



Effective catalytic hydrodechlorination of *o*-, *p*- and *m*-chloronitrobenzene over Ni/Fe nanoparticles: Effects of experimental parameter and molecule structure on the reduction kinetics and mechanisms

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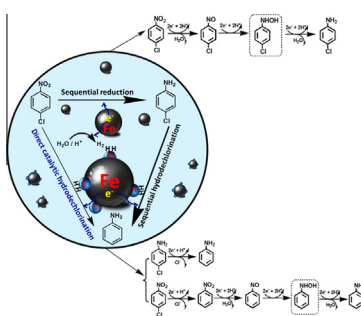
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HIGHLIGHTS

- ZVI shows a high efficiency and selective reduction of *p*-chloronitrobenzene (*p*-CNB).
- Ni as an effective catalyst favors hydrogen atom transfer in dechlorination of *p*-CNB.
- Complete reduction mechanisms of *p*-CNB over ZVI and Ni/Fe nanoparticles are provided.
- The dechlorination reactivity decreases in the order: *p*-CNB > *o*-CNB > *m*-CNB.
- The energy gap between HOMO and LUMO can predict the dechlorination reactivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Zero-valent iron (ZVI) reductive dechlorination is a promising approach for the abatement of chlorinated organic pollutants in the environment. In this study, ZVI and Ni/Fe bimetal nanoparticles were synthesized and applied for the treatment of chloronitrobenzenes (CNBs) in water. The pre- and post-reaction nanoparticles samples were characterized by SEM and XRD respectively. Here we show that ZVI nanoparticles can effectively perform the selective reduction of *p*-CNB to *p*-chloroaniline (*p*-CAN) with a selectivity of ca. 100% in 10 min without dechlorination throughout the research. Catalytic reduction of *p*-CNB over Ni/Fe nanoparticles could be divided into two sequential processes: the first is the conversion of *p*-CNB to *p*-CAN, and the second is the reductive hydrodechlorination of *p*-CAN with aniline formation. Direct catalytic hydrodechlorination of *p*-CNB as a side route was also observed. Results indicate that ZVI initiates the electron transfer process for the reduction of *p*-CNB to *p*-CAN, whereas Ni catalyst is in favor of hydrogen transfer as the dominant pathway for the dechlorination reactions. The complete reduction mechanisms of *p*-CNB over ZVI and Ni/Fe nanoparticles were discussed, and the kinetics of dechlorination of CNBs were found to be pseudo-first order. The effects of different experimental parameters, such as solution pH, dosage of Ni/Fe nanoparticles, initial concentration of *p*-CNB and the

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Ni loading on the catalytic reduction of *p*-CNB were carefully investigated. Under the several reaction conditions tested, a complete dechlorination could be attained in 2 h. The dechlorination reactivity for mono-CNBS decreases in the order: *p*-CNB > *o*-CNB > *m*-CNB. The energy gap between HOMO and LUMO is firstly indicated as a descriptor to evaluate the dechlorination reactivity of mono-CNBS, which may provide a new insight in predicting the dechlorination reactivity for other organic chlorides.

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1. Introduction

Organic chlorides, including alkyl and aryl chlorinated compounds, are important raw materials, intermediates and organic solvents, which have been widely used in large scale in the chemical, agricultural and electronic industries [1–4]. Due to their wide uses in human activities and strong recalcitrance to biodegradation, these compounds readily accumulate in the surroundings once released into the environment, and have severe impact on the atmosphere, soil and any kind of natural water bodies (e.g. river, lake and groundwater) [1,2]. In fact, these compounds are regarded as one of the most ubiquitous contaminants that have been widely detected in environment media in recent years [5–7].

Chloronitrogenated aromatic compounds (e.g. chloronitrobenzenes and chloroanilines), as a group of typical organic chlorides, are important industrial intermediates and extensively used in the production of pesticides, antioxidants, dyes, medicines and other chemicals [3,8]. Meanwhile, these compounds are normally classified as environmentally undesirable compounds due to their harmful health effect and widely distribution in environment. For instance, they can cause cancer and other harmful effects on the central nervous system, producing fatigue, headache, vertigo, vomiting, general weakness, unconsciousness and even coma [3,9]. Therefore, various abatement technologies based on physical, chemical as well as biological methods have been developed for these recalcitrant pollutants. These methods include adsorption by some common or peculiar materials [10,11], advanced oxidation processes such as photocatalytic oxidation [12], ozonation/O₃-UV combination process [13,14], Fenton oxidation [15] and electrochemical oxidation [16], and biodegradation processes [17,18]. Although these approaches have various advantages, the sheer number of reports suggests that no single method appears to be sufficiently outstanding for chloronitrogenated aromatics removal: the adsorption method only achieves the phase transfer for pollutants, while their nature does not change [10,11]; the biodegradation method is often time-consuming due to the chemical toxicity to bacteria and more danger daughter-compound formation as a result of partial dechlorination [19,20]. Whereas advanced oxidation processes can attain a complete detoxification for chloronitrogenated aromatics resulting from mineralization reaction, the degradation of these compounds is usually quite difficult due to the presence of strong electron-withdrawing substituents such as chloro- and nitro-groups, which thus makes these processes energy intensive and costly. Nevertheless, it favors the electrophilic attack reaction thermodynamically, where the reduction of nitro-group and the C-Cl bond cleavage reaction become readily to occur [17]. Moreover, the toxicity of organic chlorides mainly arises from the chlorine(s) [18], whose removal remarkably improves the risk and biodegradability of these compounds. Catalytic hydrodechlorination over supported transition metals representing a promising technology for the abatement of organic chlorides has attracted world attention for years [21,22]. Herein, the presence of heterogeneous catalyst plays a vital role. Therefore, the preparation of peculiar catalysts with high reactivity and stability has been extensively explored over the past years.

Among them, Pd [8], Au [23], Pt [24], Rh [25], Ni [26] and Cu [27] have been found to exhibit remarkable hydrodechlorination activity for chlorinated compounds. However, for the chloronitrogenated aromatics, most studies focus on the search for the effective catalysts for the selective hydrogenation of chloronitrobenzenes (CNBs) to chloroanilines (CANs), while catalytic hydrodechlorination of these compounds is seldom considered [8]. Recently, electrochemical reductive dechlorination as another promising approach has been extensively investigated for the abatement of organic chlorides [28–32]. Importantly, interesting outcomes have been often achieved by carrying out the reaction under very mild conditions without any external reductant addition. It is noteworthy that the electrode material also plays a key role in the dechlorination reaction, where remarkable catalytic cathodes are required in order to reduce the high overpotential associated with the C-Cl bond dissociation and avoid the hydrogen evolution reaction in aqueous media. According to the works of our own and some other groups, Ag, Au, Cu and Pd-based materials are found to display outstanding electrocatalytic activities toward dechlorination of organic chlorides [28–31].

Since the first application of zero-valent iron (ZVI) into the reductive dechlorination of organic chlorides reported in 1980s [33], ZVI reduction as a cost-effective and simple approach has attracted considerable attention for the removal of these compounds. However, naked ZVI without any modifications exhibit a relatively low dechlorination rate and efficiency, and it normally takes couple of days or even weeks to achieve a complete transformation of chlorinated compounds [34,35]. To further improve the dechlorination efficiency of ZVI, different strategies like nanoparticles preparation and bimetallic catalyst synthesis are found to remarkably enhance the dechlorination efficiency [35–45]. Particularly, bimetal nanoparticles, as superior catalytic reductant, display outstanding dechlorination activity for the organic chlorides. Pd has long been recognized as the most powerful catalyst and the synthesized Pd/Fe nanoparticles have been successfully applied in the abatement of considerable chlorinated compounds, including alkyl and aryl chlorides [36–38]. For example, catalytic amination and dechlorination of CNBs have clearly been observed over Pd/Fe bimetal nanoparticles, where the dechlorination rate was significantly enhanced with the bulk loading of Pd [46,47]. However, the expenses associated with Pd-based materials contribute to increasing the processing cost. Therefore, the exploitation of catalysts devoid of noble-metal materials has drawn more attention recently. Previous publications demonstrate that Ni [39–41,45], Cu [42] and Pb [43] exhibit strong dechlorination reactivity for organic chlorides and, albeit a little weaker, all of them could be used, in principle, to replace the Pd-based materials currently used [48]. In addition to catalytic materials, the molecular structure of organic chlorides appears to be another key determinant factor for the dechlorination reactivity and even for the dechlorination mechanisms. For the specific homologues, the dechlorination reaction (kinetics) over bimetal nanoparticles is found to become thermodynamically favored with the degree of chlorination, and the position of chlorine in molecular structure also is expected to affect the dechlorination reactivity due to the potential steric hindrance and/or the inductive effects [49–52].

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