Bimetallic Nanoparticles Synthesis in Membrane Matrix:

Nanoparticle Structure and Reactive Properties

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Abstract

In this study, nanosized core-shell Fe/Pd particles were synthesized in the polyacrylic acid (PAA)/polyvinylidene fluoride (PVDF) composite membranes. The PAA/PVDF membranes were prepared by a dip-coating process. The carboxylic groups in PAA layer bind ferrous ions from aqueous solution by ion exchange at controlled pH (5~6). Subsequent reduction with sodium borohydride forms metallic Fe nanoparticles. The advantages of using PAA for nanoparticle synthesis are: prevention of particle agglomeration and control of particle size, recapture of dissolved Fe^{2+} or Fe^{3+} from solution, and easy regeneration of nanoparticles. The core-shell Fe/Pd nanoparticles can be achieved by a partial displacement reaction on Fe surface. The membranes and Fe/Pd nanoparticles were characterized by several electron microscopy techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), and high-resolution transmission electron microscopy (HRTEM). The reactive properties are dependent on the bimetallic nanoparticle structure and distribution of Fe and Pd at nano domain. A specimen-drift-free EDS mapping system was performed in STEM to determine the two-dimensional element distribution inside the membrane matrix at nano scale. The interfacial structure of Fe core and Pd shell are studied in detail using HRTEM. The reactive properties of Fe/Pd bimetallic nanoparticles in PAA/PVDF membrane were investigated toward the reductive dechlorination of 2,3,2',5'-tetrachlorobiphenyl (TeCB) at room temperature. Complete destruction of TeCB (C_0 = 12 mg L^{-1}) by membrane-based Fe/Pd (Pd = 2 wt%) nanoparticles was achieved within 2 hours. Biphenyl was formed as the main product in the first hour and the only product after 2 hours. Chlorinated intermediates (trichlorobiphenyl, dichlorobiphenyl and chlorobiphenyl) which were observed in the first hour were also quantified. Reductive dechlorination of TeCB under convective flow mode and recapture of dissolved Fe^{2+} were also investigated in this paper. This research is supported by the NIEHS-SBRP program and by U.S. EPA – STAR Program.

Keywords: Polyacrylic acid, Membrane, Fe/Pd, Nanoscale bimetallic particles, Polychlorinated biphenyl (PCB) Dechlorination

Introduction

The creation of nanosized bimetallic particles having alloy or core/shell structure inside polymer domains has received intensive attentions in the study of optical, electronic, magnetic and biological devices, and highly sensitive sensors. Application of bimetallic nanoparticles in catalytic reactions is particularly attractive[1-3] due to the unique physical and chemical properties of nanostructure over bulk structure as well as the improvement of reactive properties.

The creation and development of nanosized materials have brought important and promising techniques into the field of pollution control. Recently, various studies have been reported on the groundwater remediation through degradation of toxic chlorinated organic compounds (COCs) with non-immobilized Fe^0 based bimetallic nanoparticles (Fe/Ni, Fe/Pd)[4-5]. In this case, COCs are reduced to non-toxic (or less) hydrocarbons in the presence of the second catalytic metal (Pd or Ni) by substitution of chlorine with hydrogen. Compared to the single zerovalent Fe system (such as, iron filings) which has been used for decades for COCs degradation, this catalytic hydrodechlorination technology is developed because of enhanced reaction rate and elimination of toxic by-product formation due to the second, catalytic metal. The correlation between reactive properties and the nanoparticle structure, the distribution of first and second metal, the composition of second metal, and particle size (nano size versus bulk size) have not been clarified.

In this paper, bimetallic nanopartciels (Fe/Ni and Fe/Pd) with core/shell structure were prepared directly inside polyacrylic acid (PAA)/polyvinylidene fluoride (PVDF) membrane matrix. We investigated the role of PAA as a chelating (ion exchange) polymer for binding metal cations in the formation of nanoparticles and in the dechlorination reaction of COCs. We demonstrate the element distribution of first and second metal in the nano domain and the core/shell structure of bimetallic nanoparticles using X-ray energy dispersive spectroscopy (EDS) mapping technique performed in scanning transmission electron microscopy (STEM). Our objective is to synthesize nanostructured bimetallic particles inside a membrane matrix for reductive dechlorination of toxic COCs, understand and quantify the role of second dopant metal, the nano structure, the element distribution of first and dopant metal, and the composition of dopant metal in the reactive properties of membrane-based bimetallic nanoparticles, and reaction pathway/reaction rate changes through reaction product distribution.

Experimental Section

Chemicals

Sodium borohydride (99.995%) was obtained from Aldrich. Ferrous sulfate, nickel sulfate, ethylene glycol, obtained from Fisher Scientific. PCB congeners were obtained from UltraScientific. Polyacrylic acid (MW 50,000) was obtained from Polysciences. Commercial hydrophilized polyvinylidene fluoride (PVDF, 0.1μm pore size, 47mm in diameter, 125μm thickness) porous membrane was purchased from Millipore.

Preparation of Metal Nanoparticles[6]

Synthesis of Crosslinked PAA/PVDF Composite Membrane

Hydrophilized polyvinylidene (PVDF, 0.1μm pore size, 4.7 cm diameter, 125μm thickness, wt = 0.1 gm) microfiltration membranes obtained from Millipore was used as the support membrane layer. The PAA coating layer was attached to the surface of support membrane by a dip-coating process. After removal from the immersion bath, a thin adherent layer was left on the membrane. Aqueous coating solution contained 25 wt% PAA solutions and 4 wt% ethylene glycol as the cross-linking agent. The crosslinked PAA/PVDF composite membrane was finally obtained by heating the membrane in the oven under vacuum at 110~120°C for 3 hours. The ether bond formed between carboxylic group and ethylene glycol generate the cross-linking PAA network structure.

Synthesis of Fe/Pd nanoparticles in PAA/PVDF Membrane domain

Bimetallic Fe/Ni nanoscale particles were then produced by the following procedure. Five samples of PAA/PVDF membrane were soaked into 0.1M NaOH solution for 1 hour to convert PAA from H form to Na form. After washed with DIUF water, the membranes were immersed into 0.01M $FeCl_2$ solution for 12 hours. During this process, ferrous ions were combined with PAA by ion-exchange with Na^+. Subsequent immersion of the membrane into 0.4M $NaBH_4$ aqueous solutions for 10 minutes results in the formation of Fe^0 nanoparticles. Fe/Pd nanoparticles were prepared by soaking 4 samples of PAA/PVDF/Fe^0 composite membranes into a 50mL ethanol solution containing 0.05 wt% of potassium tetrachloropalladate (K_2PdCl_4). Pd^{2+} was reduced to Pd^0 by Fe^0 and subsequently deposited on the Fe surface.

Physical Characterization of Metal Particles

Surface of membranes containing metal nanoparticles were observed using the Hitachi S-900 Scanning Electron Microscope (SEM). A Hitachi S-3200 SEM equipped with an energy dispersive spectrometer (EDS) was also used to obtain information regarding the elements present in the nanoparticles. Particle size and distribution were characterized by SEM and transmission electron microscopy (TEM). A specimen-drift-free EDS line profile and EDS mapping system was performed in a scanning transmission electron microscopy (STEM) to determine element composition of particles at nano scale.

Batch Experiments

Batch experiments for dechlorination of 2,3,2’,5’-Tetrachlorobiphenyl (TeCB) were conducted in 22 mL serum glass vials. In each batch vial, 16 mg Fe/Pd particles (Pd=2.5 wt %) immobilized on 4 samples of membranes were loaded into the vial containing 15 mg/L TeCB in 20 mL of 50/50 vol.% ethanol/water. The serum glass vials were sealed with Teflon-lined silicon septa and placed on a wrist-action shaker throughout the duration of the experiment. Parallel control experiments with only support membrane (no metal particles) were also performed.

Method of Analyses

TeCB was analyzed by gas chromatography (Varian-3800) equipped with an ion-trap mass spectrometry (Saturn-2200). For each 20-mL experimental sample vial, 4 ml of hexane as the extractant for PCBs was added to an 8-ml vial containing 4 ml of aqueous solution which was removed from the reaction vial. After removing all the residual solution, 10 ml hexane was added into the reaction vial for membrane phase extraction. The 8-ml and reaction vials were both placed on a wrist-action shaker and mixed for 2 hours to achieve extraction equilibrium. From each extraction vial, a 1ml aliquot of the extraction solvent layer was transferred to a 1 mL GC autosampler (Combital CTC Analytics) vial for analysis. Ten microliters of naphthalene (5000mg/L in methyl chloride) was added into the GC sample vial as an internal standard. External standards of TeCB, trichlorobiphenyl (TeCB), dichlorobiphenyl (DiCB), and biphenyl in hexane obtained from Ultra Scientific were used to prepare calibration curves. The calibration curves were linear over the concentration range of 0.5~20 mg/L for all three PCB congeners, and the detection limit was approximately 0.1mg/L.

Results and Discussion

Characterization of Metal Particles

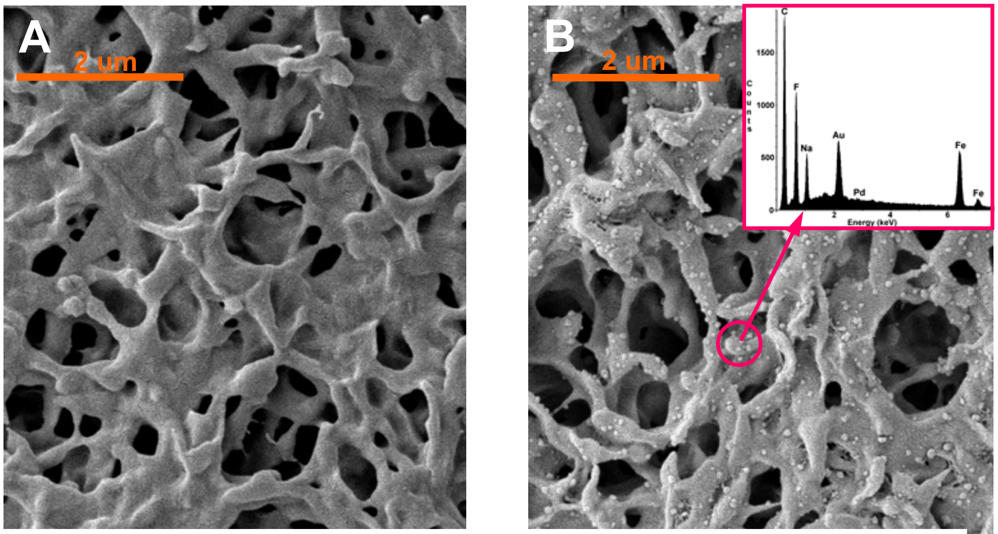

Figure 1. SEM image of (A) PVDF support membrane surface; (B) Fe/Pd (Pd = 2.5 wt %) nanoparticles in PAA/PVDF membrane.

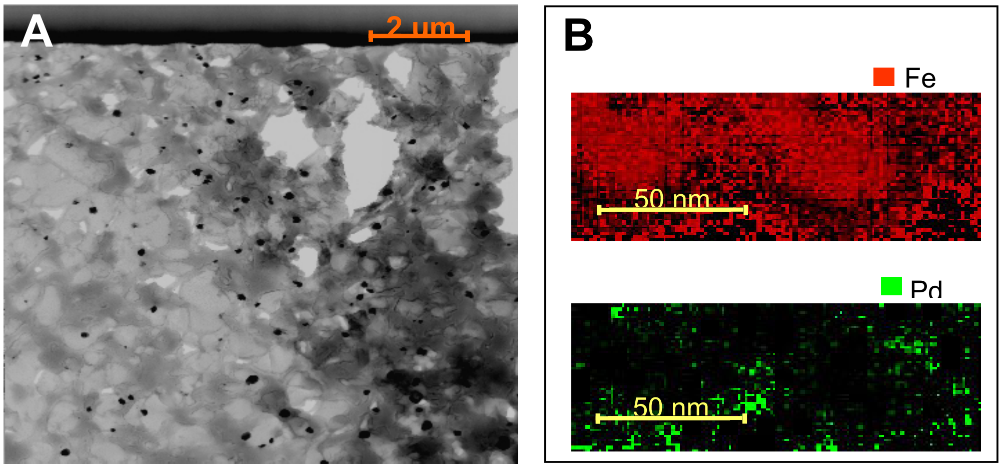

Figure 2. (A) TEM image of Fe/Pd (Pd = 2.5 wt %) nanoparticles in PAA/PVDF membrane cross-section; (B) STEM-EDS mapping image of Fe/Pd nanoparticles

To reveal the structure difference between the support membrane and the composite membrane deposited with nanoscale Fe/Ni particles, the morphology of membrane surface and was observed by SEM. As shown in Figures 1A, the PVDF microfiltration support membrane has the effective pore size of 100 nm and high porosity. After the support membrane coated with PAA solution and subsequent reduction with $NaBH_4$, the membrane surface and pores are all covered with Fe/Pd nanoparticles (Figures 1B). Nanoparticles have the diameter of 30~50 nm. A SEM energy-dispersive spectrum (SEM-EDS) analysis of the Fe/Pd particles at membrane surface is also illustrated in Figure 1B. The gold peak is from the coating process. Qualitative analysis using EDS showed that Pd content in the Fe/Pd complex is 3 wt%.

To examine the Fe/Pd nanoparticles distribution inside the membrane matrix, TEM images of membrane cross-section were taken (Figure 2A). The TEM image confirms that nanoparticles were deposited the entire membrane thickness. The EDS analysis also confirmed that these nanoparticles are Fe/pd. In order to identify the element distribution of Fe and Pd at nano scale, EDS mapping was performed in STEM mode with Fe/Pd nanoparticles (Figure 2B). The mapping images clearly demonstrate that bimetallic Fe/Pd nanoparticles having a Fe-rich core and a Pd-rich shell. This is as expected because the Pd was reduced by Fe and deposited on the Fe surface.

Batch Reaction of DiCB with Fe/Pd

Figure 3 shows the dechlorination of 15 mg/L TeCB in 50/50 vol.% ethanol/water solution with Fe/Pd (Pd: 2.5 wt%) immobilized inside PAA/PVDF membrane matrix. As shown in the figure, ccomplete degradation of TeCB by Fe/Pd in PAA/PVDF membrane was achieved within 90 mins and biphenyl was the final product. All the intermediates are only found in the low concentration in the first 60 mins. We only quantify the major intermediates at this time. Other intermediates are only in trace level which are below the detection limit. The predominance of final product biphenyl indicates the dechlorination rate of the intermediate was much faster than that of the parent compound, TeCB.

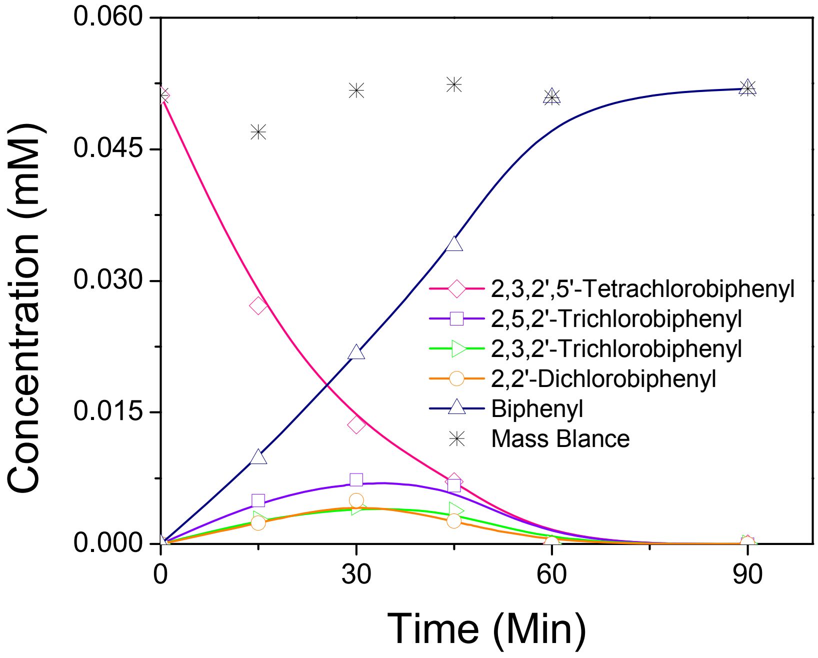

Figure 3. . Batch reaction of TeCB with nanoscale Fe/Pd (Pd = 2.5 wt%). Initial organic concentration was 15 mg/L. Metal particle loading was 16 mg/20 mL.

It is believed that the dechlorination of the TeCB occurs when it is adsorbed on the Fe/Pd surface [7]. In the bimetallic Fe/Pd system, iron serves primarily as the electron donor which provides hydrogen by the reduction of water (i.e., corrosion of iron, $Fe^0+H_2O=2Fe^{2+}+H_2+OH^-$), while the secondary metal Pd acts as a catalyst which has the ability to adsorb hydrogen into its lattice [7-9] and maintain high surface concentration of hydrogen. In the presence of the second catalytic metal Pd, TeCB was adsorbed and reductively dehalogenated on the bimetallic Fe/Pd surface by active hydrogen.

Conclusions

In summary, nanoscale Fe/Pd bimetallic particles were successfully immobilized inside the PAA/PVDF composite membrane matrix for the dechlorination of toxic organics. These nanoparticles had a quite narrow size distribution due to the presence of polymer stabilization. We demonstrate the element distribution of first and second metal in the nano domain and the core/shell structure of bimetallic nanoparticles. Complete degradation of TeCB by Fe/Pd in PAA/PVDF membrane was achieved after within 90 mins. Biphenyl was formed as the main dechlorination product. All the intermediates are only found in the low concentration in the first 60 mins.

Acknowledgements

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