Bimetallic Pd/Al particles for highly efficient hydrodechlorination of 2-chlorobiphenyl in acidic aqueous solution

Bo Yang [a,b], Shubo Deng [a], Gang Yu [a,*], Hong Zhang [b], Jinhua Wu [c], Qiongfang Zhuo [a]

[a] School of Environment, POPs Research Centre, Tsinghua University, Beijing 100084, China
[b] School of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, China
[c] School of Environmental Science and Engineering, South China University of Technology, Guangzhou 510006, China

ARTICLE INFO

ABSTRACT

Pd-based bimetallic materials have been widely studied for the effective hydrodechlorination (HDC) of aqueous chloroorganic compounds. However, the reaction functions of metal substrates and mechanism responsible for changes in reactivity have not been fully elucidated. Here, we synthesized Pd-based bimetals with Mg, Al, Mn, Zn, Fe, Sn, and Cu to explore the influence of metal substrates on HDC reactivity of 2-chlorobiphenyl (2-PCB). Bimetals exhibited disparate reactivity toward 2-PCB in acidic solution. Among these bimetals, Pd/Al particles presented the highest stability and relatively high reactivity to remove 2-PCB. The maintenance and regeneration of Al substrate are attributed to its particular corrosion properties which provide an efficient recycling between Al element and its oxide layer. The fresh and reacted Pd/Al samples were characterized by ICP-OES, SEM, XRD, and BET. The investigation of the pH effect on 2-PCB HDC further revealed the particular behaviour of Al surface. The effect of Pd loading amount on the HDC indicated that the optimal Pd content in terms of catalytic activity was related to the Pd dispersion degree. Finally, a mechanism for 2-PCB HDC on the Pd/Al surface was proposed.

© 2011 Published by Elsevier B.V.

1. Introduction

Hydrodechlorination (HDC) technology has been proved an effective degradation method for chloroorganic compounds (COC) in contaminated water [1–4]. For COC degradation, HDC mainly employs the reaction system using Pd catalyst supported on metal oxides or carbon materials with hydrogen donors and the Pd-based bimetallic system using Pd as catalytic cathode in the galvanic corrosion. The former system, e.g., the Pd–H_2 system, can rapidly dechlorinate various COC in aqueous phase [5,6]. However, H_2 which is used as the reductant is inconvenient to manipulate and possibly dangerous in practice. The latter system, with Pd depositing on metal substrate, often serves as a promising alternative HDC reagent [7]. In the system, the active hydrogen species produced from the corrosion of metal substrate is further stored in Pd lattice, to supply the HDC. Besides the catalytic function, Pd can improve reactivity through increasing the corrosion of metal substrate resulting from the formation of a galvanic couple between the active metal anode and the stable Pd cathode [8].

The bimetallic HDC technology mostly used palladized iron (Pd/Fe) particles to treat aqueous COC due to the relatively low cost, easy availability, and broad applicability of zero-valent iron (ZVI) [9]. Although Pd/Fe bimetallic particles can effectively remove COC in contaminated water, the material may not be stable for an extended run owing to ZVI corrosion. The uncontrollable corrosion would cause loss of catalyst base, iron oxide precipitation, and excessive H_2 formation, which further lead to the deactivation of Pd/Fe [10]. On the other hand, the reactivity of Pd/Fe could be greatly improved by decreasing its particle size. The Pd/Fe nanoparticles exhibit relatively high activity because of its higher intrinsic reactivity and less mass transfer restrictions [11–14]. However, due to the very high reactivity, the Pd/Fe nanoparticles tend to either react rapidly with surrounding media (e.g., O_2 or H_2O) to form iron oxide encapsulation or agglomerate rapidly into much larger particles or flocs, resulting in rapid loss in reactivity [15]. Some studies have indicated that agglomeration can be prevented by polymer or surfactant adsorption onto the surface of Pd/Fe nanoparticles or by mooring the nanoparticles onto carbon microspheres or polymeric granules [16,17]. Nevertheless, these sophisticated modification methods of Pd/Fe nanoparticles would cause more difficulty and cost-efficiency in practice.

Recently, new attempts were made by selecting other metal substrates to replace Fe for HDC in Pd-based bimetallic systems, including Mg, Zn, or nanoscale Sn particles [18–20]. Agarwal et al. reported that Pd/Mg particles can well dechlorinate PCB in neutral and alkaline H_2O [18]. As compared with Fe, Mg possesses significantly lower standard electrode potential (SEP) and unique corrosion properties, resulting in a greater force to drive the HDC

* Corresponding author. Tel.: +86 10 62796960; fax: +86 10 62794006.
 E-mail address: yg-den@tsinghua.edu.cn (G. Yu).

reaction. In this work, inspired by the study of Agarwal et al., aluminium was selected as the substrate for preparing Pd-based bimetallic material. In addition, aluminium is the most abundant metal element in the earth; moreover, zero-valent aluminium (Al) has a low SEP. So Al is likely a potential metal element for effectively reducing aqueous contaminants.

The purpose of this study was to evaluate the new class of Al particles as a substrate to support Pd for the HDC of PCB. 2-PCB was used as probe compound based on its relatively high solubility in PCB congeners, high refractory property, and a single HDC product. In the Pd-based bimetallic system, the effect of metal substrates on the HDC efficiency was investigated including Mg, Al, Mn, Zn, Fe, Sn, and Cu. The bimetallic particles were prepared by a simple cementation process. After the preliminary examinations, the HDC stability of Pd/Mg, Pd/Al, and Pd/Fe particles was further studied for the practical consideration. Due to their best stability in acidic solution, Pd/Al particles were further characterized for the content and morphology of Pd deposits using ICP-OES, SEM, XRD, and BET. The bimetallic HDC process is highly pH sensitive because protons are directly involved with hydrogen evolution. So the pH effects on 2-PCB HDC were evaluated with Pd/Al particles. The effect of Pd loading on HDC efficiency was also investigated for determining the optimal Pd content in Al particles. Finally, a mechanism for HDC in Pd/Al interface was proposed by combining the corrosion behaviour of Al with the reported bimetallic HDC processes.

2. Materials and methods

2.1. Chemicals

Al ($\geq$99%, 100–200 mesh), Mg ($\geq$99%, 100–200 mesh), Zn ($\geq$95%, 400 mesh), and Cu ($\geq$99.7%, 400 mesh) particles were purchased from Sinopharm Chemical Reagent Co., Ltd. Mn ($\geq$99.99%, 400 mesh), Fe ($\geq$97%, 100 mesh), and Sn ($\geq$99.5%, 400 mesh) particles were obtained from Tianjin Damao Chemical Reagent Plant. PdCl$_2$ ($\geq$99%) was the same as that presented in our previous paper [21]. HCl (36–38%) was from Dongguan Dongjiang Chemical Reagent Co., Ltd. 2-Chlorobiphenyl (2-PCB), biphenyl (BP), and 2,4,5,6-tetrachloro-m-xylene (TCMX) were supplied by AccuStandard, Inc. Hexane (HPLC grade), isopropanol, and acetone were provided from DikmaPure Co. All reagents were used as received.

2.2. Synthesis and characterization

The Pd/metal particles were synthesized by aqueous cementation. The stock solution of 10 mM PdCl$_2$ was prepared as indicated in our previous paper [21]. The calculated amount of PdCl$_2$ stock solution was diluted with ultrapure water. Metal particles were then added to the solution. Only for Al particles, the initial pH of deposition solution needed to be adjusted to 3.0 with HCl for accelerating cementation (Table 1). The resulting suspension was vigorously stirred for 1–3 h wherein elemental Pd deposited onto metal substrate to form the bimetallic particles. The suspended particles were then collected with vacuum filtration. The particles were washed with acetone to remove the residue on the particle surface, dried for 10 min under vacuum, and stored in a silica-gel drier. The Pd:metal ratios of the synthesized bimetallic particles were finally determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 2100DV) to analyze the concentration of Pd and metal ions from their extract of aqua regia. The BET surface areas (S_{BET}) of Al and Pd/Al particles were analyzed by nitrogen adsorption (NOVA 1200E). The Pd distribution on the Al surface was imaged by a SEM-ESB (Hitachi S-3400N II). The crystallites of Pd/Al particles were detected by XRD (Bruker D8 Advance).

2.3. HDC reactions

The HDC experiments of 2-PCB were carried out in a batch system. The stock solution of 2-PCB (18.7 μM) was prepared by dissolving pure 2-PCB in water as our previous report [22]. The 50 mL solution of 2-PCB was added into a 100 mL serum bottle; then, the bimetallic particles were put into the solution, resulting in 5.0 g/L metal loading. HCl was used to adjust the initial aqueous pH. In the batch experiment, multiple bottles of the same component were prepared. These bottles were sealed with Teflon caps and fixed on a horizontal shaker (180 rpm) at ambient temperature. At each sampling time, 0.5 mL solution was withdrawn from one of the bottles for analysis of 2-PCB and its product. The experiment was repeated twice to obtain triplicate results. Many HDC reports using bimetallic particles had shown that the catalytic reaction kinetics can be best modelled with the pseudo-first-order kinetics [4,18,23,24]. So it is introduced to analyze the reaction kinetics of this study. The reaction processes were monitored using GC/ECD and GC/MS devices through a liquid–liquid extraction method as our previous report [22].

2.4. Catalyst recycling

In order to evaluate the long-term reactivity of bimetallic catalysts, the Pd/Mg, Pd/Al, and Pd/Fe system were used in batch reactions for the HDC of 2-PCB in multiple cycles. The initial pH of reaction solution was adjusted to 3.0. Each subsequent HDC cycle was performed in the same bottle with the remaining bimetallic catalysts. At the end of each cycle, the final sample was withdrawn from the supernatant after centrifugation for analysis, while the remainder was emptied out, and the bottle was refilled with a fresh 2-PCB solution at 24 h intervals. For each cycle, the initial phase of the reaction kinetics for the 2-PCB conversions was monitored and evaluated.

3. Results and discussion

3.1. Effect of metal substrates

Metal substrates have a dramatic effect on the cementation between them and Pd. For the tested seven metals, most of metal particles achieved 57–91 wt.% of the desired Pd loading after cementation at pH 7 except Al and Sn (Table 1). The low Pd loadings for Al and Sn particles likely resulted from their compact oxide surfaces in neutral H$_2$O, which retarded the spontaneous cementation (E_H^θ[Pd^{2+}/Pd] = 0.915 V > E_H^θ[Al^{3+}/Al] = -1.676 V and E_H^θ[Sn^{2+}/Sn] = -0.136 V). The Pd loading of Al particles could be greatly improved with adjusting pH from 7 to 3 and

Table 2
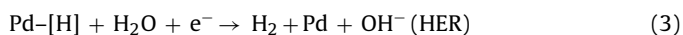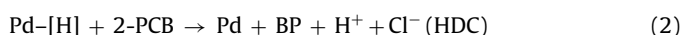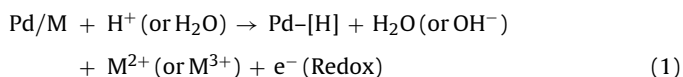Effect of metal substrates on the HDC of 2-PCB in aqueous solution containing Pd/metal particles.[a]

Metal substrates	Pd loadings (%)	$t = 5$ min		$t = 10$ min			E_H^θ (V)
		pH[b]	2-PCB concentration (μM)	pH	2-PCB concentration (μM)	BP concentration (μM)	
Mg	0.87	7.5	2.62	8.9	0.76	17.54	−2.356
Al	0.72	4.0	17.17	4.1	15.63	2.88	−1.676
Mn	0.91	7.0	3.11	7.1	1.09	17.25	−1.18
Zn	0.86	6.1	3.49	7.0	1.27	16.83	−0.7626
Fe	0.63	4.5	10.25	5.1	5.92	12.04	−0.44
Sn	0.35	4.0	18.55	4.0	18.36	0.17	−0.136
Cu	0.67	4.0	18.36	4.1	18.14	0.36	0.340

[a] Reaction parameters: $C_{0,\text{2-PCB}} = 18.7\,\mu$M, 5 g/L metal particles, 50 mL solution, initial pH = 4.0 ± 0.1, 180 rpm, reaction time = 10 min, $T = 25 \pm 2\,°$C.
[b] The pH meter (Hach sensION156) was calibrated using buffers in aqueous solution. Buffer with pH values of 4.00 and 9.00 in water gave values of 4.11 and 9.09, respectively.

increasing stirred time. But Sn particles kept the low activity to Pd cementation even after changing pH and stirred time.

The HDC tests of 2-PCB were carried out using the above Pd/metal particles. The only HDC product detected was biphenyl (BP). From Table 2, Pd/Mg particles with 0.87 wt.% Pd exhibit the highest activity for 2-PCB reduction. The conversion rate of 2-PCB arrived at 96% from 18.7 to 0.76 μM within 10-min HDC at initial pH 4.0. Agarwal et al. explained that Mg has a SEP of −2.356 V (E_H^θ[Mg^{2+}/Mg]) and thus Pd/Mg particles possess a high impetus to promote HDC reaction [18]. During the HDC of Pd/Mg particles, the pH increased from 4.0 to 7.5 within the first sampling and continuously to 8.9 within the second sampling. A very vigorous hydrogen evolution reaction (HER) was observed in this Pd/Mg system, which implied the acute corrosion behaviour of Mg surfaces. The corrosion involved consumption of H$^+$ and production of OH$^-$ resulting in the above pH profiles. For Pd/Mn and Pd/Zn systems, there were 1.09 and 1.27 μM of 2-PCB, respectively, remaining in solution after 10-min reaction. So the reaction rates of the above bimetals followed the order Pd/Zn < Pd/Mn < Pd/Mg. The order can be explained and just correlated with SEP sequence of Zn, Mn, and Mg, which determine the HER activity. Based on the widely accepted HDC mechanism in palladized materials [25], the ability of metal substrates to produce hydrogen would affect the HDC efficiencies. In addition, the solution pH using Pd/Mn or Pd/Zn particles rapidly increased from 4.0 to 7.0, which indicated that Mn or Zn rapidly depleted H$^+$ in acid solution. The final pH of Pd/Mn and Pd/Zn systems stopped at 7.0 after HDC. It is likely due to the relatively high SEP of Mn and Zn compared with Mg, which cannot successively reduce neutral H$_2$O into hydrogen atom [H] and OH$^-$. Vigorous HER also appeared in Pd/Mn and Pd/Zn systems. The phenomenon implied that metal substrates were easily exhausted by HER (side reaction) instead of HDC. The desired reaction should involve that [H] is mainly used to HDC rather than HER. The detailed processes of Pd-based bimetallic reduction reaction are listed as the following equations:

$$\text{Pd/M} + \text{H}^+ (\text{or H}_2\text{O}) \rightarrow \text{Pd–[H]} + \text{H}_2\text{O} (\text{or OH}^-)$$
$$+ \text{M}^{2+} (\text{or M}^{3+}) + \text{e}^- \text{ (Redox)} \tag{1}$$

$$\text{Pd–[H]} + \text{2-PCB} \rightarrow \text{Pd} + \text{BP} + \text{H}^+ + \text{Cl}^- \text{ (HDC)} \tag{2}$$

$$\text{Pd–[H]} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{Pd} + \text{OH}^- \text{ (HER)} \tag{3}$$

$$\text{Pd–[H]} + \text{Pd–[H]} \rightarrow \text{H}_2 + \text{Pd (HER)} \tag{4}$$

M is the metal substrate; and Pd–[H] is chemisorbed [H]. In the processes, the HDC reaction (Eq. (2)) is in competition with HER (Eqs. (3) and (or) (4)).

Pd/Fe and Pd/Al systems removed 2-PCB from 18.7 to 5.92 and 15.63 μM, respectively, during 10-min reaction (Table 2). Pd/Al particles presented an obviously lower HDC rate than Pd/Fe particles, which is likely due to the compact oxide layer of Al preventing itself

from corrosion in pH 4.0. For Pd/Sn or Pd/Cu particles, there was insignificant 2-PCB degradation in the solution. Moreover, no pH change was observed with Pd/Sn and Pd/Cu particles, suggesting that Sn and Cu substrates could not effectively convert H$^+$ or H$_2$O into [H] in pH 4.0. So the galvanic cell was not successfully coupled between Pd and Sn/Cu. The relatively high STP of Sn and Cu among these above metal substrates may result in their chemical inertia to produce hydrogen.

Based on the above results, Mg, Al, and Fe particles were selected as the further stability tests for these following reasons. Pd/Mg particles possess the highest HDC performance among these particles. Moreover, Agarwal et al. [18] reported that the OH$^-$ generated through Mg corrosion in Pd/Mg particles favors the formation of Mg(OH)$_2$, part of which repairs the protective oxide layer and makes the system self-regulated. Pd/Al or Pd/Fe presented a low HDC efficiency at initial pH 4.0, but the insignificant or slow change of pH to Al or Fe, respectively, indicated that they possess a relatively strong anti-corrosive function compared with Mn and Zn in acid solution. In addition, Fe is the widely used substrate in bimetallic HDC [1,9,26,27].

3.2. Catalyst stability

Stability tests with Pd/Mg, Pd/Al, and Pd/Fe particles were attempted to examine their long-term reactivity, which is essential to practical application. From Table 3, the HDC rate of Pd/Mg particles successively decreased from an initial activity of $k = 4.9 \times 10^{-1}$ min^{-1} in the first run to $k = 9.1 \times 10^{-2}$ min^{-1} in the third reaction cycle at the initial pH 3.0 within 10-min reaction. The decrease of Pd/Mg activity could be attributed to the loss of catalyst substrate with the dissolution of Mg into aqueous solution. Naturally, lower pH values led to higher dissolution rates. Agarwal et al. [18] reported that Pd/Mg particles formed a partially protective film of crystalline Mg(OH)$_2$ by superficial corrosion from pH near neutral to 10.6. However, Mg(OH)$_2$ film can be spontaneously dissolved in acid solution to produce the resolvable Mg^{2+}. The refreshable Mg surface loses the protective hydroxide film and then results in an undesired redundant Mg dissolution, Pd detachment, and excessive HER. During the reaction, it could be observed that there were a few fine particles of Pd black suspended in solution. To confirm this, analysis of the particle digesta of the spent 1.38 wt.% Pd/Mg indicated that Pd-leaching rate, i.e., Pd content reduction from its original state, arrived at 12.1% after the third run in the ICP-OES analysis. In addition, the excessive H$_2$ might cover the Pd islets, blocking the contact between Pd and the reactant, as reported by the previous studies [10,15]. Therefore, Pd/Mg particles are not favorable for employing to long-term HDC in acid condition.

Pd/Fe particles presented a higher HDC rate for 2-PCB than Pd/Al particles in the first cycle, but it exhibited a dramatic drop of HDC activity in the following cycles (Table 3). After the second cycle, the

Table 3
Pseudo-first-order rate constants for subsequent reaction cycles of the HDC of 2-PCB in acidic solution.[a]

	Cycle 1[b]		Cycle 2		Cycle 3	
	First-order rate constant (min^{-1})	Liner regression coefficient R^2	First-order rate constant (min^{-1})	Liner regression coefficient R^2	First-order rate constant (min^{-1})	Liner regression coefficient R^2
Pd/Mg	$4.9 \times 10^{-1} \pm 3.7 \times 10^{-4}$	9.4×10^{-1}	$2.2 \times 10^{-1} \pm 2.4 \times 10^{-4}$	8.9×10^{-1}	$9.1 \times 10^{-2} \pm 5.3 \times 10^{-4}$	9.7×10^{-1}
Pd/Fe	$1.7 \times 10^{-1} \pm 4.3 \times 10^{-4}$	9.4×10^{-1}	$1.2 \times 10^{-1} \pm 3.5 \times 10^{-4}$	9.0×10^{-1}	$6.7 \times 10^{-2} \pm 7.8 \times 10^{-4}$	9.6×10^{-1}
Pd/Al	$7.8 \times 10^{-2} \pm 2.3 \times 10^{-4}$	9.6×10^{-1}	$8.3 \times 10^{-2} \pm 6.7 \times 10^{-4}$	9.0×10^{-1}	$7.9 \times 10^{-2} \pm 1.9 \times 10^{-4}$	9.8×10^{-1}

[a] These bimetallic materials were exposed to repeated injection of 2-PCB solution at 24-h intervals, and pseudo-first-order rate constants were quantified for each cycle.

[b] All reported values are the average of three experimental results using the reuse of the same catalyst sample (1.40 ± 0.03 wt.% Pd loading/Mg, Al, and Fe particles) without changing the reaction condition ($C_{0,2\text{-PCB}}$ = 18.7 μM, initial pH = 3.0 ± 0.1, 180 rpm, reaction time = 10–60 min, T = 25 ± 2 °C).

HDC rate of Pd/Fe particles was below that of Pd/Al particles. The pseudo-first-order rate constants of Pd/Fe particles decreased from 1.7×10^{-1} min^{-1} to 6.7×10^{-2} min^{-1} within three cycles. To probe this drop, the analysis of the used 1.41 wt.% Pd/Fe digesta showed that the leaching rate of Pd from the virgin Pd/Fe after the third cycle was 2.9%. This result indicates that Pd deposited on Fe particle surface may disengage when Fe substrate corrodes. The Pd-leaching rate of Pd/Fe was evidently lower than that of Pd/Mg, which is likely due to the appearance of iron oxide shell during reaction. It results in that Pd islets encapsulated by the iron oxides formed and then its HDC efficiency decreased. Chun et al. and Zhu et al. have specifically proved that the Fe^0-core–oxide shell structure exists on the Pd/Fe particles [14,15]. In fact, the dislodgment and encapsulation of Pd islets is always a potential setback to the practical utilization of Pd/Fe because Pd provides the only active sites in the HDC [28].

In this study, Pd/Al particles took on a relatively stable HDC efficiency at initial pH 3.0 compared with Pd/Mg and Pd/Fe particles. The k values kept at 7.8–8.3×10^{-1} min^{-1} for 2-PCB degradation during three reaction runs. The Pd-leaching rate on 1.43 wt.% Pd/Al particles was only 0.1% after three cycles. Moreover, different from pH increasing in Pd/Mg and Pd/Fe systems, the initial pH 3.0 in Pd/Al system was almost not changed during HDC. Those results

may be attributed to the different corrosion behaviours among Al, Mg, and Fe surfaces in acid solution. For Al, the protective oxide film could effectively regulate its corrosion rate and enhance its utilization efficiency to HDC. In a control test, Pd-free Al particles showed insignificant HDC and HER even in the solution of pH 1.0. So the protective film inhibits the reductive capacity of Al when it reacts with H$^+$ or H$_2$O in acidic solution. After palladizing, HDC and HER took place at once. The emerging reaction may be attributed to increased rate of Al corrosion resulting from the formation of a galvanic couple between Al and Pd. In Pd/Al particles, the Pd islets act as cathodes facilitating accelerated localized galvanic corrosion and inducing electron flow from Al to Pd. When the acidity in solution reaches a certain value, Pd slowly breaks the stable alumina film and then Al substrate as anode starts corroding and producing [H]. Meanwhile, the new alumina film spontaneously forms as the protective oxide layer. The surface recycling between Al corrosion and alumina formation leads to a slow rate of Al consumption and the steady HDC performance of Pd/Al. Moreover, the Pd islets can anchor more firmly on the stable Al surface than the Mg and Fe surfaces. So a low Pd-leaching rate on Pd/Al particles appeared in this study. In addition, the insignificant change of pH with Pd/Al during HDC provides the evidence for the slow corro-
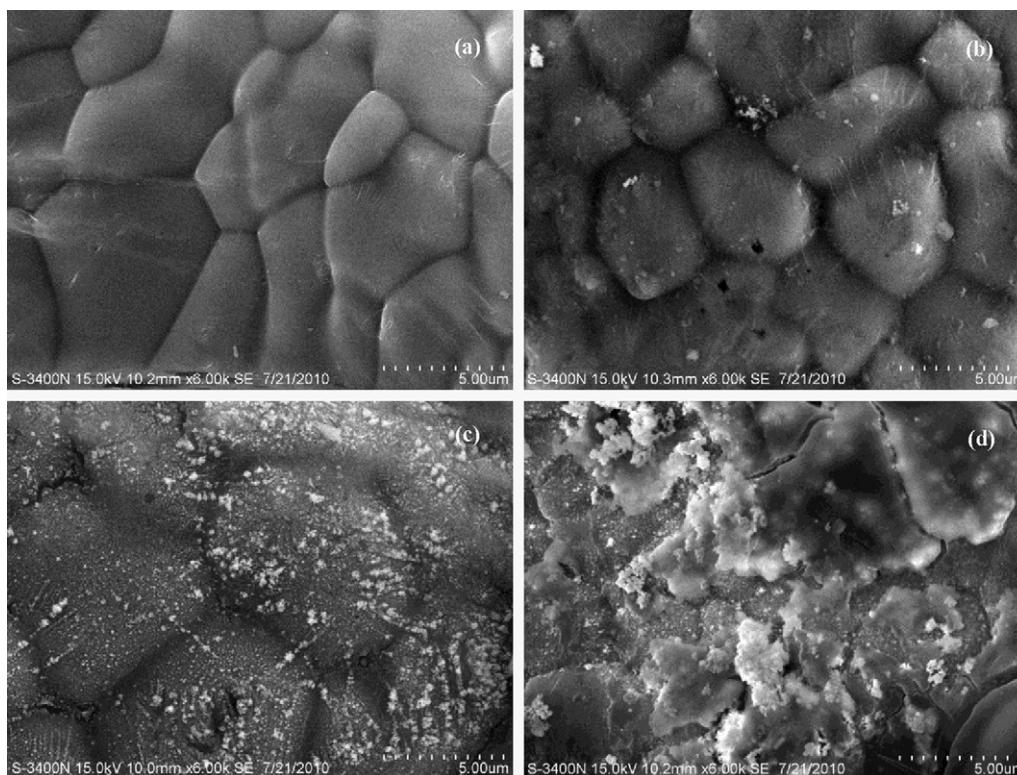

Fig. 1. SEM micrographs of (a) the surface of a raw Al particle, (b) a Pd/Al particle with 0.46 wt.% Pd, (c) a Pd/Al particle with 1.43 wt.% Pd loading, and (d) a Pd/Al particle with 2.47 wt.% Pd. The adopted magnifications are shown in the SEM micrographs.

sion of Al substrate and high utilization efficiency of [H] to HDC. The [H] producing from H^+ or H_2O reduction on Pd/Al was firstly used for HDC rather than HER, which maintain the mass balance of H^+ in solution. Considering the long storage time of the catalyst, the Pd/Al activity tests confirm its stability well. After stored in neutral H_2O or exposed in air for one month, it was carefully ensured that hardly any activity of Pd/Al for 2-PCB HDC was lost during the long storage time (k still approximately kept at 8.0×10^{-1} min^{-1}, not shown in Table 3 for clarity). The results demonstrate that the Pd/Al bimetallic particles have the potential for recycling and reuse at a high activity level. The passive oxide film formed on Pd/Al particles enables storage in ambient conditions without compromising HDC potential. Breakdown of the protective film in acid solution by corrosion at localized cathodes produces HDC again on the Pd surface. So it is evident that pH plays an important role on the Pd/Al activity, which will be discussed in the following sections.

3.3. Characterizations

SEM images of Pd/Al particle samples with different Pd loadings are shown in Fig. 1. For the raw Al particles, its morphology is a smooth surface with only 0.18 m^2/g S_{BET} (Fig. 1a). Pd islets with 0.46 wt.% loading show a tiny size distribution between 10 and 100 nm and are sparsely distributed on the Al surface. After further palladized, the S_{BET} of Pd/Al particle drastically increased up to 16.53 m^2/g at 1.43 wt.% Pd loading. It would lead to a significant increase in the active site on the Pd/Al surface for HDC. Its SEM image reveals that tiny Pd islets were uniformly dispersed on Al particle surface (Fig. 1c). A few agglomerations of Pd crystallites were observed at 1.43 wt.% Pd. But Pd islets tended to assemble into clusters or films at 2.47 wt.% of Pd loading (Fig. 1d).

The XRD patterns taken for fresh and/or spent Pd/Al particles with 1.43 and 2.47 wt.% Pd loadings are shown in Fig. 2. The diffraction peaks of the Pd/Al sample with 1.43 wt.% Pd exhibited peaks attributed to diffraction for the Al element alone, suggesting that Pd was present in a well-dispersed state on the support, and therefore small Pd particles could not be detected by XRD (Fig. 2a). The peaks for Pd appeared when Pd loading increases to 2.47 wt.% (Fig. 2c). No Al$_2$O$_3$ peak in these particles means this type of particles has a rather thin oxide layers. In addition, the XRD patterns of the 1.43 wt.% Pd/Al particles indicate that there is insignificant difference for the main crystal peaks between the fresh and the spent samples. This suggests that the microcosmic crystal pattern did not change after HDC, which was consistent with the long-term stability of Pd/Al during reaction.

3.4. pH effects

The average results of 2-PCB HDC in various initial pH solutions using Pd/Al particles from three repeated batches are plotted in Fig. 3. In the neutral H_2O, 2-PCB conversion was not statistically significant with Pd/Al bimetallic particles. In solutions of pH between 5.0 and 7.1, Pd/Al particles exhibited a very low rate to HDC. Only 19.4% of 2-PCB was degraded at initial 5.0 during 60-min reaction. When the solution pH decreased to 4.1, the conversion rates presented a significant increase. Then, the conversion rates increased rapidly, with decreasing solution pH from 4.1 to 1.1. 2-PCB was completely dechlorinated at initial pH 1.1 within 20 min. This trend is similar to the study of Bokare and Choi [29], in which the corrosion of zero-valent Al is subject to a very low rate at weak acidity and its rate becomes increasingly rapid at pH below 4.0. In this study, it can be speculated that the alumina film just resembles an automatic valve to open or close the surface of elemental Al substrate through pH triggering. In these experiments, there were
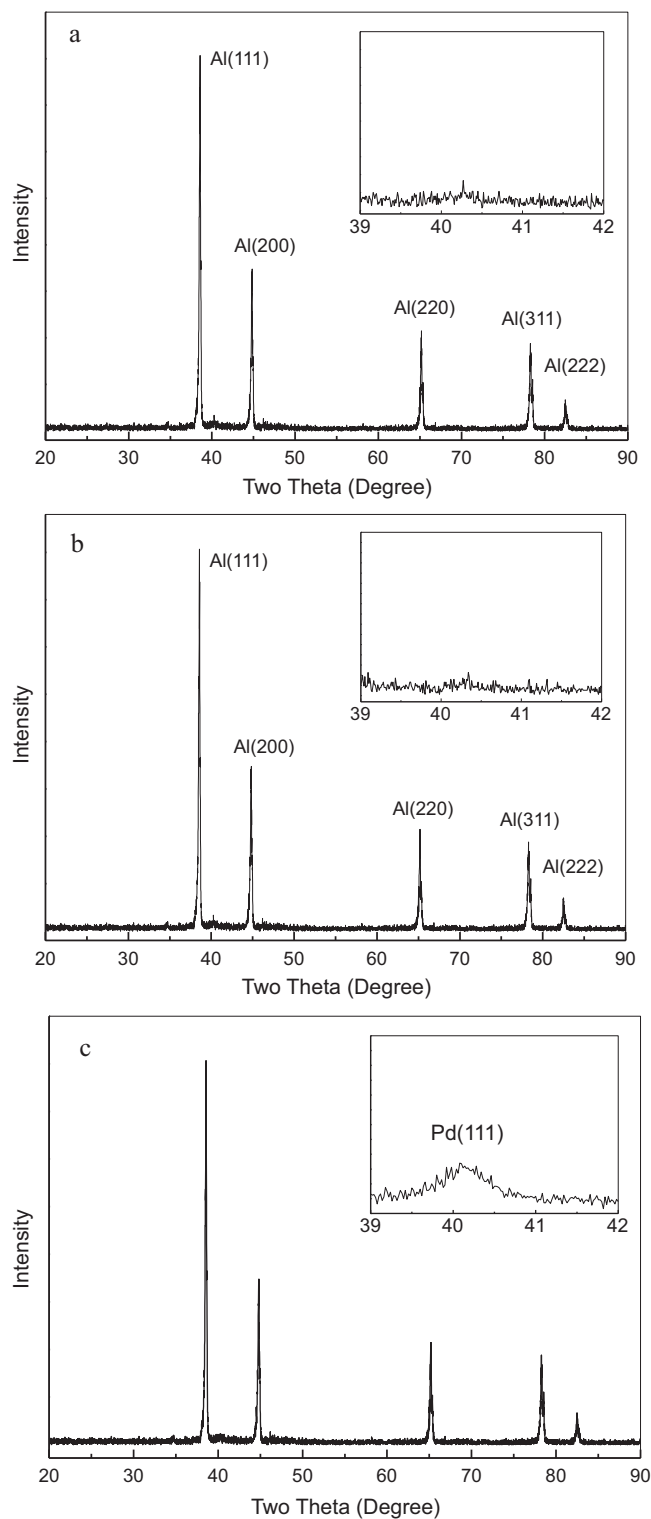

Fig. 2. XRD patterns of (a) fresh 1.43 wt.% Pd/Al particles, (b) spent 1.43 wt.% Pd/Al particles after three reaction recycles, and (c) fresh 2.47 wt.% Pd/Al particles.

insignificant changes for solution pH values during reaction, especially for low pH. This trend implies the protective oxide layer can defend Al substrate against excessive consumption since the excess corrosion of Al would visibly lead to the pH increasing. So the pH controls the competition between Al corrosion and alumina formation, making the system self-regulated. From a practical point of view, the Pd/Al activity and its long-term stability can be efficiently controlled by adjusting the solution pH. The Pd/Al can be
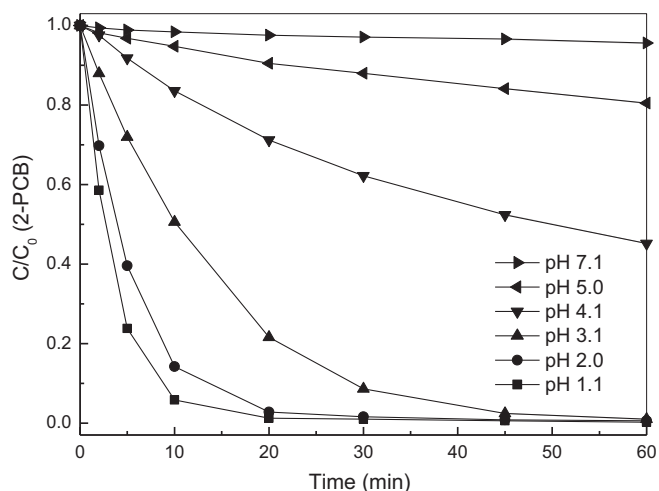
Fig. 3. Effect of the initial pH on 2-PCB conversion using Pd/Al particles with 1.43 wt.% Pd loading.

Fig. 4. Effect of Pd loading on 2-PCB conversion and catalytic activity. Inset is the HDC of 2-PCB with different Pd loadings over time.

stably conserved in neutral or weak acidic H_2O and then start HDC in relatively strong acid solution with low wastage.

In addition, Pd-free Al particles could not execute 2-PCB HDC even at pH 1.0. This suggests that the HDC process was not a direct reduction, which is consistent with our previous studies [30]. It was speculated that the HDC rate of 2-PCB would be related to Pd distributing on Pd/Al. Fang and Al-Abed reported that the HDC is proportionally related to the active hydrogen species dissolved in the Pd lattice [31]. Therefore, an attempt was made to confirm the effect of Pd content (or surface concentration) in Pd/Al on HDC rate in the following section.

3.5. Effect of Pd loading

Fig. 4 shows the effect of Pd loading on the catalyst efficiency of Pd/Al in 2-PCB HDC. 2-PCB conversion obviously increased as a function of Pd loading, with 2.47 wt.% Pd/Al exhibiting the highest conversion rate. But a very low promotion in the conversion rate appeared after Pd loading arriving at 2.06 wt.%. So the catalytic activity, defined as the intrinsic rates, moles of 2-PCB transformed per gram of Pd per minute, measured by the amount of 2-PCB dechlorinated in the initial 20 min, was employed to determine the catalytic performance [30]. From Fig. 4, the highest catalytic activity was at the 1.43 wt.% Pd loading. Before reaching it, the rapid increase in 2-PCB conversion was considered due to greater surface concentration or dispersion of Pd islets (Fig. 1). With increase in Pd loading, Pd crystallites grew larger and then agglomerated, which
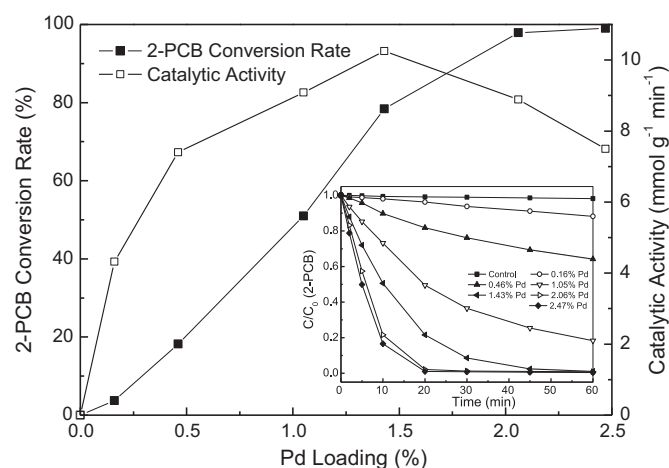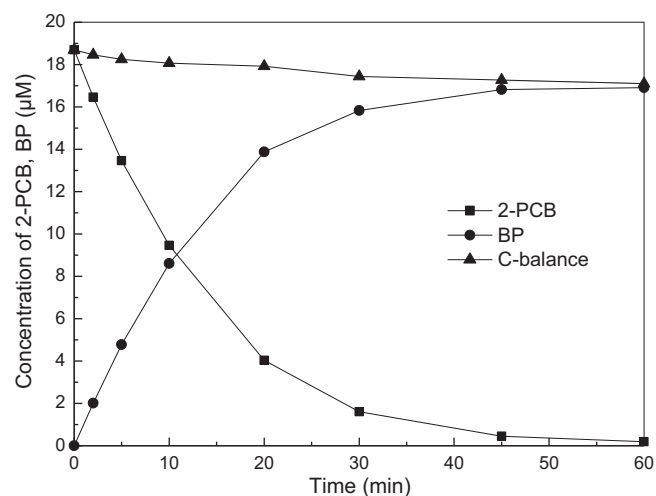

Fig. 5. Carbon-mole balance for the HDC of 18.7 μM 2-PCB using Pd/Al particles with 1.43 wt.% Pd loading (reaction parameters: 18.7 μM 2-PCB, 5 g/L metal particles, initial pH = 3.0 ± 0.1, 180 rpm, reaction time = 60 min, T = 25 ± 2 °C).

inhibited further increase in the surface concentration of Pd and resulted in a relative constant 2-PCB conversion at 2.06–2.47 wt.% Pd loadings. The smaller Pd crystallites may lead to higher HDC efficiency; however, the Pd clusters were not favorable because only the outside surface could serve as active sites.
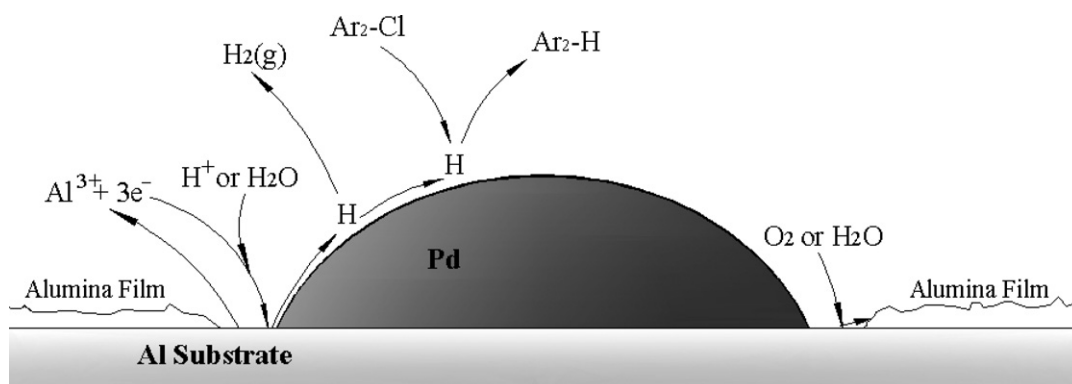

Fig. 6. Proposed mechanism for the HDC of 2-PCB on Pd/Al bimetallic particle in acidic solution.

3.6. HDC mechanism

2-PCB with an initial concentration of 18.7 μM was completely dechlorinated into BP within 60 min by the 1.43 wt.% Pd/Al particles. Its carbon balance curve is illustrated in Fig. 5. Lower than 10% deficit in the carbon mass balance shows that HDC is the major reaction. The loss of mass may be attributed to the further undetectable hydrogenation of BP and/or the loss of the compounds via irreversible adsorption in the bimetallic system.

According to the S_{BET} results, the surface area of the Al particles (S_{BET}: 0.18 m^2/g) is much smaller than that of the Pd/Al particles with 1.43 wt.% Pd loading (S_{BET}: 16.53 m^2/g). It is speculated that the main adsorbed species were located on the large surface area of Pd particles. Pd-free Al particles exhibited no activity for 2-PCB conversion. Therefore, the direct conversion of 2-PCB to BP can be rationalized with the HDC occurring mainly at the palladium surface.

Consulting the reported bimetallic HDC mechanism [7,10,21,25], the HDC mechanism on the Pd/Al bimetallic interface is proposed in Fig. 6. Firstly, H$^+$ or H$_2$O is spontaneously reduced into [H] at the exposed Al substrate on the edge of a Pd particle. The [H] then diffuses to other surface area in the Pd particle by hydrogen spillover. The diffusion processes provide a wide access to the total available surface than the original hydrogen evolution area so that [H] can react with 2-PCB adsorbed on the Pd surface. On the other hand, quick formation of a protective oxide layer inhibits the reductive capacity of Al element when it contacts with O$_2$ or H$_2$O. However, the palladized Al particles become sensitive to the pH change in solution, resulting from the formation of a galvanic couple between Pd catalyst and Al substrate. As a result, the pH can effectively make a compromise between Al corrosion and alumina formation and further maintain the HDC efficiency and long-term activity of Pd/Al bimetallic particles. Therefore, the highly efficient conversion of 2-PCB on the Pd/Al particles may be attributed to the creation, maintenance, and regeneration of catalytic activity with adjusting pH.

4. Conclusions

This study investigated the catalytic HDC of 2-PCB in aqueous solution with Pd-loaded bimetal particles including the substrates of Mg, Al, Mn, Zn, Fe, Sn, and Cu. It was found that Pd/Al particles presented the highest stability and relatively high reactivity to dechlorinate 2-PCB in acid aqueous solution among these bimetals. The solution pH and Pd loadings have the important influence on the HDC efficiency. 2-PCB with an initial concentration of 18.7 μM was completely dechlorinated into BP within 60 min by the 1.43 wt.% Pd content on Al particles at initial pH 3.0. From a practical viewpoint, results from this study provide information useful for the new bimetallic material in acid solution on the basis of reactivity, stability, and cost efficiency. Al substrate is potentially available for treatment of aqueous chloroorganics because of enhanced stability and low cost, which likely becomes an alternative candidate of ZVI as the support of Pd catalyst, especially in acidic wastewater. The understanding obtained from this work may lead our future study to investigate the technical and economic feasibility of HDC in acidic wastewater containing chloroorganics using some low-cost scrap aluminium and Al bimetals.

Acknowledgments

References

[1] F. Alonso, I.P. Beletskaya, M. Yus, Metal-mediated reductive hydrodehalogenation of organic halides, Chem. Rev. 102 (2002) 4009–4091.

[2] S. Ordonez, H. Sastre, F.V. Diez, Hydrodechlorination of aliphatic organochlorinated compounds over commercial hydrogenation catalysts, Appl. Catal. B: Environ. 25 (2000) 49–58.

[3] H.L. Lien, W.X. Zhang, Nanoscale Pd/Fe bimetallic particles: catalytic effects of palladium on hydrodechlorination, Appl. Catal. B: Environ. 77 (2007) 110–116.

[4] M.O. Nutt, J.B. Hughes, M.S. Wong, Designing Pd-on-Au bimetallic nanoparticle catalysts for trichloroethene hydrodechlorination, Environ. Sci. Technol. 39 (2005) 1346–1353.

[5] G. Yuan, M.A. Keane, Liquid phase hydrodechlorination of chlorophenols over Pd/C and Pd/Al$_2$O$_3$: a consideration of HCl/catalyst interactions and solution pH effects, Appl. Catal. B: Environ. 52 (2004) 301–314.

[6] C.H. Xia, Y. Liu, S.W. Zhou, C.Y. Yang, S.J. Liu, J. Xu, J.B. Yu, J.P. Chen, X.M. Liang, The Pd-catalyzed hydrodechlorination of chlorophenols in aqueous solutions under mild conditions: a promising approach to practical use in wastewater, J. Hazard. Mater. 169 (2009) 1029–1033.

[7] W.X. Zhang, C.B. Wang, H.L. Lien, Treatment of chlorinated organic contaminants with nanoscale bimetallic particles, Catal. Today 40 (1998) 387–395.

[8] D.W. Elliott, W.X. Zhang, Field assessment of nanoscale biometallic particles for groundwater treatment, Environ. Sci. Technol. 35 (2001) 4922–4926.

[9] C. Grittini, M. Malcomson, Q. Fernando, N. Korte, Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system, Environ. Sci. Technol. 29 (1995) 2898–2900.

[10] G.N. Jovanovic, P. Znidarsic-Plazl, P. Sakrittichai, K. Al-Khaldi, Dechlorination of p-chlorophenol in a microreactor with bimetallic Pd/Fe catalyst, Ind. Eng. Chem. Res. 44 (2005) 5099–5106.

[11] V. Nagpal, A.D. Bokare, R.C. Chikate, C.V. Rode, K.M. Paknikar, Reductive dechlorination of gamma-hexachlorocyclohexane using Fe–Pd bimetallic nanoparticles, J. Hazard. Mater. 175 (2010) 680–687.

[12] Z. Zhang, Q.H. Shen, N. Cissoko, J.J. Wo, X.H. Xu, Catalytic dechlorination of 2,4-dichlorophenol by Pd/Fe bimetallic nanoparticles in the presence of humic acid, J. Hazard. Mater. 182 (2010) 252–258.

[13] H. Hildebrand, K. Mackenzie, F.D. Kopinke, Highly active Pd-on-Magnetite nanocatalysts for aqueous phase hydrodechlorination reactions, Environ. Sci. Technol. 43 (2009) 3254–3259.

[14] C.L. Chun, D.R. Baer, D.W. Matson, J.E. Amonette, R.L. Penn, Characterization and reactivity of iron nanoparticles prepared with added Cu, Pd, and Ni, Environ. Sci. Technol. 44 (2010) 5079–5085.

[15] B.W. Zhu, T.T. Lim, Catalytic reduction of Chlorobenzenes with Pd/Fe nanoparticles: reactive sites, catalyst stability, particle aging, and regeneration, Environ. Sci. Technol. 41 (2007) 7523–7529.

[16] F. He, D.Y. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water, Environ. Sci. Technol. 39 (2005) 3314–3320.

[17] J.J. Zhan, B. Sunkara, L. Le, V.T. John, J.B. He, G.L. McPherson, G. Piringer, Y.F. Lu, Multifunctional colloidal particles for in situ remediation of chlorinated hydrocarbons, Environ. Sci. Technol. 43 (2009) 8616–8621.

[18] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, Enhanced corrosion-based Pd/Mg bimetallic systems for dechlorination of PCBs, Environ. Sci. Technol. 41 (2007) 3722–3727.

[19] J.H. Choi, Y.H. Kim, Reduction of 2,4,6-trichlorophenol with zero-valent zinc and catalyzed zinc, J. Hazard. Mater. 166 (2009) 984–991.

[20] C.J. Lin, Y.H. Liou, S.L. Lo, Supported Pd/Sn bimetallic nanoparticles for reductive dechlorination of aqueous trichloroethylene, Chemosphere 74 (2009) 314–319.

[21] B. Yang, G. Yu, J. Huang, Electrocatalytic hydrodechlorination of 2,4,5-trichlorobiphenyl on a palladium-modified nickel foam cathode, Environ. Sci. Technol. 41 (2007) 7503–7508.

[22] B. Yang, S. Wang, G. Yu, Y.R. Zhou, Electrocatalytic reduction of 2-chlorobiphenyl in contaminated water using palladium-modified electrode, Sep. Purif. Technol. 63 (2008) 353–359.

[23] D.M. Cwiertny, S.J. Bransfield, K.J.T. Livi, D.H. Fairbrother, A.L. Roberts, Exploring the influence of granular iron additives on 1,1,1-trichloroethane reduction, Environ. Sci. Technol. 40 (2006) 6837–6843.

[24] J.H. Kim, P.G. Tratnyek, Y.S. Chang, Rapid dechlorination of polychlorinated dibenzo-p-dioxins by bimetallic and nanosized zerovalent iron, Environ. Sci. Technol. 42 (2008) 4106–4112.

[25] I.F. Cheng, Q. Fernando, N. Korte, Electrochemical dechlorination of 4-chlorophenol to phenol, Environ. Sci. Technol. 31 (1997) 1074–1078.

[26] R. Cheng, W. Zhou, J.L. Wang, D.D. Qi, L. Guo, W.X. Zhang, Y. Qian, Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: role of nano-Ni and its size effect, J. Hazard. Mater. 180 (2010) 79–85.

[27] N.R. Zhu, H.W. Luan, S.H. Yuan, J. Chen, X.H. Wu, L.L. Wang, Effective dechlorination of HCB by nanoscale Cu/Fe particles, J. Hazard. Mater. 176 (2010) 1101–1105.

[28] W.L. Yan, A.A. Herzing, X.Q. Li, C.J. Kiely, W.X. Zhang, Structural evolution of Pd-doped nanoscale zero-valent iron (nZVI) in aqueous media and implications for particle aging and reactivity, Environ. Sci. Technol. 44 (2010) 4288–4294.

[29] A.D. Bokare, W. Choi, Zero-valent aluminum for oxidative degradation of aqueous organic pollutants, Environ. Sci. Technol. 43 (2009) 7130–7135.

[30] S. Wang, B. Yang, T.T. Zhang, G. Yu, S.B. Deng, J. Huang, Catalytic hydrodechlorination of 4-chlorophenol in an aqueous solution with Pd/Ni catalyst and formic acid, Ind. Eng. Chem. Res. 49 (2010) 4561–4565.

[31] Y. Fang, S.R. Al-Abed, Correlation of 2-chlorobiphenyl dechlorination by Fe/Pd with iron corrosion at different pH, Environ. Sci. Technol. 42 (2008) 6942–6948.