

Enhanced catalytic degradation process of *o*-nitrochlorobenzene by palladium-catalyzed Fe⁰ particles

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Abstract: Over Pd/Fe bimetallic catalyst, *o*-nitrochlorobenzene (*o*-NCB), at a concentration of 20 mg/L in aqueous solutions, is rapidly converted to *o*-chloroaniline (*o*-CAN) first, and then quickly dechlorinated to aniline (AN) and Cl⁻, without other intermediate reaction products. The aminated and dechlorinated reactions are believed to take place on the surface site of the Pd/Fe. The *o*-NCB removal efficiency and the next dechlorination rate increase with an increase of bulk loading of palladium and catalysts addition due to the increase of both the surface loading of palladium and the total surface area. These results indicate that reduction, amination and dechlorination of *o*-NCB by palladium-catalyzed Fe⁰ particles, can be designed for remediation of contaminated groundwater.

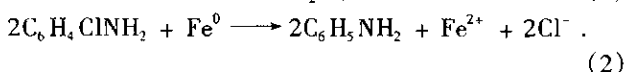
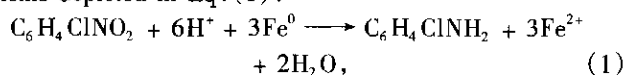
Keywords: palladium-catalyzed Fe⁰; amination; dechlorination; *o*-NCB

Introduction

o-Nitrochlorobenzene (*o*-NCB, C₆H₄ClNO₂) is a chemical intermediate used for the synthesis of various industrial chemicals, including explosives, pesticides, dyes/pigments, and engineering polymers. It is also used as a raw material for *o*-nitroaniline. By their nature, the above are highly toxic and poorly biodegradable compounds that are now established as a class of priority environmental pollutants by the US EPA (USEPA, 1988).

The use of zero valent iron (Fe⁰) for the treatment of contaminants in wastewaters and groundwaters has been the focus of much recent research. Researchers have studied different classes of compounds such as halogenated organics (Muftikian, 1995; Xu, 2003; 2004), azoaromatics (Weber, 1996), nitroaromatics (Scherer, 2001) and inorganics (Su, 2001). The majority of these studies are concerned with chlorinated organics, because they are widespread, mobile, and represent important environmental contaminants.

Chloronitrobenzenes are more difficult to dechlorinate than chlorinated aliphatic hydrocarbons. Research regarding reductive dechlorination with zero valent iron led to the discovery that a bimetallic preparation for iron and palladium was a superior reductant for chlorinated organics. Pd/Fe bimetal dramatically accelerated the reductive dechlorination (Liu, 2001; Xu, 2003; 2004). Laboratory research in the past few years has shown that Fe⁰ could degrade many chlorinated organic compounds, including some herbicides and pesticides. These reactions also have obvious commercial implications; therefore, it is important to investigate the factors that may affect the rate of dechlorination. Previous studies focused on monitoring the disappearance of chlorobenzenes in the presence of Fe⁰, and no detailed reaction kinetics has been reported. In this study, *o*-NCB was chosen as a model compound. The reduction of nitrochlorobenzene by Pd/Fe bimetal may occur via the scheme depicted in Eq. (1).



The purpose of this research was to identify the

parameters that might affect rates of *o*-NCB reduction (reduce to *o*-CAN) and then its dechlorination by Pd/Fe bimetallic catalysts, the toxicity will be reduced, and the biodegradability will be improved when the *o*-NCB is reduced to aniline.

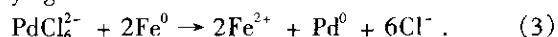
1 Experiments and methods

1.1 Chemicals

All chemicals used for the experiments were of AR grade. Potassium hexachloropalladate (99%, Aldrich, USA), *o*-NCB (>99%) and *o*-CAN (>98.5%), methanol (HPLC grade, >99.9%), iron powder reduced (>200 mesh, >98.0%), acetone, sulfuric acid (H₂SO₄) and other reagents were analytical grade. These reagents, except potassium hexachloropalladate, were purchased from Shanghai Chemical Reagents Company, China.

1.2 Pd/Fe catalyst preparation and characterization

Pd/Fe bimetallic catalysts were prepared in an anaerobic glovebox (under nitrogen gas). Iron powder was washed using 0.1 mol/L H₂SO₄, then acetone, and rinsed with distilled water so as to remove surface oxide layers and undesired organic compounds prior to palladization. An aqueous solution of potassium hexachloropalladate was added to a bottle containing iron powder; Pd/Fe bimetallic particles were then prepared following the reaction as indicated in Eq. (3). The solution in the bottle was continuously stirred until the dark orange solution turned to pale yellow. The deposition of palladium on the surface of iron particles resulted in a bimetallic surface (Pd/Fe). Then, the palladized iron was rinsed twice with deionized water and used for the reaction without drying.



Surface areas (BET area) of iron and palladized iron were measured by employing the nitrogen adsorption method with a ST-03 surface analyzer (Beijing, China). The morphology of the particles was obtained using a scanning electron microscope (SEM) (S-570 Hitachi, Japan) at 20 kV under a magnification of 20000.

1.3 Batch experimental procedures

The desired concentration of the *o*-NCB stock solution was adjusted using methanol as the solvent, and the solution was stored in a refrigerator at about 5°C. An *o*-NCB solution

of 50 mg/L was prepared by further dilution of the stock solution. Batch experiments for *o*-NCB dechlorination were conducted in 75 ml bottles. In most cases the bottles, containing 1–3 g Pd/Fe, were then filled with *o*-NCB solution, leaving no headspace, and were sealed immediately with butyl rubber septa. Each bottle was placed in an incubator shaker (200 r/min, $25 \pm 1^\circ\text{C}$). Aliquots of the samples were withdrawn at the indicated times from the supernatant using a syringe, and filtered through a piece of membrane filter with a pore size of $0.45 \mu\text{m}$ for subsequent analyses.

1.4 Analytical method

Organic compounds such as aniline, *o*-CAN, *o*-NCB, etc. were measured by Waters High Performance Liquid Chromatography with a column of Nova-Pak C18, $4 \mu\text{m}$, $3.9 \times 150 \text{ mm}$; mobile phase: MeOH/H₂O (80/20 v/v), flow rate: 1.0 ml/min; detector: UV at 254 nm; column temperature: 35°C ; sample volume: $20 \mu\text{l}$.

Chloride analysis was performed by ion chromatography (792 Basic IC, Metrohm) equipped with Metrosep A Supp4 column with a size of $4 \times 250 \text{ mm}$. Suppressed conductivity detector was applied. The flow rate of eluent (1.7 mmol/L NaHCO₃ + 1.8 mmol/L Na₂CO₃, with chemical suppression) was 1.0 ml/min. The sample volume is $20 \mu\text{l}$. Before being injected, sample solutions were always filtered through a $0.45 \mu\text{m}$ membrane filter.

2 Results and discussion

2.1 Reduction and dechlorination of *o*-NCB

Catalytic amination and dechlorination of *o*-NCB over Pd/Fe catalysts with 1 g and 5 g loading are shown in Fig. 1 and Fig. 2. *o*-NCB was first transformed to *o*-chloroaniline then quickly reduced to aniline. It seemed both *o*-NCB and chloroaniline were absorbed on the surface of Pd/Fe bimetal during dechlorination, so part of the *o*-NCB was reduced to chloroaniline and dechlorinated to aniline directly on the surface of Pd/Fe without returning to the solution. It can also be seen that no other intermediates or final products were generated besides chloroaniline and aniline. A typical catalytic amination and dechlorination process resulting from the batch tests are shown in Fig. 1. As seen from the figures, the aqueous concentration of the *o*-NCB declined rapidly and dropped below the detectable limit of the HPLC within 30 min at the Pd/Fe mass concentration of 5 g/75 ml with 0.02% Pd. Final reaction products in the solution were determined to be aniline and inorganic chloride.

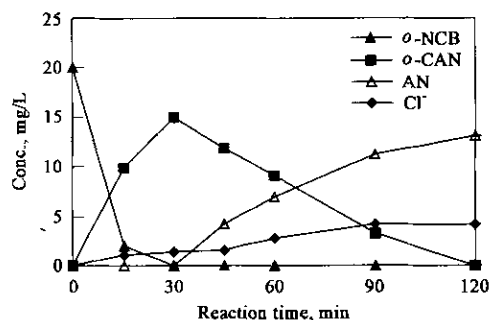


Fig. 1 Transformation plot of *o*-NCB over Pd/Fe catalysts as a function of time

$C_0 = 20 \text{ mg/L}$, Pd loading 0.020%, Pd/Fe powder 5 g/75 ml, $T = 25^\circ\text{C}$, pH = 6.5

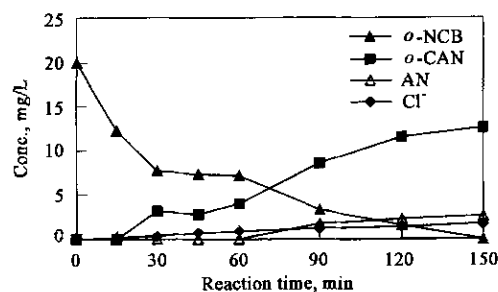


Fig. 2 Transformation plot of *o*-NCB over Pd/Fe catalysts as a function of time

$C_0 = 20 \text{ mg/L}$, Pd loading 0.020%, Pd/Fe powder 1 g/75 ml, $T = 25^\circ\text{C}$, pH = 6.5

2.2 Effects of experimental factors on transformation efficiency

2.2.1 Effects of the mass fraction of Pd in the bimetal

The variation of removal efficiency during the reaction period under different Pd mass fractions in the bimetal is presented in Fig. 3. With the increase of Pd loading, the removal efficiency of *o*-NCB increases as shown in Fig. 3a. The removal percentage of *o*-NCB reaches 78.2% in 15 min for particles with 0.03% Pd, and 100% *o*-NCB was removed in 30 min. In contrast, only 50.4% of removal efficiency is obtained in 15 min for particles with 0.01% Pd, and needs more than 90 min to remove all *o*-NCB. The presence of palladium on the surface of iron speeds up the reduction reaction dramatically as shown Fig. 3b. For particles with 0.01% Pd, also all *o*-NCB was removed after 90 min reaction, but no aniline was found at the end of reaction (at 150 min), the *o*-CAN reaches the maximum concentration at 150 min, so just the amination reaction occurred, and no dechlorination reaction happened. In contrast, the intermediate reaction product of *o*-CAN reaches the maximum attainable amount at 45 min for particles with above 0.02% Pd, and then rapidly reduced to the final

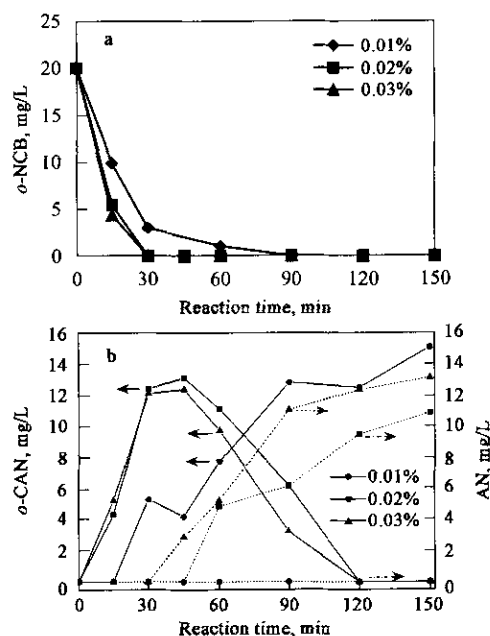


Fig. 3 Effect of Pd mass-fraction on the *o*-NCB removal efficiency

$C_0 = 20 \text{ mg/L}$, Pd loading 0.01%–0.03%, Pd/Fe powder 3 g/75 ml, $T = 25^\circ\text{C}$, pH = 6.5

reaction product, aniline (product of dechlorination), at the end of reaction, almost all *o*-CAN was reduced to aniline.

2.2.2 Effects of Pd/Fe mass concentration

Fig.4 shows the increase of *o*-NCB removal efficiency with reaction time at the selected Pd/Fe mass concentrations. At the Pd/Fe mass concentration of 1 g/75 ml, only 38.7% of *o*-NCB could be removed in 15 min. However, 72.69% and 90.05% of *o*-NCB were removed at the Pd/Fe mass concentrations of 3 g/75 ml and 5 g/75 ml respectively at the same reaction time, and 100% of *o*-NCB was removed in 30 min with 5 g /75 ml and 3 g/75 ml catalysts in Fig.4a. The intermediate reaction product of *o*-CAN reached the maximum concentration at 30 min at the Pd/Fe mass concentration of 5 g/75 ml, while 45 and 150 min for catalysts addition of 1 g/75 ml and 3 g/75 ml respectively. And 2.567, 10.89 and 13.27 mg/L aniline were found with 150 min at the Pd/Fe mass concentration of 1 g/75 ml, 3 g/75 ml and 5 g/75 ml, respectively, which also means that the dechlorination efficiency of *o*-NCB increased with the increase of Pd/Fe mass concentrations. It is believed that the reduction, and then dechlorination reaction, occurs on the Pd/Fe surface. As the Pd/Fe mass concentration increases, the reactive Fe

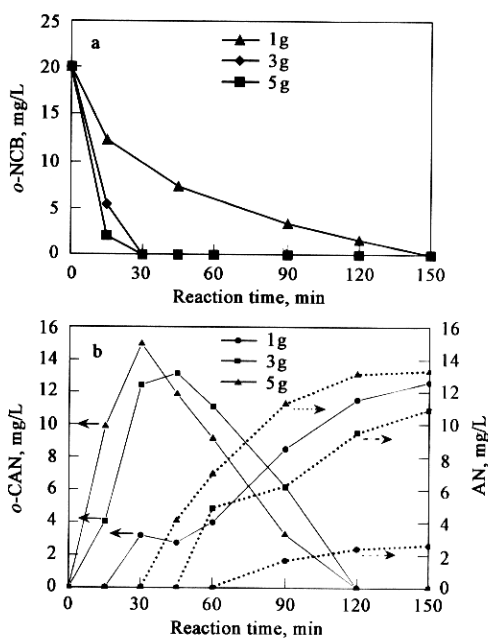
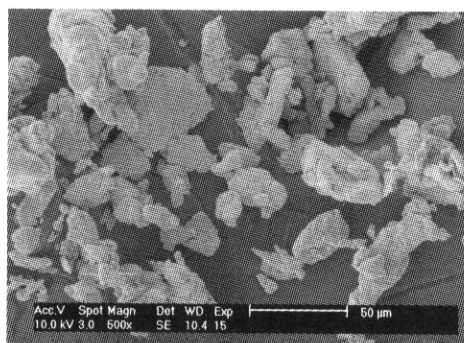
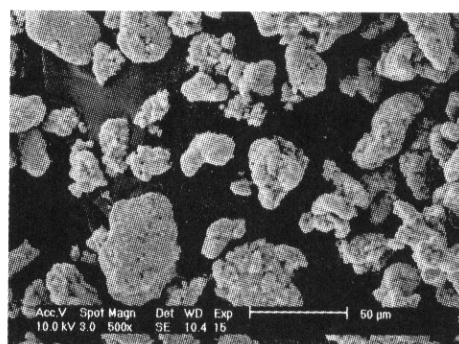


Fig.4 Effect of Pd/Fe additions on the *o*-NCB removal efficiency
 $C_0 = 20$ mg/L, Pd loading 0.020%, Pd/Fe powder 1–3 g/75 ml, $T = 25^\circ\text{C}$, $\text{pH} = 6.5$



a Before dechlorination



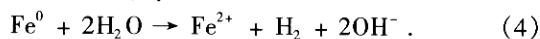
b After dechlorination

Fig.5 SEM images of Fe powers

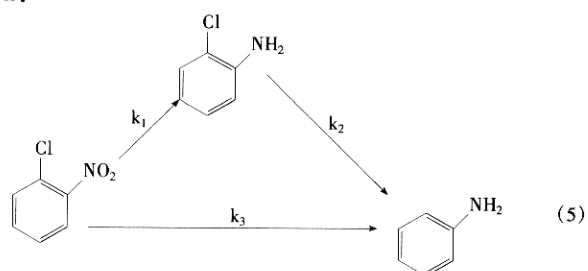
site concentration and adsorptive Pd site concentration increase simultaneously, which leads to the increase of reaction rate.

2.3 Reduction and dechlorination mechanism of *o*-NCB

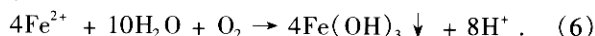
It is hypothesized that the reduction and dechlorination of *o*-NCB occurs when adsorbed on the surface of Pd/Fe. The Pd on the Fe surface acts as a collector of hydrogen gas produced by the reaction of Fe with water, i. e., the corrosion reaction of iron:



On the palladium surface, the produced hydrogen is dissociated into H atoms. The *o*-NCB adsorbed on the Pd/Fe surface is reductively dechlorinated through the following reaction:



The reaction products, chloroaniline, aniline and chloride ion, are released into the solution. The chlorine in *o*-NCB is substituted by hydrogen with the formation of aniline. The hydrogen atom is solely supplied by H_2O as proved by an experiment conducted in a D_2O solution (Liu, 2001). In the presence of dissolved oxygen under weak acidic or neutral conditions, the following reaction also occurs:



After reaction, surface passivated layers are formed due to the precipitation of metal hydroxides and metal carbonates on the surface of iron and Pd/Fe (Fig.5).

3 Conclusions

The Pd/Fe catalytic reductants showed prominent activity in the reductive dechlorination of *o*-NCB at ambient temperature and pressure. The reduction and dechlorination are believed to take place on the surface site of the catalyst following a pseudo-first-order reaction. The final reduced product for chloroaniline is aniline. The conversion rate depends on the reaction Pd loading and the addition of Pd/Fe, and so on. Chloroaniline represents stable partially reduction intermediates in the generation of aniline. The removal efficiency of *o*-NCB rate benefited from the increase

in bulk loading of palladium due to the increase of both the surface loading of palladium and the total surface area. The present finding can be valuable in designing *in situ* treatment of chlorobenzene contaminated groundwater and soil.

References:

- Burris D R, Campbell T J, Manoranjan V S, 1995. Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron-water system[J]. *Environ Sci Technol*, 29: 2850—2855.
- Keum Y S, Li Q X, 2004. Reduction of nitroaromatic pesticides with zero-valent iron[J]. *Chemosphere*, 54: 255—263.
- Liu Y H, Yang F L, Yue P L *et al.*, 2001. Catalytic dechlorination of chlorophenols in water by palladium/iron[J]. *Water Res*, 35: 1887—1890.
- Muftikian R, Fernando Q, Korte N, 1995. A method for the rapid dechlorination of low molecular weight chlorinated hydrocarbons in water[J]. *Water Res*, 29: 2434—2439.
- Scherer M M, Johnson K M, Westall J C, 2001. Mass transport effects on the kinetics of nitrobenzene reduction by iron metal[J]. *Environ Sci Technol*, 35: 2804—2811.
- Schultz C A, Grundl T J, 2000. pH dependence on reduction rate of 4-Cl-nitrobenzene by Fe(II)/montmorillonite systems[J]. *Environ Sci Technol*, 34: 3641—3648.
- Shin E J, Keane M A, 1999. Detoxification of dichlorophenols by catalytic hydrodechlorination using a nickel/silica catalyst[J]. *Chem Eng Sci*, 54: 1109—1120.
- Su C, Puls R W, 2001. Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride[J]. *Environ Sci Technol*, 35: 4562—4568.
- USEPA (US Environmental Protection Agency), 1988. National pollutant discharge elimination system[S]. Code of Federal Regulations, 40, Part 122. US Government Printing Office, Washington, DC.
- Weber E J, 1996. Iron-mediated reductive transformations: investigation of reaction mechanism[J]. *Environ Sci Technol*, 30: 716—719.
- Xu X H, Zhou H Y, Wang D H, 2003. Catalytic dechlorination of chlorobenzene in water by Pd/Fe system[J]. *Chin Chem Lett*, 14: 700—703.
- Xu X H, Liu Y, Wei J J *et al.*, 2004. Catalytic dechlorination and influencing factors of 2,4-DCP by nanoscale Pd/Fe bimetallic system[J]. *Chin J Catal*, 25: 138—142.

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