

## Catalytic Dechlorination of Chlorobenzene in Water by Pd/Fe System

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**Abstract:** Chlorobenzene was dechlorinated by Pd/Fe bimetallic system in water through catalytic reduction. The dechlorination rate increases with increase of bulk loading of Pd due to the increase of both the surface loading of the Pd and the total surface area. For conditions with 0.005% Pd/Fe, 45% dechlorination efficiency was achieved within 5 h. The dechlorinated reaction is believed to take place on the bimetal surface in a pseudo-first-order reaction, with the rate constant being  $0.0043 \text{ min}^{-1}$ .

**Keywords:** Reductive dechlorination, catalytic, Pd/Fe, chlorobenzene.

Chlorinated organic compounds have been used on a large scale in the chemical and petrochemical industries. They are carcinogenic and stable, and also very difficult to be treated by biodegradation. Incinerating is feasible, but leads to the release of even more toxic compounds, also cannot always be destroyed by advanced oxidation processes<sup>1</sup>. Chlorinated organic compounds can be adsorbed by macromolecule resin, but cannot be decomposed, need to be desorbed and treated by other method<sup>2</sup>. Reductive dechlorination method promoted by zero-valent metals has been a very active research area since Gillham<sup>3</sup>. Iron can be used in this capacity in field tests, which has recently been used to rapidly dechlorinate organic compounds of wide range, including trichloroethene (TCE), perchloroethene (PCE), polychlorinated biphenyls (PCBs), *etc.* Ni, Zn, Mg also can be used as catalysts for dechlorination, but often leads to secondary pollution<sup>4-5</sup>. Reduction of nitro aromatic compounds and aromatic azo compounds by iron has also been reported<sup>6-11</sup>. Recently, it has been found that the addition of Pd as a catalyst can speed up the dechlorination. The dechlorination reaction between Pd/Fe and low-molecule hydrocarbons was found to be so fast that it is suitable for treating wastewater<sup>12-14</sup>.

### Experimental

Palladium/iron (Pd/Fe) powder was prepared by wet impregnation of the iron powder with an aqueous solution of potassium hexachloropalladate. The iron powder was washed with 0.1mol/L H<sub>2</sub>SO<sub>4</sub> then acetone and rinsed with distilled water to remove surface oxide layers and undesired organic compounds *prior* palladization. An aqueous

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solution of potassium hexachloropalladate was prepared and added to a bottle containing iron powder. The solution in the bottle was continuously stirred until the dark orange solution turned to pale yellow. Then, the palladized iron was rinsed twice with deionized water and used for reaction without drying.

Surface area (BET area) of iron and Pd/Fe were measured using the nitrogen adsorption method with a ST-03 surface analyzer (Beijing).

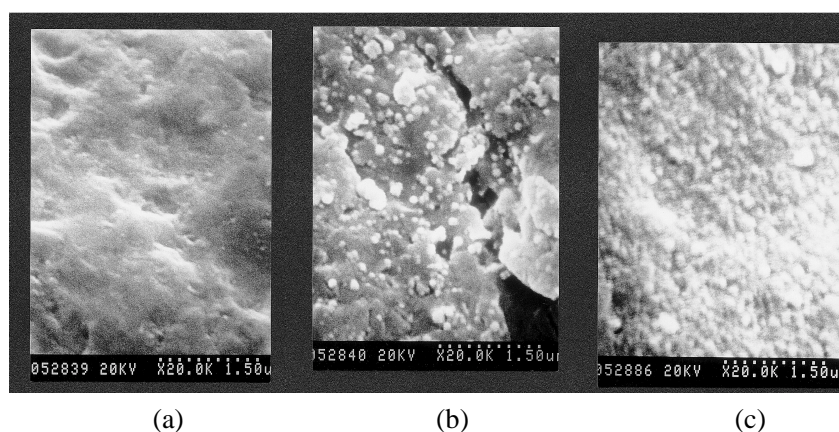
Batch experiments for chlorobenzene dechlorination were conducted in 30mL bottles, each bottle was placed in an incubator shaker (200 rpm,  $25\pm 1^\circ\text{C}$ ). At varying times, samples were withdrawn and filtered with a piece of  $0.45\ \mu\text{m}$  filter film, then used for analysis. Chlorobenzene and benzene were determined by HPLC system, chloride analysis was performed by ion chromatography (792 Basic IC, Metrohm).

## Results and Discussion

### *Characterization results of the catalyst*

The surface morphology of both the Fe and Pd/Fe is shown in **Figure 1**. The surface of Pd/Fe is rough with palladium deposited on the iron surface, and the more Pd loading, the more white dots. The total surface area of the Fe and Pd/Fe (0.005%) measured by BET- $\text{N}_2$  was  $0.49\ \text{m}^2/\text{g}$  and  $0.62\ \text{m}^2/\text{g}$ , respectively. The increased surface indicated that the Pd is dispersed on the surface of iron rather than clustered. That is consistent with the information revealed in the SEM image of the catalyst. Similar results were reported by Liu Y.H. *et al*<sup>14</sup>.

**Figure 1** SEM image of (a) Fe powder, (b) Pd/Fe (0.005%), (c) Pd/Fe (1%)

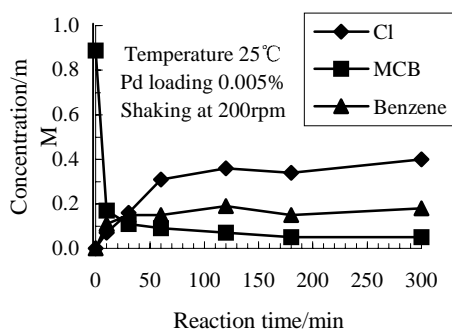


### *Dechlorination of chlorobenzene*

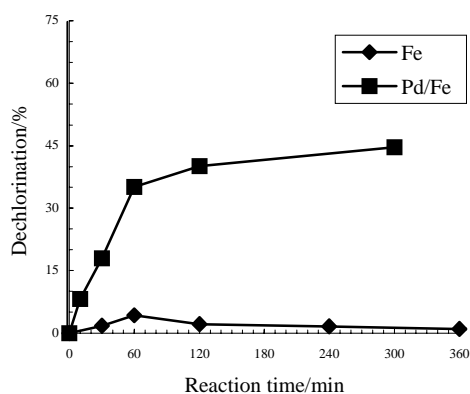
In all experiments, initial MCB concentration was 100 mg/L; metal to solution ratio was 2 g/30 mL. As seen from the **Figure 2**, the aqueous concentration of the MCB declined rapidly at the first 10 minutes, and then almost complete degradation was achieved within 5 hours. No byproducts were observed by GC-MS, benzene was the only

product of MCB dechlorination. The concentration of benzene and free chloride were gradually increased. Although close to 95% degradation was observed at the end of the experiment, the free chloride formation observed was just 48% of the maximum attainable. It is supposed that most of the MCB remained adsorbed to the iron surface until complete dechlorination is achieved. This need further study to confirm it. **Figure 3** showed the comparison of the dechlorination rates with Fe, Pd/Fe for MCB. The dechlorination efficiency for Fe was less than 6% during the 3 days experiment, while 45% for Pd/Fe within 5 h. It is obvious that Pd as the catalyst accelerated the reductive dechlorination reaction.

**Figure 2** Reduction of chlorobenzene (MCB) and respective formation of benzene

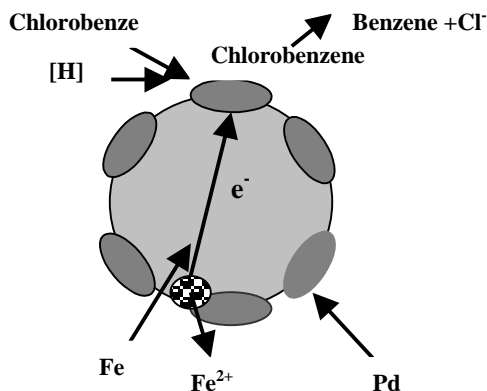


**Figure 3** Comparison of the dechlorination rates of Fe and Pd/Fe



#### *Catalytic reduction mechanism*

Evidence strongly suggests that, within a bimetallic system, one metal likely serves as catalyst (Pd) while the other as electron donor (Fe) as illustrated in **Figure 4**. Iron is a very effective reductant.

**Figure 4** Scheme of dechlorination of chlorobenzene with the bimetallic particle catalyst

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