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Structure relationship for catalytic dechlorination rate of dichlorobenzenes in water

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Abstract

Three isomers of dichlorobenzene (*o*-, *m*- and *p*-DCB) were dechlorinated by Pd/Fe catalyst in aqueous solutions through catalytic reduction. The dechlorination reaction took place on the surface site of the catalyst via a pseudo-first-order kinetics, and resulted in benzene as the final reduction product. The rate constants of the reductive dechlorination for the three dichlorobenzenes (DCBs) in the presence of Pd/Fe as a catalyst were measured experimentally. In all cases, the reaction rate constants were found to increase with the decrease in the Gibbs free energy of the formation of DCBs. The reaction rate constant for *o*-, *m*- and *p*-DCBs in the presence of 0.020% (w/w) Pd/Fe at 25 °C was determined to be 0.0213, 0.0223, and 0.0254 min^{-1}, respectively. While the activation energy of each dechlorination reaction was measured to be 102.5, 96.6 and 80.0 kJ mol^{-1} for *o*-, *m*- and *p*-DCBs, respectively. The results demonstrated that *p*-DCBs were reduced more easily than *o*- or *m*-DCBs, and the order of the tendency of the dechlorination was *p*-DCB > *m*-DCB > *o*-DCB. The presented data show the catalytic reduction using Pd/Fe as a catalyst is a fast and easy approach for the dechlorination of DCBs.

Keywords: Pd/Fe; Dechlorination; Structure; DCBs

1. Introduction

Chlorobenzenes are so widely used that they are nearly ubiquitous in all major environmental compartments. For example, chlorobenzenes have a wide range of industrial and domestic uses, such as intermediates in the synthesis of other chemicals, solvents, hygiene products, and components of dielectric fluids (Meharg et al., 2000). They are hazardous pollutants contained in various waste oils and other organic liquids. By their nature, they are highly toxic and poorly biodegradable compounds that are now established as a class of priority environmental pollutants by the US EPA (1988). There is a definite need for efficient methods of dechlorination that are suitable for eliminating chlorobenzenes from both concentrated industrial effluents and diluted polluted groundwater (Meharg et al., 2000).

Recently, chemical reduction of hazardous compounds such as chlorinated organic compounds (COCs) and nitroaromatic compounds (NACs) using zero-valent metals has been intensively studied for either in situ or aboveground treatment of contaminated water. For instance, the use of zero-valent iron for the treatment of

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contaminants in wastewaters and ground waters has been the focus of much recent research. Iron has successfully utilized in the treatment of chlorinated organic solutions. Zero-valent iron was found to serve as a donor of electrons (or the reducing agent) in the reaction (Matheson and Tratnyek, 1994). Zero-valent iron also reacts with water producing hydrogen gas (which can react with COCs) and hydroxide ions (which lead to the increase of the pH of the water solutions). The treatment of COCs by zero-valent iron represents one of the latest innovative technologies for environmental remediation. A passive remediation technology involving zero-valent iron as the reactive material in subsurface barriers was developed (Gillham and O'Hannesin, 1994a,b). In another study, Orth and Gillham (1996) proposed basic mechanisms of the reductive transformation of COCs by metallic iron. Recently, it was also found that the addition of palladium as a catalyst can speed up the dechlorination. The dechlorination reaction between Pd/Fe and small molecule hydrocarbons was found to be fast enough for treating wastewater in situ (Rosy et al., 1995). The catalytic dechlorination reaction in the presence of Pd/Fe was also reported for other classes of compounds, these include halogenated organics (Muftikian et al., 1995; Arnold and Roberts, 2000; Farrell et al., 2000; Kim and Carraway, 2000; Xu and Zhang, 2000; Dombek et al., 2001; Liu et al., 2001; Xu et al., 2003), azoaromatics (Weber, 1996; Nam and Tratnyek, 2001), nitroaromatics (Mantha et al., 2001; Scherer et al., 2001) and inorganics (Melitas et al., 2001). Most of these studies were concerned with chlorinated organics, as chlorinated organics are widespread and mobile, and they represent important environmental contaminants.

In the present work, we report the experimental determination of first-order rate constants (k) for the catalytic dechlorination of three isomers of dichlorobenzene (namely *o*-, *m*- and *p*-DCBs) in the presence of a zero-valent bimetallic Pd/Fe catalyst, and their reaction activation energies. The structure relationship for the catalytic dechlorination of three dichlorobenzenes in water is discussed. Thus it is the purpose of this study to identify further molecular structural characteristics and their corresponding structural descriptors relevant to dechlorination of chlorobenzenes by Pd/Fe bimetal.

2. Experiments and methods

2.1. Chemicals

Potassium hexachloropalladate (99%, Aldrich, USA), *o*-DCB, *m*-DCB and *p*-DCB (>98.5%), chlorobenzene (>98.5%), methanol (reagent for HPLC, >99.9%), iron powder reduced (>200 mesh, >98.0%), benzene, acetone, sulfuric acid (H_2SO_4) and other reagents are analytical grade.

2.2. Pd/Fe preparation and characterization

Pd/Fe powders were prepared in an anaerobic glovebox (under nitrogen gas). Prior to palladization, iron powders were pretreated by washing using 0.1 M H_2SO_4 then acetone and rinsed with distilled water in order to remove the lower Fe-layers and undesired organic compounds. An aqueous solution of potassium hexachloropalladate was added to a bottle containing iron powders. 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 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 observed by XL30ESEM (Philips, Netherlands) scanning electron microscopy (SEM).

2.3. Batch experimental procedures

The stock solutions of DCBs with desired concentrations were prepared using methanol as the solvent, and stored in a refrigerator at about 4 °C. Individual (*o*-, *m*- and *p*-) DCB solution of 50 mg l^{-1} was prepared by pipetting the corresponding stock solution and using water as the solvent. Batch experiments for DCBs dechlorination were carried out in 75-ml bottles. In most cases, the bottles containing 4 g Pd/Fe were then filled with DCBs solutions, leaving no headspace, and sealed immediately with butyl rubber septa. Each bottle was placed in an incubator shaker (200 rpm, 25 ± 1 °C). Aliquots of samples were withdrawn at times from the supernatant using a syringe, and filtered with a piece of 0.45 μm filter film for later-on analysis.

2.4. Analytical method

The organic compounds such as benzene, chlorobenzene, DCBs, etc. were measured by HPLC. Analysis parameters were as follows: Instrument: Waters High Performance Liquid Chromatography. Column: Nova-Pak C18, 4 μm, 3.9 × 150 mm, Mobile phase: MeOH/H_2O (80/20). Flow rate: 1.0 ml min^{-1}. Detector: UV at 254 nm. Column temperature: 35 °C. Sample size: 20 μl.

Chloride analysis was performed by ion chromatography (792 Basic IC, Metrohm). Column: Metrosep A Supp4, Column size: 4 × 250 mm. Analysis condition: Eluent: 1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3 (with chemical suppression), Sample size: 20 μl, Flow rate:

1.0 ml min^{-1}, Detector: suppressed conductivity detector. Before injected, sample solutions were always filtered through a 0.45 μm membrane filter.

Each dechlorination efficiency of DCBs was calculated using the ratio between free chloride measured experimentally and free chloride calculated theoretically by the complete dechlorination of DCBs.

3. Results and discussion

3.1. Characterization of Pd/Fe

The surface morphology of Pd/Fe was shown in Fig. 1. The surface of Pd/Fe became much rough with palladium deposited on the iron surface. BET specific surface area of the Pd/Fe particles was 0.62 $m^2\ g^{-1}$. In comparison, the fine iron powder, which is commercially available, has a specific surface area of about 0.49 $m^2\ g^{-1}$. The increased surface area indicated that the Pd was dispersed on the surface rather than clustered, which was consistent with the information revealed in the SEM image of the Pd/Fe catalyst.

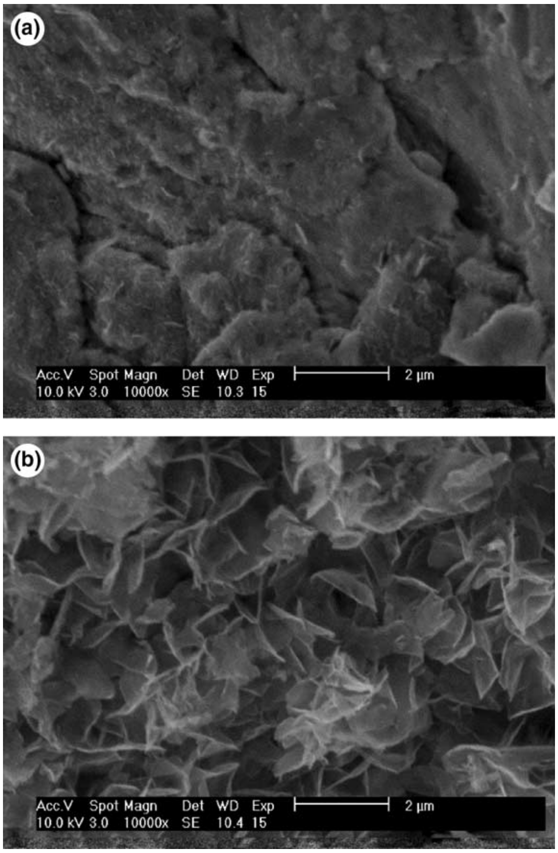


Fig. 1. SEM images of Pd/Fe bimetallic powders: (a) before dechlorination; (b) after dechlorination.

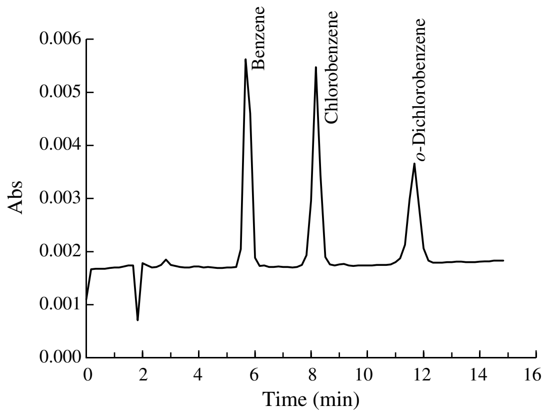


Fig. 2. HPLC chromatograms of the reaction mixture during reaction.

3.2. Dechlorination of DCBs

Fig. 2 illustrates the HPLC chromatograms during the dechlorination of *o*-DCB. *o*-DCB is first transformed to chlorobenzene then reduced to benzene quickly, because *o*-DCB or chlorobenzene was absorbed on the surface of Pd/Fe bimetal during the dechlorination, some *o*-DCB is reduced to chlorobenzene and dechlorinated to benzene directly on the surface of Pd/Fe and did not return to the solution. The reduction products for *m*- and *p*-DCB were also chlorobenzene and benzene.

A typical concentration profile resulting from the batch tests was shown in Fig. 3. As seen from the figure, the aqueous concentration of the *o*-DCB declined rapidly and dropped below detectable limits within 60 min. Final reaction products in the solution were determined to be benzene and inorganic chloride. In the solution, little chlorobenzene was identified and remained

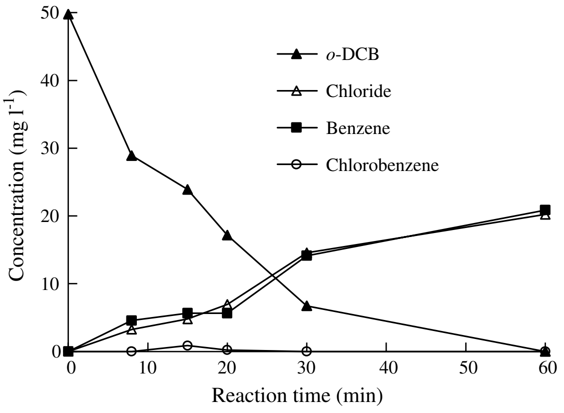
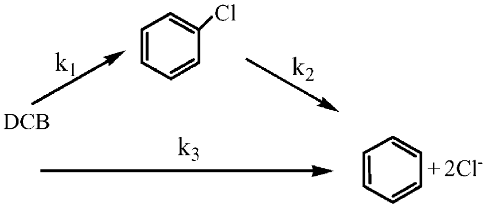


Fig. 3. Transformation of *o*-dichlorobenzene over Pd/Fe catalysts, $C_0 = 50$ mg l^{-1}, Pd loading 0.020%, Pd/Fe powder 4 g 75 ml^{-1}, $T = 25$ °C, pH = 6.5.

lower concentration throughout the experiment. The chloride formation detected was only 84.0% of the maximum attainable when all *o*-DCB and chlorobenzene were removed. It was most likely that *o*-DCB and chlorobenzene could be absorbed or covered by surface passivating layers due to the precipitation of metal hydroxides and metal carbonates on the surface of iron and Pd/Fe (see Fig. 1(b)), in fact, chloride ion also can be covered or absorbed, so the dechlorination efficiency was commonly less than 100% in all reactions under study, but *o*-DCB could be removed 100%. Our results were in very good agreement with previous findings (Burris et al., 1995). The dechlorinations of *m*- and *p*-DCB also show the same results as *o*-DCB.

3.3. Catalytic reduction rate constants

In these dechlorination reactions, most DCBs are first transformed to chlorobenzene then reduced to benzene quickly, while a small amount of DCBs are reduced to benzene directly. The reaction pathway for the conversion of DCBs by Pd/Fe bimetal is illustrated as follows:



(1)

The dechlorination rate of DCBs by Pd/Fe in a batch system can be determined by the following equation:

$$\ln\left(1-\frac{C_{\mathrm{Cl}^-}}{2C_{\mathrm{DCB0}}}\right) = -k_{\mathrm{obs}}t \tag{2}$$

where Cl^- is the concentration of chloride ion generated in the aqueous phase (mM); C_{DCB0} is the concentration of DCBs, and k_{obs} is the observed first-order reaction rate constant (min^{-1}).

The dependence of the reaction rate constant on the structure of the substrates is not surprising. Dolfing and Harrison (1992) have shown that the rate constant for the reduction of halogenated aromatics in anaerobic estuarine sediment was proportional to the Gibbs free energy or the activation energy of formation E_a. E_a is one of the physical chemical parameters of compounds that reveals the difference in molecular structures.

The integrated form of the proposed pseudo-first-order kinetic equation was

$$\ln k = A - \frac{E_a}{RT} \tag{3}$$

where E_a is the activation energy (kJ mol^{-1}), A the pre-exponential factor, k the observed pseudo-first-order reaction rate constant (min^{-1}), R the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the reaction temperature (K).

The effect of reaction temperature on the effectiveness of the dechlorination efficiency was studied by varying the reaction temperature from 287 to 313 K. By rearranging the experiment data at 25 °C shown in Fig. 3, a linear decrease of $\ln(C_{o\text{-DCB}}/C_{o\text{-DCB0}})$ with time is obtained as shown in Fig. 4. This linear relationship reveals a pseudo-first-order reduction reaction regarding the dechlorination efficiency. As a result, the reaction rate constants (k) were determined to be 0.0016, 0.0213, 0.0315, 0.0350 and 0.0651 min^{-1}, respectively, with a reaction temperature of 14, 25, 30, 35 and 40 °C (Fig. 4).

The reaction rate constants (k) of *m*-DCB and *p*-DCB at difference temperatures also can be determined from Fig. 5 as 0.0033, 0.0223, 0.0347, 0.0380 and 0.0789 min^{-1}, respectively, with the temperature 17, 25, 30, 35 and 40 °C for *m*-DCB, and 0.0045, 0.0254, 0.0355, 0.0473 and as 0.0690 min^{-1}, respectively, with the temperature 15, 25, 30, 35 and 40 °C for *p*-DCB.

The results are plotted in Figs. 4 and 5. As seen in figures, an increase in the reaction temperature can enhance the reaction rates significantly. The k values calculated at various temperatures were correlated by Eqs. (4)–(6) and shown in Fig. 6, which gives rise to an estimated activation energy of 102.5, 96.6 and 80.0 kJ mol^{-1}, respectively, for *o*-, *m*- and *p*-DCB:

$$\ln k = 36.92 - \frac{12333}{T} \tag{4}$$

$$\ln k = 34.685 - \frac{11616}{T} \tag{5}$$

$$\ln k = 28.26 - \frac{9627.5}{T} \tag{6}$$

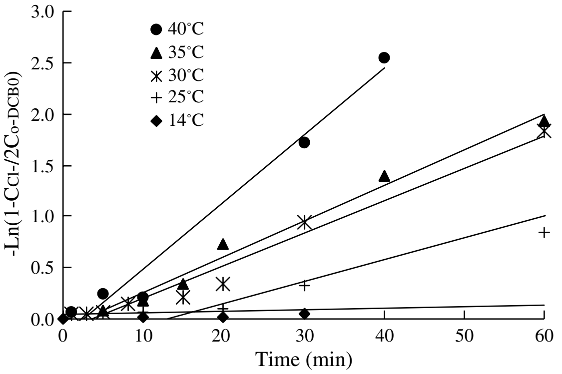


Fig. 4. Linear decrease of normalized dechlorination efficiency (ln) with the reaction time under different temperatures for *o*-dichlorobenzene, $C_0 = 50$ mg l^{-1}, Pd loading 0.020%, Pd/Fe powder 4 g 75 ml^{-1}, pH = 6.5.

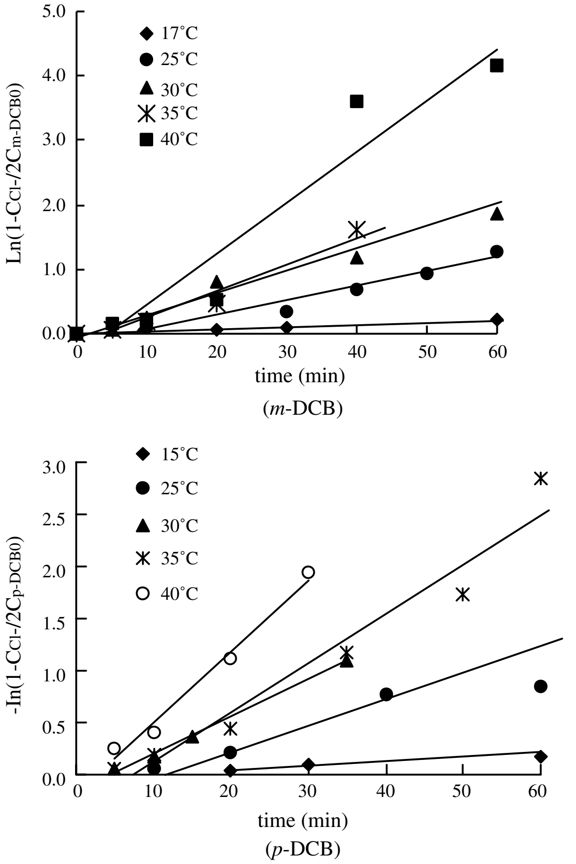


Fig. 5. Linear decrease of normalized dechlorination efficiency (ln) with the reaction time under different temperatures for *m*-dichlorobenzene and *p*-dichlorobenzene, $C_0 = 50$ mg l^{-1}, Pd loading 0.020%, Pd/Fe powder 4 g 75 ml^{-1}, pH = 6.5.

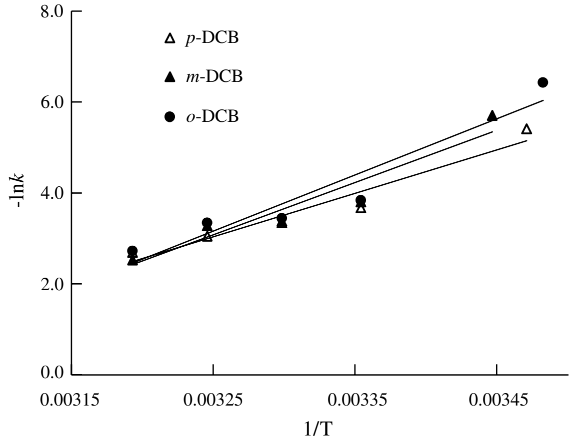


Fig. 6. Correlation for reaction rate constant *k* with reaction temperature for three isomers of dichlorobenzene.

The results revealed higher chlorine-substituted homologues were reduced more easily than lower-substituted congener and the tendency of rate constant follows *p*-DCB > *m*-DCB > *o*-DCB.

4. Conclusions

The reductive dechlorination of DCBs in the presence of Pd/Fe is found to be a pseudo-first-order reaction, and occurs primarily at the catalyst surface. The reaction rate constant increases with the decrease in the Gibbs free energy of the formation of DCBs, with the rate constant being 0.0213, 0.0223 and 0.0254 min^{-1}, respectively, for *o*-, *m*- and *p*-DCBs with 0.020% Pd/Fe at 25 °C. The activation energy of the reaction was determined to be 102.5 kJ mol^{-1} for *o*-dichlorobenzene, 96.6 kJ mol^{-1} for *m*-dichlorobenzene and 80.0 kJ mol^{-1} for *p*-dichlorobenzene. Molecular structural descriptors that are significantly relevant to log*k* and the activation energy include the descriptors describing the overall character of the molecules and the descriptors describing the nature of the chlorine atoms. Our results show *p*-DCBs were reduced more easily than *o*- and *m*-DCBs, and the rate constant of the dechlorination for each DCB was *p*-DCB > *m*-DCB > *o*-DCB. Pd/Fe catalytic reduction provides a fast and easy means for the dechlorination of all three DCBs. The present finding can be valuable in designing in situ treatment of dichlorobenzenes contaminated water.

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