Effect of reduction temperature on the preparation of zero-valent iron aerogels for trichloroethylene dechlorination

Jihye Ryu**, Dong Jin Suh*, Young-Kwon Park**, and Young-Woong Suh**†

*Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
**Faculty of Environmental Engineering, University of Seoul, Seoul 130-743, Korea

(Received 7 January 2008 • accepted 27 April 2008)

Abstract—Zero-valent iron (ZVI) aerogels have been synthesized by sol-gel method and supercritical CO2 drying, followed by H2 reduction in the temperature range of 350-500 °C. When applied to trichloroethylene (TCE) dechlorination, the ZVI aerogel reduced at 370 °C showed the highest performance in the conditions employed in this study. Thus, the effect of reduction temperature in preparing ZVI aerogels has been investigated by several characterizations such as BET, XRD, TPR, and TEM analyses. As the reduction temperature decreased from 500 to 350 °C, the BET surface area of the resulting aerogels increased from 6 to 30 m2/g, whereas their Fe0 content decreased up to 64%. It was also found that H2 reduction at low temperatures such as 350 and 370 °C leads to the formation of ZVI aerogel particles consisting of both Fe0 and FeO in the particle cores with a different amount ratio, where FeO is a mixture of maghemite and magnetite. It is, therefore, suggested that reduction at 370 °C for ZVI aerogel preparation yielded particles homogeneously composed of Fe0 and FeO in the amount ratio of 87/13, resulting in high TCE dechlorination rate. On the other hand, when Pd- and Ni-ZVI aerogels were prepared via coprecipitation and then applied for TCE dechlorination, we also observed a similar effect of reduction temperature. However, the reduction at 350 or 370 °C produced Pd- or Ni-ZVI aerogel particles in which Fe0 and FeO co-exist homogeneously. Since both Fe0 and FeO are advantageous in TCE dechlorination, the activities of Pd- and Ni-ZVI aerogels reduced at 350 °C were comparable to those of both aerogels reduced at 370 °C, although the former aerogels have less Fe0 content.

Key words: Zero-valent Iron, Aerogel, Dechlorination, Trichloroethylene, Thermal Reduction

INTRODUCTION

Chlorinated organic compounds, which are most commonly detected in surface water, groundwater, and soil, are persistent to natural degradation. Various technologies have been explored for removal of chlorinated compounds, including bioremediation, thermal treatment, permeable reactive barriers, etc. One cost-effective method for remediation of contaminated groundwater is the installation of permeable reactive zones or barriers within aquifers [1,2], where zero-valent metals (ZVM) have played a crucial role in reduction of chlorinated organic compounds, toxic metals, and harmful organic species due to their ability to undergo electron-transfer reactions [3]. Among various metals which have proven to be effective in this application, zero-valent iron (ZVI; Fe0) particle is widely considered to be one of the most active catalysts in terms of the cost, reduction efficiency, and environmentally benign impact. Such ZVI particles can directly supply electrons for reduction have been applied to the reductive dechlorination of a wide range of environmental pollutants including polychlorinated biphenyls (PCBs), tetrachlorinated ethylene (PCE), and trichloroethylene (TCE), or to the reduction of water-soluble metal ions such as Cr6+, Pb2+, TeO4−, etc [4,5]. Among them, TCE is the most frequently targeted probe molecule since more toxic compounds such as dichloroethylene (DCE) isomers and vinyl chloride (VC) rather than the parent compound were produced through the ZVI-promoted reduction [6].

However, the commercial ZVI samples have been found to show a low rate in TCE dechlorination due to their micro-sized particles. Since the reaction on Fe0-based particles is a surface-mediated process, the TCE dechlorination rate strongly depends on the surface area of ZVI particles. Hence, a large number of researches have been focused on increasing the surface area of ZVI particles to enhance the reaction rate. To achieve this goal, nano-sized ZVI particles have been variously prepared, typically by a reductive precipitation of iron salts with NaBH4 (ZVI-BH4) [7]. It has been reported that such nanoparticles with a broad size distribution of 1-100 nm showed a BET surface area of ~33.5 m2/g, which leads to much higher TCE dechlorination rate than the micro-sized ZVI particles [8]. The as-received samples of ZVI-BH4 were, in addition, shown to consist of a metal core, a thin iron oxide layer, and an outer layer that is mostly oxidized B (borate) with some reduced B (boride), as reported in the literature [9-12]. However, the role of the B-rich shell in ZVI-BH4 samples is still ambiguous, although the activities of ZVI-BH4 samples are greater than those of H2-reduced ZVI samples for CCl4 dechlorination in terms of the mass-normalized rate constant [8].

Recently, nano-sized ZVI particles could be prepared by reduction of goethite particles with H2 at high temperatures of 200-600 °C, followed by allowing the iron particles to stand in water for up to 30 days, yielding the BET surface area of 5-60 m2/g [13]. These particles (ZVI-T), supplied by Toda Kogyo Corp., were also known to be a two-phase material consisting of Fe3O4 in the core and FeO in the shell [8,13], where the magnetite layer at the surface of particles can protect inside Fe, resulting in the prolonged catalytic ac-
tivity. Since the activity of ZVI particles is, in general, gradually deteriorated by oxidation of iron metal at their surface, the properties of ZVI particles appear to be unique for the TCE degradation.

On the other hand, the iron oxide layer is produced at the ZVI surface by Fe oxidation in aqueous system due to the thermodynamic instability of ZVI: the electrons released by Eq. (1) can produce H₂ and OH⁻ (Eq. (2)), so that the pH value is getting higher [14]. The consequent rise in pH can precipitate ferrous hydroxide, as shown in Eq. (3). This hydroxide is thermodynamically unstable and can be further oxidized to form magnetite (Fe₃O₄) according to Eq. (4) [15].

\[
\begin{align*}
\text{Fe}^0 & \rightarrow \text{Fe}^2+2e^- \quad (1) \\
2\text{H}_2\text{O}+2e^- & \rightarrow \text{H}_2+2\text{OH}^- \quad (2) \\
\text{Fe}^2++2\text{OH}^- & \rightarrow \text{Fe}(_2\text{O}_3)\text{H}_2\text{O} \quad (3) \\
\text{Fe(OH)}_2(aq) & \rightarrow \text{Fe}_3\text{O}_4(s)+\text{H}_2\text{O} \quad (4)
\end{align*}
\]

The resulting magnetite, which is electrically conductive, can transfer a charge through the interface oxide and, in turn, induce reductive dechlorination, although the degradation rate is lower because the charge transfer rate through the oxide is slower than on an exposed metal surface [16-18]. As the precipitate ages with time, Fe₃O₄ is oxidized to form non-electron-conducting maghemite (γ-Fe₂O₃) at the inner layer of the Fe₃O₄ film with a neutral pH, which interferes with electron transfer from the Fe₀ core and then inhibits the redox reaction [16].

Considering the above-mentioned physical properties of nano-sized ZVI required for TCE dechlorination, one could anticipate that catalytic activity could be maintained and/or enhanced by using the ZVI sample with high surface area consisting of the iron-rich core and the Fe₃O₄-rich shell. In this study, we have utilized a synthetic method of aerogels which are well known to show a high specific surface area and well-developed mesoporosity. To render Fe₃O₄ exist in ZVI aerogel particles, thermal reduction by H₂ was also carried out at temperatures lower than 400°C. The resulting ZVI aerogels were applied to the dechlorination of TCE at 20°C, where the effect of reduction temperature on the preparation of ZVI aerogels has been investigated. Also, a similar study was performed using Pd- and Ni-incorporated ZVI aerogels synthesized via cogelation, since nano-sized Pd- and Ni-containing ZVI particles could enhance the dechlorination rate and simultaneously prevent the production of chlorinated intermediates [6,19,20].

**EXPERIMENTAL**

1. Preparation of ZVI Aerogel

Iron oxide aerogel was synthesized by the sol-gel method and supercritical CO₂ drying, which is similar to the literature method [21]. For preparing iron oxide wet gel, iron chloride hexahydrate (FeCl₃·6H₂O, Sigma-Aldrich, >98%) was first dissolved in 35 mL of ethanol (Merck, 99.9%) to make a 0.35 M of iron solution. After stirring for 1 h, distilled water was added for the hydrolysis, followed by stirring for another 1 h. To this solution, propylene oxide (Sigma-Aldrich, 99%) as a gelation promoter was added dropwise by a syringe pump at a rate of 1 mL/min with stirring. Then, the molar ratio of FeCl₃·6H₂O, water, propylene oxide, and ethanol in all samples was 1 : 3 : 7 : 49. During the gel formation, the solution color gradually changed from reddish brown to dark brown while the viscosity increased with heat evolving. The ethanol solvent in wet gels was then exchanged with supercritical CO₂ for 3-4 h at a pressure of 3,000 psi at 60°C.

The resulting iron oxide aerogel was reduced in 5% H₂/Ar at a flow rate of 400 mL/min by ramping the temperature with 1°C/min to the desired temperature in the range of 350-500°C and holding for 2 h. Finally, ZVI aerogels were obtained after a treatment in 1% O₂/N₂ at a flow of 60 mL/min for 1 h at room temperature, due to the pyrophoric character of iron. The physical properties of ZVI aerogels reduced at different temperatures are summarized in Table 1 (entries 1-4), where the number in aerogel samples’ name stands for the reduction temperature.

2. Preparation of Pd- and Ni-ZVI Aerogels

Palladium- or nickel-containing iron oxide aerogel was prepared by the same procedure as the ZVI aerogel, except that palladium

---

**Table 1. Physical properties of ZVI, Pd- and Ni-ZVI aerogels reduced at various temperatures**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>Reduction temperature (°C)</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
<th>Fe⁰ content (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZVI-350</td>
<td>350</td>
<td>30</td>
<td>0.284</td>
<td>33.05</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>ZVI-370</td>
<td>370</td>
<td>25</td>
<td>0.147</td>
<td>22.34</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>ZVI-400</td>
<td>400</td>
<td>19</td>
<td>0.045</td>
<td>9.07</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>ZVI-500</td>
<td>500</td>
<td>6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Pd-ZVI-350</td>
<td>350</td>
<td>21</td>
<td>0.102</td>
<td>19.64</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>Pd-ZVI-370</td>
<td>370</td>
<td>18</td>
<td>0.066</td>
<td>15.80</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>Pd-ZVI-400</td>
<td>400</td>
<td>12</td>
<td>0.040</td>
<td>15.24</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>Ni-ZVI-350</td>
<td>350</td>
<td>28</td>
<td>0.158</td>
<td>23.34</td>
<td>77</td>
</tr>
<tr>
<td>9</td>
<td>Ni-ZVI-370</td>
<td>370</td>
<td>21</td>
<td>0.090</td>
<td>16.59</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>Ni-ZVI-400</td>
<td>400</td>
<td>13</td>
<td>0.042</td>
<td>14.49</td>
<td>99</td>
</tr>
</tbody>
</table>

*Calculated from the following formula: Fe⁰ content = −51.387X² + 151.88X, where X represents an intensity ratio of D₁₁₀/(D₁₁₀+D₃₁₁).

*Not determined.

*Commercial Fe⁰ particles (Alfa, <10 micron).