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Structure relationship of nitrochlorobenzene catalytic degradation process in water over palladium-iron bimetallic catalyst^{*}

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Abstract: Two isomers of nitrochlorobenzene (*o*-, and *p*-NCB) were treated by a Pd/Fe catalyst in aqueous solutions through catalytic amination and dechlorination. Nitrochlorobenzenes are rapidly converted to form chloroanilines (CAN) first through an amination process, and then rapidly dechlorinated to become aniline (AN) and Cl⁻, without the involvement of any other intermediate reaction products. The amination and dechlorination reaction are believed to take place predominantly on the surface site of the Pd/Fe catalysts. The dechlorination rate of the reductive degradation of the two isomers of nitrochlorobenzene (*o*-, and *p*-NCB) in the presence of Pd/Fe as a catalyst was measured experimentally. In all cases, the reaction rate constants were found to increase with the decrease in the Gibbs free energy (correlation with the activation energy) of NCBs formation; the activation energy of each dechlorination reaction was measured to be 95.83 and 77.05 kJ/mol, respectively for *o*- and *p*-NCB. The results demonstrated that *p*-NCBs were reduced more easily than *o*-NCBs.

Key words: Pd/Fe, Catalytic degradation, Structure, NCBs

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INTRODUCTION

Nitrochlorobenzenes (C₆H₄ClNO₂) or NCBs are chemical intermediates used for the synthesis of various industrial chemicals, including explosives, pesticides, dyes/pigments, and engineering polymers and are also used as raw materials in the manufacturing of nitroaniline. By their nature, NCBs are highly toxic and poorly biodegradable compounds that have long been established as a class of priority environmental pollutants by the US EPA (US EPA, 1988).

The use of zero valent iron (Fe⁰) for treating contaminants in waste and groundwater has been the

focus of much recent research. Researchers have studied different classes of compounds such as halogenated organics (Muftikian *et al.*, 1995; Arnold and Roberts, 2000; He and Zhao, 2005), azoaromatics (Weber, 1996), nitroaromatics (Scherer *et al.*, 2001) and inorganics (Su and Puls, 2001). Nitrochlorobenzenes are generally more difficult to be dechlorinated than chlorinated aliphatic hydrocarbons. Research regarding reductive dechlorination with zero valent iron led to the discovery that a bimetallic composite consisting of both iron and palladium was a superior reductant for chlorinated organics. Pd/Fe bimetal dramatically accelerated the reductive dechlorination (Liu *et al.*, 2001; Xu *et al.*, 2003; 2004). In this study, two isomers of NCBs (*o*-, and *p*-NCB) were chosen as model compounds, the structure relationship of the catalytic degradation of two nitrochlorobenzenes in water is discussed. This study is aimed at further

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identifying molecular structure characteristics and their corresponding structural descriptors relevant to the degradation of nitrochlorobenzenes by Pd/Fe bimetal catalyst.

MATERIALS AND METHODS

Materials

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

Pd/Fe powders were prepared in an anaerobic glovebox (under nitrogen gas). Prior to palladization, iron powders were pretreated by washing using 0.1 mol/L H₂SO₄ then acetone, followed by rinsing with copious amount of 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.

Batch experiments

In order to prepare solutions with different concentrations ranging from 20~50 mg/L NCBs in water, we first dissolved them in methanol due to their poor solubility in water. The desired concentration of the NCBs stock solution was adjusted using methanol as the solvent (NCBs concentration, 1000 mg/L), and the solution was stored in a refrigerator at about 5 °C. An NCB solution of 20~50 mg/L was prepared by further dilution of the stock solution using deionized water before batch experiment. Batch experiments for NCB dechlorination were conducted in 75-ml bottles. In most cases, the bottles containing 1~3 g Pd/Fe particles were then filled with NCBs solution, leaving no headspace, and sealed immediately with butyl

rubber septa. Each bottle was placed in an incubator shaker (200 r/min, (25±1) °C). Aliquots of the samples were withdrawn at times from the supernatant using a syringe, then filtered through a piece of membrane filter with pore size of 0.45 µm for subsequent analyses.

Analytical method

Organic compounds such as NCBs, CANs and AN, etc. were measured by HPLC. Analysis parameters were as follows: instrument: waters high performance liquid chromatography; column: Nova-Pak C18, 4 µm, 3.9 mm×150 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 size: 20 µl.

Chloride analysis was performed by ion chromatography (792 Basic IC, Metrohm). Column: Metrosep A Supp4, Column size: 4 mm×250 mm. Analysis condition: eluent: 1.7 mmol/L NaHCO₃+1.8 mmol/L Na₂CO₃ (with chemical suppression), sample size: 20 µl, flow rate: 1.0 ml/min, detector: suppressed conductivity detector.

RESULTS AND DISCUSSION

Catalytic amination and dechlorination of NCBs

The catalytic amination and dechlorination of *p*-NCB in the presence of Pd/Fe catalysts is shown in Fig.1. NCB was first transformed into chloroaniline then rapidly reduced to aniline. It seemed both NCB and chloroaniline were absorbed on the surface of Pd/Fe bimetal during the dechlorination, so part of the NCB was reduced to chloroaniline and dechlorinated to aniline directly on the Pd/Fe surface without returning to the solution. As also seen from Fig.1, the aqueous concentration of the *p*-NCB decreased rapidly and dropped below the detectable limit within 30 min at Pd/Fe mass concentration of 3 g/(75 ml) with 0.03% Pd. Final reaction products in the solution were determined to be aniline and inorganic chloride. In the solution, minimal chloroaniline was identified and remained at low concentration during the experiment. Ninety percent of Cl⁻ was observed in the end. It was possible that all *p*-NCB, chloroaniline and aniline were 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 particles. It was shown previously that chloride ion could also be covered or absorbed, so the dechlorination efficiency was commonly less than 100%, but *p*-NCB and *p*-CAN could be removed completely in short reaction time (Burris *et al.*, 1995).

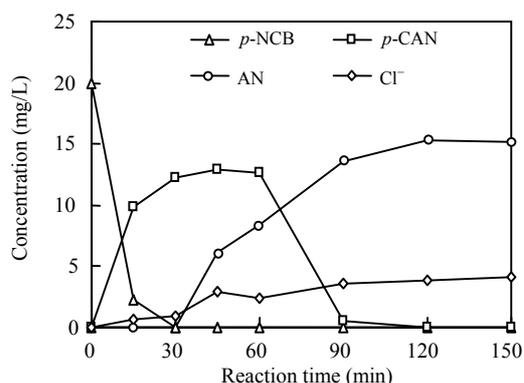
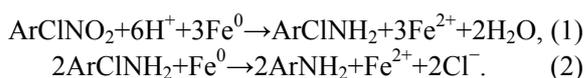


Fig.1 Transformation plot of *p*-NCB over Pd/Fe catalysts as a function of time. $C_0=20$ mg/L, Pd loading 0.03%, Pd/Fe powder 3 g/(75 ml), $T=25$ °C, pH=6.5

Structure relationship of catalytic degradation process

In catalytic degradation process, most NCBs are first transformed into CAN then reduced rapidly to AN, while a small amount of NCBs are reduced to AN directly. The reaction pathway for the conversion of NCBs by Pd/Fe bimetal is as follows:



The dependence of the reaction rate constant on the structure of the substrates is not surprising. Dolfing and Harrison (1992) showed 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 E_a formation, where E_a is one of the physical chemical parameters of compounds differing in molecular structures.

The catalytic degradation process of *o*- and *p*-nitrochlorobenzene during the same reaction period is presented in Fig.2. The results demonstrated that *p*-NCBs were reduced more easily than *o*-NCBs, especially for the dechlorination reaction of intermediate reaction product CAN. The removal percentage

of *p*-NCB reached 78.84% in 15 min for particles with 0.02% Pd and 3 g/(75 ml) catalyst additions, while 72.69% of removal efficiency was obtained for *o*-NCB. The structure relationship is more clear through the detailed analysis of intermediate reaction products, the *p*-CAN reached maximum concentration at 15 min, and then rapidly reduced to the final reaction product, aniline (product of dechlorination), at the end of reaction, when almost all *p*-CAN was reduced to aniline. The yield of intermediate reaction products *p*-CAN remained less than 50.0% (maximum concentration 8.099 mg/L). In contrast, *o*-CAN concentration maximized at 45 min; the degradation reaction appeared to be much slower than that of *p*-NCB, the dechlorination process of *o*-CAN was also slower than that of *p*-CAN, in which the yield of intermediate reaction products *o*-CAN remained at 81.2% (maximum concentration 13.14 mg/L), and then slowly reduced to the final reaction product, aniline (product of dechlorination).

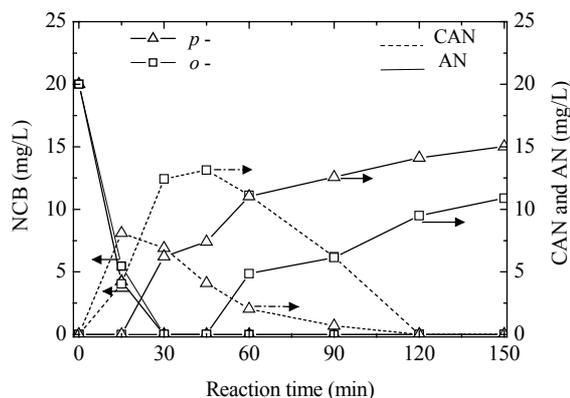


Fig.2 Structure relationship of catalytic degradation process of *o*- and *p*-nitrochlorobenzene by Pd/Fe system. $C_0=20$ mg/L, Pd loading 0.02%, Pd/Fe powder 3 g/(75 ml), $T=25$ °C, pH=6.5

With increase of Pd loading, the removal efficiency of *p*-NCB increased correspondingly, and *p*-NCBs were also reduced more easily than *o*-NCBs during the increase of Pd loading. The catalytic degradation process of *o*- and *p*-nitrochlorobenzene for particles with 0.03% Pd and 3 g/(75 ml) catalyst additions is presented in Fig.3. The removal percentage of *p*-NCB reached 88.76% in 15 min. In contrast, only 78.2% of removal efficiency was obtained for *o*-NCB.

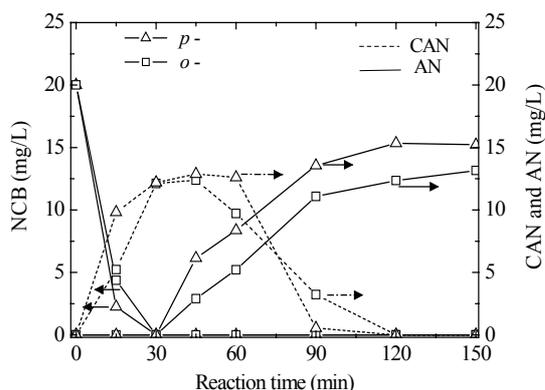


Fig.3 Structure relationship of catalytic degradation process of *o*- and *p*-nitrochlorobenzene by Pd/Fe system. $C_0=20$ mg/L, Pd loading 0.03%, Pd/Fe powder 3 g/(75 ml), $T=25$ °C, pH=6.5

Catalytic dechlorination rate constants

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

$$\ln\left(1 - \frac{C_{Cl^-}}{C_{NCB_0}}\right) = -k_{obs}t, \quad (3)$$

where C_{Cl^-} is the concentration of chloride ion generated in the aqueous phase (mmol/L); C_{NCB_0} is the initial concentration of NCBs, and k_{obs} is the observed first-order reaction rate constant (min^{-1}). 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 is:

$$\ln k = A - E_a/RT, \quad (4)$$

where E_a is the activation energy (kJ/mol), 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·K)), 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 293 to 313 K. As a result, the reaction rate constants (k) were determined to be 0.0009, 0.0030, 0.0045, and 0.0067 min^{-1} , respectively, with a reaction temperature of 20, 30, 35 and 40 °C for *p*-NCB, and 0.0005, 0.0021,

0.0036, and 0.0061 min^{-1} , respectively, with the same four temperatures for *o*-NCB. Increase in the reaction temperature can enhance the reaction rates significantly. The k values calculated at various temperatures were correlated by Eq.(4) and shown in Fig.4, which gives rise to an estimated activation energy of 95.83 and 77.05 kJ/mol, respectively for *o*- and *p*-NCB; the results demonstrated that the rate constant is in the order *p*-NCB > *o*-NCB.

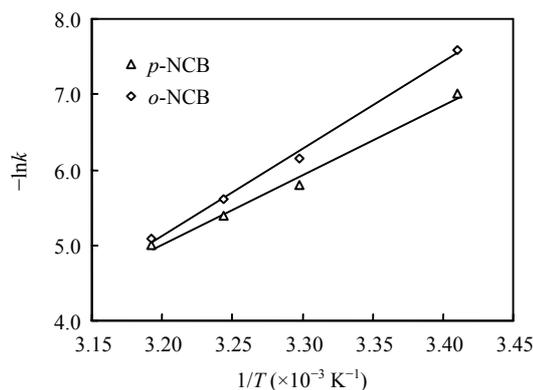
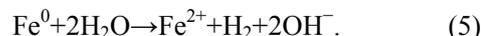


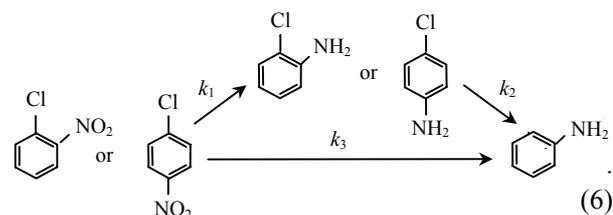
Fig.4 Correlation of reaction rate constant k with reaction temperature for two isomers of NCBs. $C_0=20$ mg/L, Pd loading 0.02%, Pd/Fe powder 3 g/(75 ml), pH 6.5

Catalytic reduction and dechlorination mechanism of NCBs

It is hypothesized that the reduction and dechlorination of NCBs occurs when they are adsorbed on the surface of Pd/Fe particles. 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 adsorbed hydrogen is dissociated into H atoms. The NCBs adsorbed on the Pd/Fe surface are reductively dechlorinated through the following reactions:



In all cases, the reaction rate constants were found to increase with the decrease in the Gibbs free energy of NCBs formation, so the catalytic degradation process of *p*-NCBs was much faster than that of *o*-NCBs.

CONCLUSION

Our experimental results suggest that Pd/Fe catalytic reductants showed prominent activity in removing *o*- and *p*-NCB and their intermediate reaction products (i.e. *o*- and *p*-CAN) at ambient conditions, after reductive amination and subsequent dechlorination reactions. As a result, the toxicity of these pollutants are greatly reduced and the biodegradability is improved when the NCBs are reduced to aniline. The reaction rate constant increases with the decrease in the Gibbs free energy (correlating to the activation energy) of NCBs formation. Molecular structure descriptors that are significantly relevant to $\ln k$ and the activation energy include the descriptors describing the overall character of the molecules, and the descriptors describing the nature of the chlorine atoms, NO₂-(nitryl) or NH₂-(amidocyanogen). Our results show *p*-NCBs are reduced more easily than *o*-NCBs, the same results were also found for intermediate reaction products *p*-CAN and *o*-CAN. The present finding can be valuable for designing in situ treatment of nitrochlorobenzenes-contaminated water.

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