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Catalytic dechlorination of monochlorobenzene with a new type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant

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Abstract

A unique type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant was prepared and used for dechlorination of monochlorobenzene (MCB). The sample Ni(B)/Fe(B) was synthesized by an electroless plating method, in which nanoscale Ni(B) was deposited on the surface of nanoscale Fe(B) synthesized by chemical reduction. The results suggest that the nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant has higher dechlorination efficiency than Ni/Fe(B) catalytic reductant prepared by replacing Fe(B) with Ni^{2+} in aqueous solution. The Ni content was found to be an important factor in catalytic dechlorination, with the dechlorination rate increasing with Ni content. The electroless plating method improve the efficiency of the Ni^{2+} in the solution. Dechlorination takes place with the existence of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant *via* a pseudo-first-order reaction.

Keywords: Iron; Nickel; Dechlorination; Monochlorobenzene

1. Introduction

Chlorinated organic compounds are widely used as industrial chemicals, intermediates for organic synthesis, and organic solvents. However, almost all of the chlorinated organic compounds, especially the chlorinated aromatics, are environmentally toxic chemicals. Most are hard to degrade and are listed as priority pollutants by the US EPA (1988). In recent years, numerous methods have been used for the degradation of chlorinated organic compound, such as zero-valent metal reduction (Kim et al. 2004; Christ et al., 2005; Doong and Lai, 2005; Hrapovic et al, 2005; Lin et al., 2005), biodegradation (Slater et al., 2001; Chen et al., 2005), wet oxidation (Kojima et al., 2005) and other methods (Epling et al., 1998; Zhang and Rusling, 1993).

In situ groundwater remediation using zero-valent iron, first demonstrated in the 1990s (Gillham and O'Hannesin, 1994), represents one of the latest innovative technologies for environmental treatment (Schrick et al., 2002). Compared with conventional iron, nanoscale iron and bimetallic particles based on iron exhibit higher dechlorination efficiency for their higher specific surface area and higher surface reactivity (Zhang, 2003; Liu et al., 2005a; Wei et al., 2006; Cheng et al., 2007). Because nanoscale bimetallic particles usually have much higher activity than nanoscale iron alone, these have been widely researched recently for environmental treatment (Zhang and Manthiram, 1997; Zhang et al., 1998; Xu and Zhang, 2000; Lowry and Johnson, 2004; Feng and Lim, 2005; Liu et al., 2005b; Song and Carraway, 2005; Nurmi et al., 2005). In bimetallic particles, iron acts as the electron donor (reductant), while the second metal (such as Pd, Pt, Ni or Ag) acts as a catalyst to collect hydrogen gas in aqueous solution and dissociate it to produce active hydrogen atoms to be the real reductant (Mallouk et al., 2002; Zhang et al., 2006). Palladium (Pd) shows

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outstanding high dechlorination efficiency in the Pd/Fe bimetallic catalytic reductant (Muftikian et al., 1995; Cheng and Wu, 2000; Liu et al., 2001). However, the high price of Pd will limit its application. It is preferable to find a more economic metal, such as nickel, to be the catalytic component.

Co-reducing by borohydride and substitution are widely used in preparing bimetallic catalytic reductants. Co-reduction method is to reduce the aqueous mixture of Ni^{2+} and Fe^{2+} by borohydride solution (Muftikian et al., 1995; Cheng and Wu, 2000; Liu et al., 2001). The samples prepared by co-reduction are bulk alloy, in which a portion of the second metal are covered by zero-valent iron and not utilized to collect and dissociate hydrogen. Thus, it is necessary to locate the second metal on the surface of the bimetallic catalytic reductant. When the substitution method is induced by replacing M^{2+} with zero-valent iron in aqueous solution, the second metal is easily dispersed on the surface of M/Fe (M = Pd, Pt, Ag, Cu or Ni, etc.). However, the second metal might form a layer structure that prevents the zero-valent iron from adsorbing and reacting with chlorinated organic compounds and H_2O.

Here we reported a method for preparing Ni/Fe bimetallic reductant by electroless plating. In this sample, designated Ni(B)/Fe(B), nanoscale Ni(B) particles were deposited on the surface of the nanoscale Fe(B). Monochlorobenzene (MCB) was chosen as a representative of the kind of environmentally toxic chemicals widely used as organic solvents and dye intermediates.

2. Experimental methods

2.1. Chemicals

Analytical grade ferrous chloride ($FeCl_2 \cdot 4H_2O$, Tianjin Guangfu Fine Chemical Research Institute, China), nickel sulfate ($NiSO_4 \cdot 6H_2O$, Tianjin Guangfu Fine Chemical Research Institute, China), potassium borohydride (KBH_4, Tianjin Chemical Reagent Institute, China), ethylenediamine (1,2-diaminoethane, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), sodium hydroxide (Tianjin Chenmical Reagent No. 3 Plant, China) and monochlorobenzene (Tianjin Chemical Reagent No. 2 Plant, China) were used in catalyst preparations. HPLC grade methanol (Tianjin Concord Tech Co., Ltd., China) was used for analysis.

2.2. Preparation of nanoscale Fe(B) and Ni(B)/Fe(B) bimetallic catalytic reductant nanoparticles

The nanoscale Fe(B) was prepared by chemical reduction method as we previously reported (Han et al., 2008). An aqueous solution of potassium borohydride (1.0 mol L^{-1}) was added to 0.05 mol L^{-1} ferrous sulfate aqueous solution, using a pump, while stirring vigorously. The molar ratio of BH_4^-:Fe^{2+} was 3:1, and the temperature was 298 K. The reaction system was protected from oxidation by an argon atmosphere. The resulting nanoscale Fe(B) was washed thoroughly with distilled water and anhydrous ethanol in series and then dried in vacuum at 323 K for 2 h. The product was metallic iron with small quantity of B element which was introduced by the reductant KBH_4 and inert in this reaction. The sample was denoted as Fe(B) in this work and so was the sample Ni(B) mentioned below.

The plating solution, consisting of nickel sulfate (12.0 g L^{-1}), ethylenediamine (11.1 g L^{-1}), potassium borohydride (5 g L^{-1}) and sodium hydroxide (6.7 g L^{-1}), was stable below 333 K. Nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant was prepared by the reaction between 1.0 g Fe(B) and different volumes of plating solution at 313 K. The reaction was also protected by argon atmosphere. Hydrogen gas was generated during the reaction. The products were separated from the plating solution immediately when no significant bubbles were observed, and then washed and dried as above. The volumes of plating solution used in the reaction were 37.5 mL (Ni(B)/Fe(B)-1), 50 mL (Ni(B)/Fe(B)-2), 75 mL (Ni(B)/Fe(B)-3), 150 mL (Ni(B)/Fe(B)-4) and 200 mL (Ni(B)/Fe(B)-5). Another series of nanoscale Ni/Fe catalytic reductants, designated as Ni/Fe(B)-1, Ni/Fe(B)-2, and Ni/Fe(B)-3 were prepared for comparison by replacing 1.0 g Fe(B) with 75 mL, 150 mL and 200 mL 12.0 g L^{-1} Ni^{2+} in aqueous solution, respectively.

2.3. Dechlorination experiments

Batch experiments were conducted in a three-necked bottle. MCB aqueous solution (200 mg L^{-1}) was added to the bottle, which contained 0.8 g nanoscale Ni/Fe catalytic reductant, until it was full, leaving no headspace. The total volume of the solution was 350 mL. The reactions were carried out at 298 K while mechanical stirring at a rate of 300 rpm.

2.4. Method of analysis

At different reaction times, aqueous samples were withdrawn using a 5 mL syringe and filtered through a 0.45 μm membrane for analysis. The concentrations of the parent chlorobenzene and products were measured using a high-performance liquid chromatograph (HPLC, Wufeng, Shanghai) equipped with a UV-1575 detector and C18 column (4 μm, 3.9 × 150 mm). A mobile phase of 70% methanol and 30% water was employed at a flow rate of 0.8 mL min^{-1}, and the detector wavelength was set at 254 nm.

The Ni content in the Ni/Fe catalytic reductant was determined by inductively coupled plasma (ICP) analysis using an IRIS Advantage spectrometer. The transmission electron micrographs were obtained using a Philips Tecnai G2 T20ST. Samples for observation were dispersed in ethanol and treated with ultrasound for 5 min and then placed on a copper grid coated with carbon film.