicals were analytical grade except HPLC grade solvents. Deionized water (DIW, 18 MΩ·cm) was prepared using ELGA PURELAB Classic system and purged with argon gas for 4 hr to prepare deaerated and deionized water (DDIW). DDIW was used in all experiments except dissolving second metal in DIW. Unless otherwise stated, every chemical was used as received without further treatment.

2.2 Synthesis of bimetallic catalysts

Several bimetallic catalysts on hematite were synthesized using impregnation method (Jung *et al.* 2012) to find out the most efficient combination of noble and second metals. Hematite (1 g) as a support material was mixed with 100 mL DIW and exposed for 6 min to ultrasonic vibration prior to addition of second and noble metal precursors. Each second metal precursor solution (10 wt.%) dissolved in DIW and each noble metal precursor solution (1 wt.%) in 0.5 M HCl were sequentially introduced to the hematite suspension and they were mixed under continuous stirring for 2 hr, respectively. The solution containing second metal and noble metal precursors was dried in an oven at 105°C for 24 hr and calcinated at 350°C for 2 hr. The calcinated bimetallic catalyst was then reduced by dropwise addition of 0.01 M NaBH₄ as following representative reactions



The suspension with the reduced bimetallic catalyst on hematite was centrifuged, the supernatant were decanted, and the precipitate (catalyst particles) was washed with DDIW twice to remove residual chemicals under an anaerobic condition. The washed catalyst was freeze-dried and stored in an anaerobic chamber. The catalyst was used for the catalytic reductive dechlorination of PCE.

2.3 Experimental procedures

The reductive dechlorination of PCE by bimetallic catalyst was performed in a 250 mL glass serum bottle as a batch reactor, which was equipped with an aluminum cap with center opening Teflon-faced rubber septa. Thirty mM MOPS buffer solution (pH 7, 150 mL) was introduced to

the reactor containing 0.2 g bimetallic catalysts on hematite under 4% H₂ condition. The catalytic PCE reduction was initiated by addition of 250 μ L PCE stock solution (300 mM) to obtain an initial concentration of 0.5 mM at room temperature ($25 \pm 0.5^\circ\text{C}$). Unless stated otherwise, the experimental condition was fixed at 10 wt.% Ni, 1 wt.% Pd, 4% H₂ concentration, and pH 7 adjusted by 30 mM MOPS buffer. The bottle was rapidly taken out of the anaerobic chamber and mounted on a tumbler that provided end-over-end rotation at 8 rpm. The degradation kinetics of PCE by bimetallic catalysts on hematite were determined by sacrificial sampling and monitoring the concentration of the target compounds at each sampling point.

The PCE reduction tests were also carried out with different combination of bimetallic catalysts consisted of four second metals and three noble metals and controls (DDIW, MOPS buffer, hematite only, Ni/hematite, and Pd/hematite) to compare their PCE removals to that by 10% Ni in hematite catalyst with 1% Pd (Ni(10)-Pd(1)/H). Three different pHs (4, 7, and 10), five different loadings of Ni (1, 2, 5, 10, and 20 wt.%) and Pd (0.5, 1, 2, 3, and 6 wt.%), three different H₂ concentrations (0, 2, and 4%) were used to investigate their effects on the PCE removals. The three H₂ conditions were provided by adjusting the H₂ concentration in the anaerobic chamber and preparing the experimental samples in the atmosphere. An optimal catalyst combination showing the highest production of non-toxic products such as acetylene, ethylene, and ethane was determined at different combinations of second and noble metals, and a formation of those products was also observed at an optimal composition of Ni and Pd (10:1) at the same experimental condition. All experiments were conducted in duplicate.

2.4 Analytical procedures

PCE concentration was measured using a gas chromatograph with an electron capture detector (GC/ECD, GC-2010 Plus, Shimadzu, Co.) equipped with HP-5 column (30 m length, 0.32 mm i.d., and 0.25 μ m film thickness, Agilent Technologies, Inc.). From the batch reactors sacrificed at each sampling time, an aliquot of a supernatant (50 μ L) was taken and transferred to 2 mL vial containing an extractant (1.85 mL of n-hexane with 0.05 mM 1,2-DBP as an internal standard). Extraction was conducted by shaking the vial for 30 min using an orbital shaker at 200 rpm and 1 μ L of extractant was automatically introduced into the GC injector with a split ratio of 30:1. The temperature of injector and detector was 200 and 230 $^\circ\text{C}$, respectively, and oven temperature was isothermal at 100 $^\circ\text{C}$. Nitrogen with 99.999% purity was used as a carrier gas at a constant flow rate of 2.6 mL/min.

Chlorinated and non-toxic products transformed from PCE degradation were analyzed using the following procedures. The batch reactors at each sampling time were centrifuged at $2535 \times g$ for 2 min, and 10 mL of supernatants were transferred to clear borosilicate glass vials (23.4 mL). The vials were shaken for 1 hr using an orbital shaker at 200 rpm to equilibrate the chemicals between gas and liquid phases and then allowed to stand for 1 hr at room temperature. One hundred milliliter of gas-phase was collected two times using two gas-tight micro-syringes (100 μ L, Hamilton, Reno, NV) at each sampling time, which one was for the chlorinated products (i.e., TCE, 1,1-DCE, cis-DCE, trans-DCE, and VC) and the other was for the non-toxic products (i.e., acetylene, ethylene, and ethane).

Chlorinated products formed during PCE degradation were analyzed by a gas chromatograph/mass spectrometer (GC/MS), composed of Hewlett-Packard (HP) 5890II GC with a 5971 mass selective detector, under scan mode. The headspace samples (100 μ L) obtained by the gas-tight micro-syringe (100 μ L) were injected manually into the injection port of the GC. The

separation was carried out through DB-VRX column (30 m length, 0.25 mm i.d., and 1.4 μm film thickness, Agilent Technologies, Inc.). The temperature of detector was set at 220°C. The temperature at injector was 200°C. The initial oven temperature was 45°C, held for 1 min, and then ramped to 155°C at a rate of 10°C/min. There was no solvent delay time, and the temperature of the transfer line was set at 185°C. Mass spectra were recorded at 3 scans/sec in the mass range of 50–550 amu. The gas sample (100 μL) was injected using the gas-tight syringe (100 μL). Helium with 99.9999% purity was used as a carrier gas at a constant flow rate of 1 mL/min.

Non-toxic products' concentration was quantified using a GC (YL6500GC, Young Lin Instrument Co.) equipped with a flame ionization detector and GS-Alumina column (30 m length, 0.53 mm i.d., Agilent Technologies, Inc.). The headspace samples (100 μL) obtained by the gas-tight micro-syringe (100 μL) were injected manually into the injection port of the GC. The temperature of detector was set at 275°C. The temperature at injector was 250°C. The initial oven temperature was isothermal at 100°C.

H₂ concentration was measured using a GC (Cow Mac series 580, Cow Mac Instrument) equipped with a thermal conductivity detector and stainless-steel column (1.8 m length, 3.2 mm o.d., Supelco) packed with Molecular Sieve 5A (60/80 mesh). The headspace samples (100 μL) were obtained by the gas-tight micro-syringe (100 μL) and those were injected manually into the injection port of the GC. The temperature of detector was set at 90°C. The temperature at injector was 80°C. The initial oven temperature was isothermal at 50°C.

3. Results and discussion

3.1 Reductive dechlorination of PCE by bimetallic catalyst

Fig. 1 shows the degradation of PCE by various combinations of bimetallic catalysts on hematite supporter at pH 7. Control (DDIW) sample showed no significant losses due to the sorption on reactor wall and volatilization from the reactor (Fig. 1(a)). Among the combinations using 4 second metals and 3 noble metals, Pd groups showed the enhanced degradation of PCE, irrespective of the second metal type. The range of PCE removals by different bimetallic catalysts on hematite was 14.3–75.8%, which the highest removal (75.8%) was attained by Ni(10)-Pd(1)/H. The formation of non-toxic products which were sum of acetylene, ethylene, and ethane was in the order of Ni-Pd (39.8%) > Co-Pd (34.1%) > Cu-Pd (21.3%) > Zn-Pd (19.9%) (Fig. 1(b)). Monitoring of the non-toxic products confirmed that Ni-Pd/H composition was the optimum bimetallic catalyst for the degradation of PCE at pH 7. PCE removals and formation of non-toxic products by other composition of bimetallic catalysts except Pd groups were less than 52.1% and 16.7%, respectively.

Fig. 2(a) shows the effect of each component on PCE degradation by Ni-Pd/H catalyst. PCE removals in 3 controls (DDIW, buffer, and support material) were less than 5%, showing that no significant losses by volatilization from reactor system and sorption on catalyst surface occurred during experimental runs. At the condition of Ni(5)/H (13.7%), PCE was degraded less than at the same condition with Ni(10)/H (20.6%). The result indicates that zero-valent Ni (Ni⁰) on hematite can degrade PCE in the absence of Pd. The enhanced PCE removal at higher Ni content in the catalysts also indicates that more PCE can be reductively degraded as the electrons from the catalyst surface are more abundant due to the increased Ni⁰ content. Meanwhile, removals of PCE were rarely influenced by the experimental condition of different Pd amounts although those by Pd

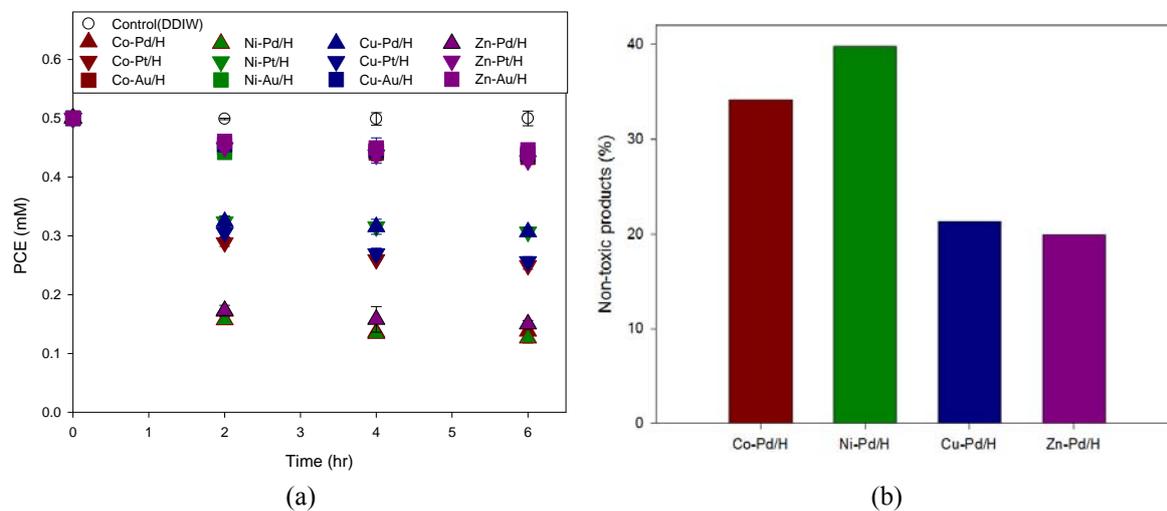


Fig. 1 (a) Degradation of PCE by various combinations of bimetallic catalysts on hematite supporter and (b) its non-toxic products in 6 hr. Experimental conditions: $[PCE]_0 = 0.5$ mM, $[catalyst]_0 = 0.2$ g/150 mL, $[second\ metal]:[noble\ metal]:[hematite] = 0.1:0.01:1$ based on wt.%, $[H_2]_0 = 4\%$, and pH 7

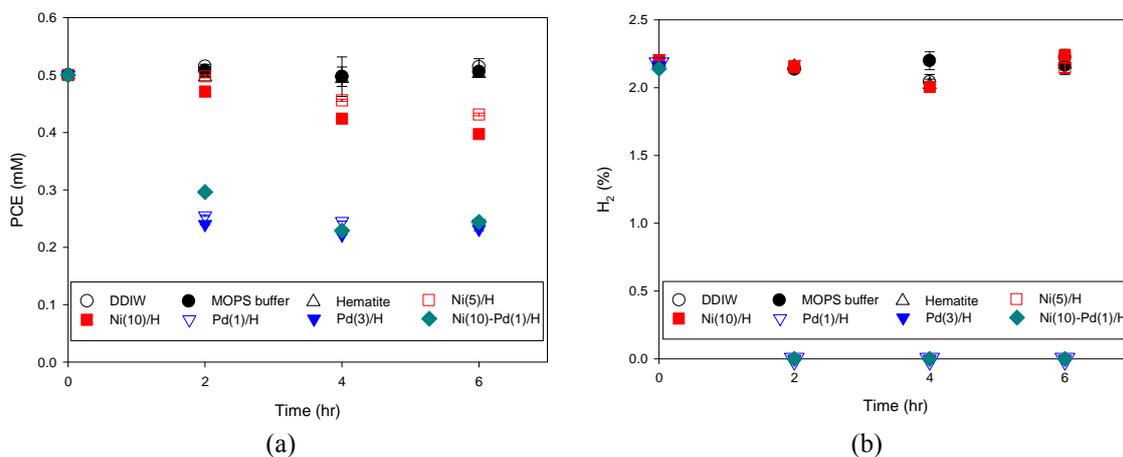


Fig. 2 (a) Degradation of PCE by various combinations of bimetallic catalysts on hematite supporter and (b) H_2 gas concentration throughout the reaction. Experimental conditions: $[PCE]_0 = 0.5$ mM, $[catalyst]_0 = 0.2$ g/150 mL, $[second\ metal]:[noble\ metal]:[hematite] = 0.1:0.01:1$ based on wt.%, $[H_2]_0 = 4\%$, and pH 7

were higher (~52%) than those by Ni (13.7-20.6%). The results for the effect of Ni and Pd metals on PCE degradation by bimetallic catalyst show that Ni^0 and Pd^0 reduced by sodium borohydride can transfer their electrons to PCE and the electrons can be used to reductively dechlorinate PCE. Analysis on H_2 gas was carried out to investigate reaction mechanism of PCE degradation by Ni-Pd/H catalyst. Fig. 2(b) shows the role of H_2 gas in reductive dechlorination of PCE by each

metal component. H_2 gas concentration in the reaction system decreased only when catalysts containing Pd (i.e., Pd(1)/H, Pd(3)/H, and Ni(10)-Pd(1)/H) were used to degrade PCE. This is presumably due to hydrogen atom which may be dissociated on Pd sites and the dissociated hydrogen atoms (H^*) are likely responsible for the bimetallic reactivity.

The results shown above support the fact that catalysts containing Pd can promote PCE dechlorination by using H_2 gas. However, mixture type of bimetallic catalyst (Ni-Pd/H) did not show higher PCE removal (51.2%) than Pd/H catalysts did (51.7-53.7%) (Figs. 2(a)-(b)). It is different from our expectation, which bimetallic catalyst composed of Ni and Pd on hematite may degrade PCE more than monometallic catalyst consisted of Ni or Pd on hematite. The bimetallic catalyst did not show the enhanced PCE removal. This is presumably due to the complicated transfer (or unexpected consumption) of electrons between different metals or between each metal and PCE. Fig. 3 shows the reductive dechlorination of PCE by Ni-Pd/H catalyst, which was a result derived from an experimental condition optimized in advance. The reaction kinetics of PCE was properly described by a pseudo-first-order rate law ($0.4664 \pm 0.0551 \text{ hr}^{-1}$). The results from Figs. 2 and 3 suggest that the experimental conditions including the concentration of target contaminants affect the experimental verification.

3.2 Effect of pH, contents of Ni and Pd, and H_2 gas concentrations on the reductive dechlorination of PCE

Fig. 4 shows the effect of pH on the reductive dechlorination of PCE by Ni-Pd/H catalyst. PCE removals at pH 4 and 7 by the bimetallic catalyst were similar throughout the reaction (86.7% and 90.0%, respectively) while that at pH 10 was 10.1%. The deteriorated PCE removal at pH 10 was presumably due to the passivation of bimetallic catalyst surface (Alessi and Li 2001). The result indicates that acidic to neutral pH conditions were favourable to the degradation of PCE, compared to the alkaline condition.

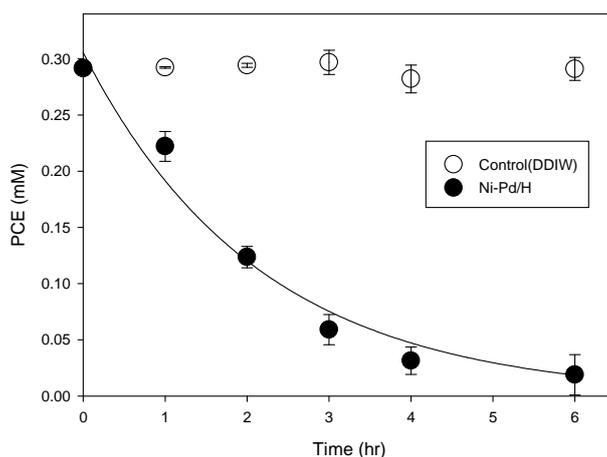


Fig. 3 Reductive dechlorination of PCE by Ni-Pd/H catalyst. Experimental conditions: $[PCE]_0 = 0.3 \text{ mM}$, $[catalyst]_0 = 0.2 \text{ g/150 mL}$, $[second \ metal]:[noble \ metal]:[hematite] = 0.1:0.01:1$ based on wt.%, $[H_2]_0 = 4\%$, and pH 7

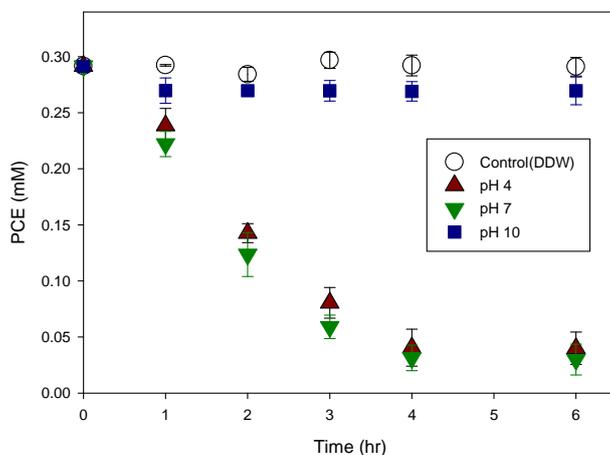


Fig. 4 Effect of pH on the reductive dechlorination of PCE by Ni-Pd/H catalyst. Experimental conditions: $[PCE]_0 = 0.3$ mM, $[catalyst]_0 = 0.2$ g/150 mL, $[second\ metal]:[noble\ metal]:[hematite] = 0.1:0.01:1$ based on wt.%, and $[H_2]_0 = 4\%$

Previous study on nitrate removal using the similar bimetallic catalyst showed that increasing a metal content to maximum did not guarantee the highest removal of target contaminants (Jung *et al.* 2012). Therefore, the effect of different contents of Ni and Pd with the same hematite amount on the reductive dechlorination of PCE was tested (Fig. 5). As Ni contents increased from 1% to 10%, PCE removals increased from 70.6% and reached 89.8% in 6 hr. However, increasing the Ni content more than 10% did not increase the PCE removal (74.2% at 6 hr). This can be explained

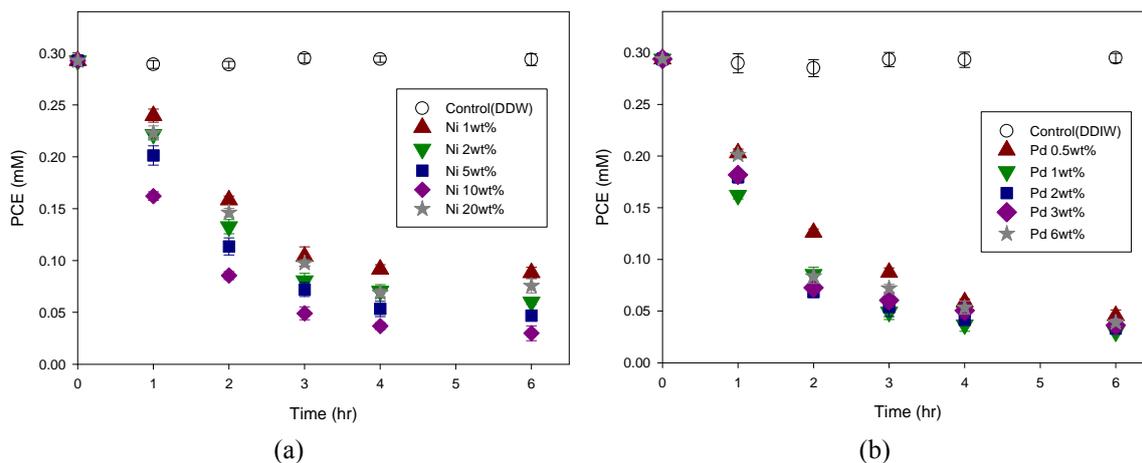


Fig. 5 Effect of contents of (a) Ni and (b) Pd on the reductive dechlorination of PCE by Ni-Pd/H catalyst. Experimental conditions: $[PCE]_0 = 0.3$ mM, $[catalyst]_0 = 0.2$ g/150 mL, $[H_2]_0 = 4\%$, and pH 7

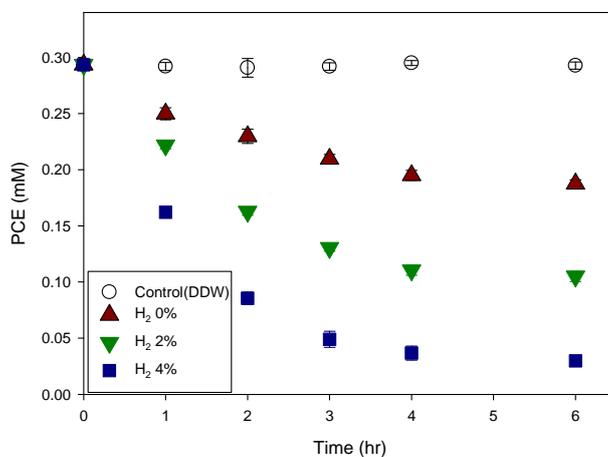


Fig. 6 Effect of H₂ gas concentrations on the reductive dechlorination of PCE by Ni-Pd/H catalyst. Experimental conditions: [PCE]₀ = 0.3 mM, [catalyst]₀ = 0.2 g/150 mL, [second metal]:[noble metal]:[hematite] = 0.1:0.01:1 based on wt.%, and pH 7

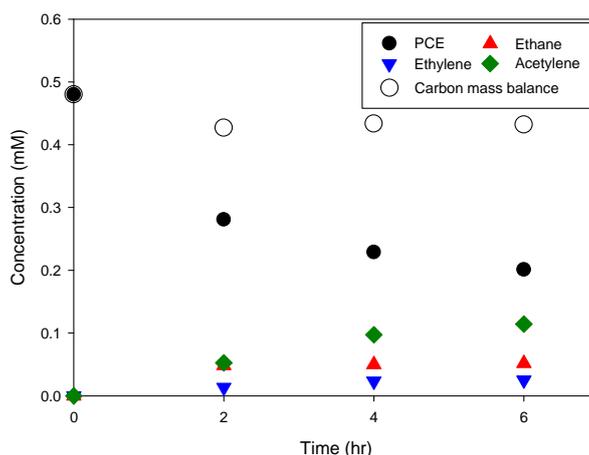


Fig. 7 Variation of measured concentrations of transformation products during PCE dechlorination by Ni-Pd/H catalyst. Experimental conditions: [PCE]₀ = 0.5 mM, [catalyst]₀ = 0.2 g/150 mL, [second metal]:[noble metal]:[hematite] = 0.1:0.01:1 based on wt.%, [H₂]₀ = 4%, and pH 7

by the intrusion of Pd sites by excessive Ni. PCE removals increased as Ni contents increased to an optimal level in the presence of limited Pd sites. However, the Pd sites seem to be covered by the excessive Ni when the Ni content exceeded the level of 10%. Increasing Pd contents to 1% increased PCE removal to approximately 90% in 6 hr. Similarly with the effect of Ni contents on PCE removal, increasing the Pd content more than 1% did not increase the PCE removal and showed the decreased PCE removal patterns (86.8% at 6 hr) with increasing Pd contents to 6%. Rare difference of PCE removals at more than 1% Pd contents might be due to the limited amount of H^{*}. Fig. 2(b) shows the complete consumption of H₂ gas in the presence of catalysts containing

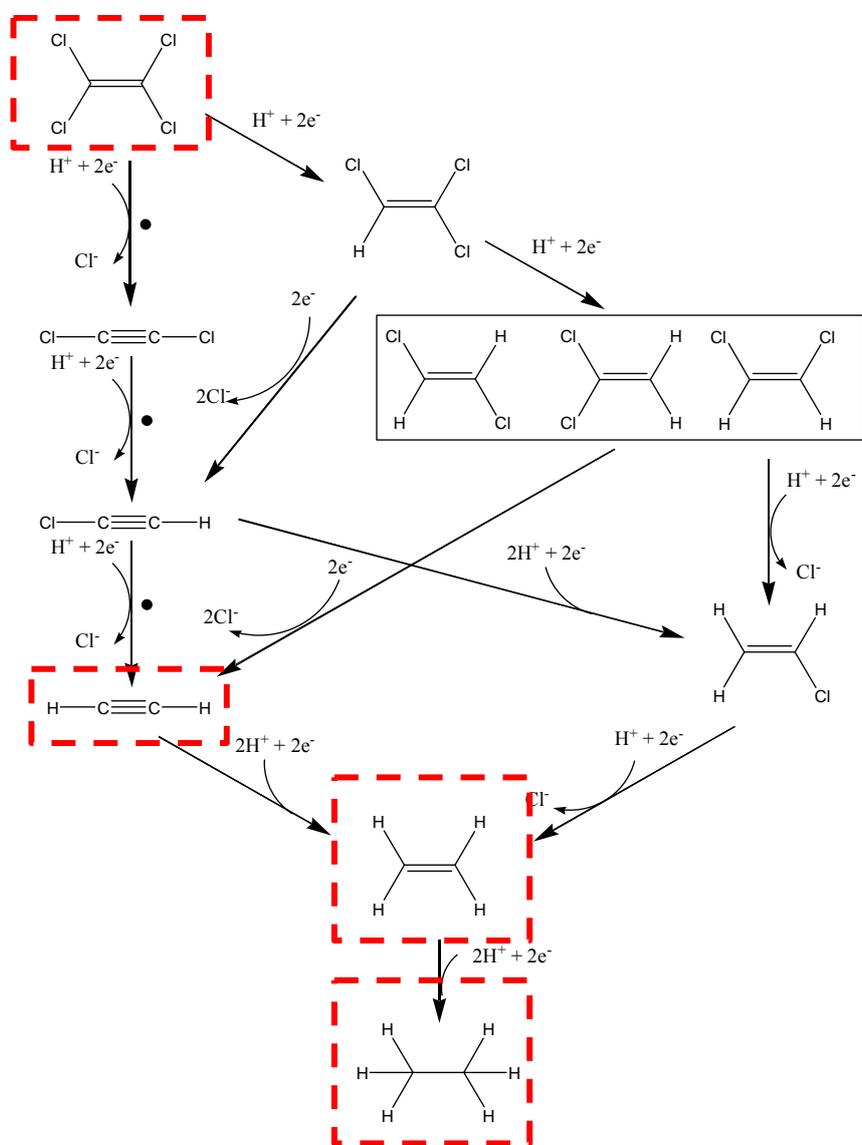


Fig. 8 Proposed degradation pathway for reductive dechlorination of PCE by Ni-Pd/H catalyst

Pd (Pd(1)/H, Pd(3)/H, and Ni(10)-Pd(1)/H). This indicates that the limited H_2 gas concentrations of 4% were not enough to produce H^* sufficiently in the presence of Pd when the contents were more than 1% level in the bimetallic catalyst.

Fig. 6 shows that the effect of H_2 gas concentrations on the reductive dechlorination of PCE by Ni-Pd/H catalyst. PCE removals increased from 36.1% to 64.1% as the H_2 gas concentrations increased from 0% to 2%. Increasing the H_2 concentration increased the removal of PCE (approximately 90.0%) until 4% H_2 content, which was maximum concentration applied in this study. This might be because the increased H_2 gas to 4% was sufficient for producing the H^* on Pd

surface. Applying H₂ concentration higher than 4% might enhance the reductive dechlorination of PCE by Ni-Pd/H catalyst, however it was not tested due to the safety concerns.

3.3 Degradation pathway of PCE by Ni-Pd/H catalyst

Fig. 7 shows formation and distribution of transformation products of PCE by Ni-Pd/H catalyst. Approximately 60% of PCE was degraded by the bimetallic catalyst in 6 hr. PCE was transformed to acetylene (24%), ethylene (5%), and ethane (11%) at 6 hr in bimetallic catalyst system. The percentage was calculated by dividing a molar concentration of each product at 6 hr by initial molar concentration of PCE. Total carbon mass of PCE accounted for 90.0% at last sampling time and unrevealed portion (10.0%) may be transformed to other hydrocarbons such as 1,3-butadiene (Amir and Lee 2012). Chlorinated products such as TCE, 1,1-DCE, cis-DCE, trans-DCE, and VC were not observed in 6 hr. Based on the formation and distribution of measured products, PCE degradation by Pd-Ni catalyst on hematite seems to follow the β -elimination pathway (Fig. 8).

4. Conclusions

A novel technology using bimetallic catalyst consisted of second and noble metals on hematite for the treatment of PCE was investigated. Ni and Pd were selected as second and noble metals for the best metal composition. Effect of each component on PCE degradation by Ni-Pd/H catalyst showed that Ni⁰ and Pd⁰ can transfer their electrons to PCE and that the electrons can be used to reductively degrade PCE. PCE was dechlorinated less by Ni(5)/H catalyst than by Ni(10)/H catalyst at the same condition. Removals of PCE were rarely influenced by the experimental condition of different Pd amounts (Pd(1)/H and Pd(3)/H). H₂ concentration in the reaction system decreased only when catalysts containing Pd were used to degrade PCE. This might be explained by the dissociated hydrogen atoms which may be generated on Pd sites and likely responsible for the bimetallic reactivity.

Acidic to neutral pH conditions were favorable to the degradation of PCE, compared to the alkaline condition. PCE removal might be deteriorated due to the passivation of catalyst surface at high pH. Increasing Ni contents to 10% increased the PCE removal, but the removal decreased at Ni 20% content. Meanwhile, increasing Pd contents to 6% showed no difference in PCE removals at Pd content of more than 1%. Increasing H₂ concentration increased the removal of PCE until 4% H₂ content. Chlorinated products such as TCE, 1,1-DCE, cis-DCE, trans-DCE, and VC were not formed while PCE was transformed to acetylene, ethylene, and ethane by Ni-Pd/H catalyst in 6 hr. The result obtained from this study can provide a fundamental knowledge to understand reductive dechlorination of chlorinated organics by bimetallic catalyst composed of second and noble metals and a soil mineral supporter and apply the bimetallic catalyst technology to the treatment of groundwater and wastewater contaminated by chlorinated organics.

Acknowledgments

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2012-C1AAA001-M1A2A2026588) and Korean Ministry of Environment as "The GAIA Project" (ARQ201202076).

References

- Alessi, D.S. and Li, Z. (2001), "Synergistic effect of cationic surfactants on perchloroethylene degradation by zero-valent iron", *Environ. Sci. Technol.*, **35**(18), 3713-3717.
- Amir, A. and Lee, W. (2011), "Enhanced reductive dechlorination of tetrachloroethene by nano-sized zero valent iron with vitamin B12", *Chem. Eng. J.*, **170**(2-3), 492-497.
- Amir, A. and Lee, W. (2012), "Enhanced reductive dechlorination of tetrachloroethene during reduction of cobalamin (III) by nano-mackinawite", *J. Hazard. Mater.*, **235-236**, 359-366.
- Bae, S. and Lee, W. (2010), "Inhibition of nZVI reactivity by magnetite during the reductive degradation of 1,1,1-TCA in nZVI/magnetite suspension", *Appl. Catal. B*, **96**(1-2), 10-17.
- Borch, T., Kretzschmar, R., Kappler, A., Cappellen, P.V., Ginder-Vogel, M., Voegelin, A. and Campbell, K. (2010), "Biogeochemical redox processes and their impact on contaminant dynamics", *Environ. Sci. Technol.*, **44**(1), 15-23.
- Dong, Y., Liang, X., Krumholz, L.R., Philp, R.P. and Butler, E.C. (2009), "The relative contributions of abiotic and microbial processes to the transformation of tetrachloroethylene and trichloroethylene in anaerobic microcosms", *Environ. Sci. Technol.*, **43**(3), 690-697.
- Elsner, M., Schwarzenbach, R.P. and Haderlein, S.B. (2004), "Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants", *Environ. Sci. Technol.*, **38**(3), 799-807.
- Gander, J.W., Parkin, G.F. and Scherer, M.M. (2002), "Kinetics of 1,1,1-trichloroethane transformation by iron sulfide and a methanogenic consortium", *Environ. Sci. Technol.*, **36**(21), 4540-4546.
- Jeong, H.Y. and Hayes, K.F. (2007), "Reductive dechlorination of tetrachloroethylene and trichloroethylene by mackinawite (FeS) in the presence of metals: Reaction rates", *Environ. Sci. Technol.*, **41**(18), 6390-6396.
- Jung, J., Bae, S. and Lee, W. (2012), "Nitrate reduction by maghemite supported Cu-Pd bimetallic catalyst", *Appl. Catal. B*, **127**, 148-158.
- Kenneke, J.F. and Weber, E.J. (2003), "Reductive dehalogenation of halomethanes in iron- and sulfate-reducing sediments. 1. Reactivity pattern analysis", *Environ. Sci. Technol.*, **37**(4), 713-720.
- Lee, W. and Batchelor, B. (2003), "Reductive capacity of natural reductants", *Environ. Sci. Technol.*, **37**(3), 535-541.
- Lee, C.C. and Doong, R.A. (2008), "Dechlorination of tetrachloroethylene in aqueous solutions using metal-modified zerovalent silicon", *Environ. Sci. Technol.*, **42**(13), 4752-4757.
- Lee, W., Batchelor, B. and Schlautman, M.A. (2000), "Reductive capacity of soils for chromium", *Environmental technology*, **21**(8), 953-963.
- Maymó-Gatell, X., Nijenhuis, I. and Zinder, S.H. (2001), "Reductive Dechlorination of cis-1,2-Dichloroethene and Vinyl Chloride by "Dehalococcoides ethenogenes"", *Environ. Sci. Technol.*, **35**(3), 516-521.
- US Environmental Protection Agency (2012), "Edition of the Drinking Water Standards and Health Advisories; EPA 822-S-12-001", EPA Office of Water, Washington, D.C., USA.
- US Environmental Protection Agency (2014), "Integrated Risk Information System (IRIS, <http://www.epa.gov/iris/>)".
- Van der Zee, F.P. and Cervantes, F.J. (2009), "Impact and application of electron shuttles on the redox (bio)transformation of contaminants: A review", *Biotechnol. Adv.*, **27**(3), 256-277.
- Zhao, Z., Fang, Y.L., Alvarez, P.J.J. and Wong, M.S. (2013), "Degrading perchloroethene at ambient conditions using Pd and Pd-on-Au reduction catalysts", *Appl. Catal. B*, **140-141**, 468-477.