Preparation of Zero-valent Iron Aerogels for TCE Dechlorination

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Introduction

It is well known that trichloroethylene (TCE), one of the most common chlorinated organic compounds detected in soil and groundwater, is persistent to natural degradation. Removal of TCE by chemical reduction has been a challenging task for decades. Among various technologies for the dechlorination of TCE, zero-valent iron (ZVI; Fe^0) particles appear to be one of the most promising technologies. However, micro-sized Fe^0 particles have been found to show a low TCE reduction rate with half-lives in the order of days or longer. To enhance the dechlorination rate, many researchers have paid their attention to increasing the surface area of ZVI since dechlorination on Fe^0-based particles is a surface-mediated process. One of the effective methods to achieve this goal is to prepare nano-sized ZVI particles, for example, by reductive precipitation with $NaBH_4$ [1]. Here we present the synthesis of ZVI aerogels using supercritical drying and gas-phase reduction, which is similar to the literature method [2], and their application to the dechlorination of TCE.

Materials and Methods

For preparing iron oxide wet gels, $FeCl_3 \cdot 6H_2O$, water, propylene oxide and ethanol were used with a molar ratio of 1:3:7:49. The solvent was exchanged with $CO_2(l)$ and dried under the supercritical condition. The resulting aerogels were reduced in 5% H_2/Ar at a flow rate of 400 ml/min by ramping the temperature at 1°C/min and holding the desired temperature (370 – 500°C) for 2 h. TCE dechlorination was conducted in 2 mL septum vial with zero headspace, where Fe concentration was 10 g/L. After the ZVI samples were collected by placing a magnet at the bottom of vial, the reaction mixture was extracted with hexane and then analyzed using a GC with ECD and auto injection system.

Results and Discussion

On the basis of the TPR profile (Fig. 1a) which shows that the supercritical-dried FeO_x aerogel is completely reduced at ~450°C, the effect of reduction temperature on FeO_x aerogel was investigated. As a result, reduction temperatures higher than 400°C led to the formation of ZVI particles having a BET surface area less than 19 m^2/g and a total pore volume less than 0.037 cm^3/g (Table 1, ZVI-A2 sample). We also reduced FeO_x aerogel at temperatures lower than 400°C, even if its reduction was not completely done. As seen in Table 1 and Fig. 1b, ZVI-A1 sample reduced at 370°C for 2 h has the BET surface area of 25 m^2/g and the total pore volume of 0.074 cm^3/g while the content of Fe^0 is about 72 mol% calculated from the XRD peak areas.

The TCE dechlorination rate of ZVI aerogel samples was compared to that of commercial Fe^0 particles (ZVI-C) having a very low surface area of 0.13 – 0.19 m^2/g. As shown in Table 1, the TCE conversion on commercial Fe^0 is about 4 mol% at the reaction time of 10 h. The ZVI aerogels, however, showed much higher TCE conversion. It is surprising that the ZVI aerogel reduced at 370°C ($t \approx 11$ h at 100% conversion) reductively dechlorinated TCE two times faster than the one reduced at 400°C ($t \approx 23$ h at 100% conversion). Assuming that dechlorination has the 1st order reaction rate, the initial rate constant (k) of the former is 4-fold higher than that of the latter, leading to the fact that the reaction rate is not linearly correlated with the surface area of ZVI aerogels. It is, therefore, considered that a mixture of FeO_x and Fe^0 has a favorable effect in TCE dechlorination rather than a single Fe^0, based on the observation that the ZVI-A1 sample is composed of 72% Fe^0 and 28% FeO_x. To support our results, the ZVI aerogels reduced at various temperatures are now being applied to TCE dechlorination and characterized by XRD, BET, XPS and TEM analyses.

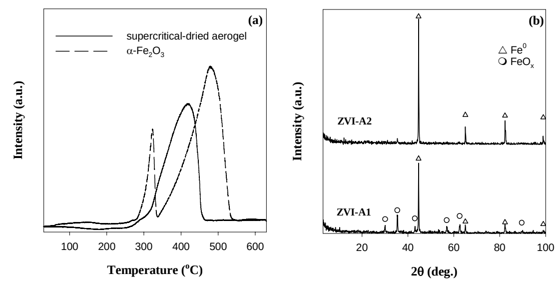

Figure 1. (a) TPR profiles of supercritical-dried FeO_x aerogel and α-Fe_2O_3 (Alfa). (b) XRD patterns of ZVI-A1 and ZVI-A2 samples reduced at 370°C and 400°C, respectively.

Table 1. Characteristics of commercial Fe^0 and ZVI aerogels

Sample	Reduction temperature (°C)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	$Fe^{0\,a}$ (mol%)	TCE conversion[b] (mol%)
ZVI-C	130	0.13-0.19[c]	0.034	100	4.3
ZVI-A1	370	25	0.074	72	96.5[d]
ZVI-A2	400	19	0.037	100	55.4[d]

[a] The content of Fe^0 in the samples was calculated from XRD peak areas. [b] Obtained after reaction for 10 h. [c] Obtained from Alfa. [d] % Error < 5%

Significance

The ZVI aerogels prepared in this study had large surface areas and showed high TCE dechlorination rates, compared to the commercial Fe^0. It is worth noting that a small fraction of FeO_x present in ZVI aerogels would be beneficial to TCE dechlorination.

References

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