



The influence of ion effects on the Pd-catalyzed hydrodechlorination of 4-chlorophenol in aqueous solutions

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ABSTRACT

The aim of this work was to study the influence of ions on the hydrodechlorination of 4-chlorophenol in water over 5% Pd/C catalyst. It was found that the presence of some ions such as Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, Cl⁻, Br⁻, CO₃²⁻, HCO₃⁻, SO₄²⁻ and NO₃⁻ etc., did not show negative effects on catalyst activity in the hydrogenation process of 4-chlorophenol in aqueous solutions. But, when Fe²⁺, Fe³⁺, Cu²⁺, Zn²⁺, Ni²⁺ and Pb²⁺ etc., were present in water, they could reduce the activity of Pd/C and even led Pd/C to deactivate.

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1. Introduction

Heterogeneously catalytic hydrogenation is a convenient method for the dehalogenation of aryl halides in organic synthesis because of its experimental simplicity, good yields and high purity of products [1]. In recent years, because the disposal of chlorinated organic waste becomes a serious environmental problem, the catalytic hydrogenolysis of organochlorines has been developed an effective, low cost and environmentally friendly procedure in the environmental catalysis, which has been applied to different types of chlorinated compounds such as chlorobenzenes, chlorophenols, halogenated hydrocarbons, polychlorobiphenyls (PCBs), dioxins etc., leading to their conversion into much less harmful substances under relatively mild conditions [2–11].

For most hydrogenation reactions of aromatic halides in liquid phase in reported literatures, organic solvents were usually used as the reaction mediums [1,12,13]. Compared to organic solvents, water is a cheaper, safer and more environmentally amicable reaction medium. In our group, we have investigated the hydrodehalogenation of aromatic halides, PCBs and dioxins in aqueous solutions and water–alcohol solutions [14–19]. It was found that the addition of water greatly improved the dechlorination rates of the catalytic hydrodechlorination of aromatic halides in organic

solvents [16–18] and the catalyst showed higher activities in aqueous solutions than organic solvents [14–19]. Furthermore, it is similar to practical process of the hydrotreatment of chlorinated organic wastewater to study the hydrodechlorination of organochlorines in aqueous solutions.

For the industrial organochlorinated wastewater, it is well known that the compositions are usually very complex. Besides chlorinated organic compounds, others organic compounds and various salts are commonly encountered in the catalytic hydrodechlorination [20]. For example, chlorinated organic wastes often contain some chlorides such as sodium chloride and HCl. The presence of such Cl-containing salts could change the activity of the catalyst [21,22]. There is so far a scarce literature on the influence of inorganic salts or ions on the catalytic hydrodechlorination in aqueous solutions in the published literatures. Therefore, it was desirable to study the effect of the presence of soluble inorganic salts on catalytic hydrodechlorination of 4-chlorophenol in water. These studies would provide an insight into the hydrodechlorination process to treat aqueous waste stream containing chlorophenols and other organochlorines by catalytic hydrotreatment in practical applications.

2. Experimental

Five percentage of Pd/C catalyst used in experiments was purchased from C&P Chemical Co., China. The catalyst was not

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pre-treated before experiments and only hermetically-sealed kept in a desiccator. 4-Chlorophenol (4-CP) (purity $\geq 98\%$) was obtained from Aldrich. The inorganic salts and NaOH, used in the experiments, were analytical reagents and were supplied by Sinopharm Chemical Reagent Co., Ltds. Water used in the reaction was deionized. The purities of hydrogen and nitrogen used in the experiments were more than 99.99%.

The reaction was carried out in a three-necked flask. Under atmospheric pressure, 4-CP (510 mg, 4.0 mmol), NaOH (168 mg, 4.2 mmol) and 5% Pd/C (20 mg, 9.5×10^{-3} mmol) were added into 50 ml water, respectively. At room temperature, 4-CP was treated with hydrogen gas over 5% Pd/C in aqueous solutions. In order to investigate the effects of ions on the dechlorination reactions, some soluble inorganic salts were added to the reaction systems. The intermediate products in the hydrodechlorination reaction of 4-CP were determined by GC/MS [14]. The compositions of the reaction system were analyzed by GC-FID.

3. Results and discussion

HCl, produced in the hydrodechlorination of chlorinated organic compounds, is usually neutralized and eliminated by a base. Chloride ion and HCl has been shown to inhibit the activity of Pd and Rh catalyst in the gas-phase and liquid-phase dechlorination of organic chlorides [23–25]. In the hydrodechlorination of 4-CP in water, NaOH was used to eliminate HCl and stoichiometric NaCl was simultaneously produced. Here, the effect of NaCl on the hydrodechlorination of 4-CP in water was investigated firstly.

It was observed in Table 1, whether adding NaCl or not, 4-CP was completely hydrodechlorinated within 35 min (Entry 1–3). Even though the amount of NaCl (1.0 g) adding to water was 50 times higher than that of the catalyst, the rate of dechlorination was almost coincident with that not adding NaCl in water (Entry 10). It means that the presence of the excess amount of NaCl had no influence on the activity of Pd/C in the hydrodechlorination of 4-CP in water. This was possibly due to that NaCl could completely ionize to produce sodium ion (Na^+) and chlorine ion (Cl^-) in water, which could not accumulate on the catalyst surface and the support [14]. But in organic solvents, NaCl formed in the hydrogenation of aromatic chlorides could result in a gradual decrease in the activity of the catalyst due to the accumulation of sodium chloride on its surface [22]. Additionally, it also implies that Na^+ and Cl^- were impossible to occupy the catalyst active sites to lead the catalyst to the deactivation in aqueous solutions. In order to further confirm the effects of the presence of the excess amount of NaCl on the activity of the catalyst, 5% Pd/C was recovered and reused three times under the same experimental conditions. At

the beginning of every recycling reaction, 0.1 g NaCl was added into water. 4-CP was completely hydrogenated within 35 min in every recycling reaction and the activity of Pd/C was hardly changed in batch reactor in recycling reactions. The results of the recycle experiments were further proved that the excess presence of Na^+ or Cl^- could not lead to the decline of the catalyst activity in the dechlorination of chlorinated organic compounds in water.

In Table 1, it was also found that the presence of NaBr did not effect the dechlorination of 4-CP in water (Entry 4). However, when 0.1 g NaI was added into water, only 80% 4-CP was hydrodechlorinated within 60 min (Entry 5). This illustrates that NaI had a disadvantageous influence on the activity of Pd/C. According to some literatures [26,27], it was due to high affinity of iodide anion to Pd to result in the inhibition effect.

Catalyst poisoning by HS^- and SO_3^{2-} in aqueous solutions has been reported [28,29]. The presence of 66 mg/l HS^- or 30 mg/l SO_3^{2-} in aqueous solutions resulted in complete catalyst deactivation in the dechlorination reaction. Fig. 1 shows the catalyst activity in the presence of high concentrations of other acid group ions, such as CO_3^{2-} , HCO_3^- , NO_3^- , and SO_4^{2-} etc., in the hydrodechlorination of 4-CP in water. The presences of NO_3^- (2.0 g/l) and SO_4^{2-} (2.0 g/l) had no negative effect on the dechlorination of 4-CP compared to the control experiment in water. This was due to NO_3^- or SO_4^{2-} did not appear to compete for the catalyst active sites with 4-CP and molecular hydrogen. Additionally, due to the presence in the ionic form in water, they did not deposit on the surface of the catalyst and block the pores of carbon support. The effects of dissolved CO_3^{2-} and HCO_3^- on the catalyst activity were also shown in Fig. 1. Comparison with the control reaction in water reveals that the presence of CO_3^{2-} (2.0 g/l) or HCO_3^- (2.0 g/l) obviously promoted the catalyst activity and accelerated the reaction, which probably resulted from the basicity of CO_3^{2-} and HCO_3^- . The presence of CO_3^{2-} or HCO_3^- accelerated the elimination of HCl thereby inhibiting HCl poisoning and improving the activity of Pd/C. The bases are often used to enhance the catalyst activity in the catalytic hydrodehalogenation reactions by neutralizing hydrogen halides produced [12,18].

In Table 1, it was also investigated the influence of alkali metal or alkali earth ions on the dechlorination of 4-CP in water. Compared to the control experiment (Entry 10), the presence of K^+ , NH_4^+ , Mg^{2+} or Ca^{2+} almost did not effect the dechlorination of 4-CP in water (Entry 6–9).

Fig. 2 showed the effects of some transitional metal ions, such as Cu^{2+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , Pb^{2+} and Zn^{2+} etc. It was clearly indicated

Table 1
The effects of ions on the activity of Pd/C in water^a.

Entry	Salts	Amount (g)	TOF (min^{-1})		DC ^c (%)
			15 min	25 min	
1	NaCl	0.01	6.9	7.2	100
2	NaCl	0.1	7.0	7.1	100
3	NaCl	1.0	6.8	7.0	100
4	NaBr	0.1	6.8	7.3	100
5	NaI ^b	0.1	3.1	2.7	80
6	KCl	0.1	7.0	7.2	100
7	NH_4Cl	0.1	6.8	7.1	100
8	CaCl_2	0.1	6.9	7.0	100
9	MgCl_2	0.1	6.8	7.0	99
10	Control	–	6.9	7.1	100

^a Reaction conditions: The mixtures were hydrogenated at room temperature under atmospheric pressure in aqueous solutions in 35 min.

^b Reaction time: 60 min.

^c DC: Dechlorination.

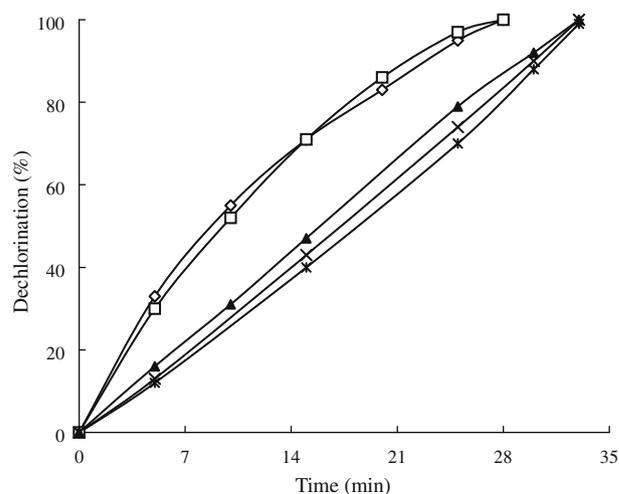


Fig. 1. The effects of the acid group ions (\blacktriangle) H_2O , (\square) NaHCO_3 , (\diamond) Na_2CO_3 , ($*$) Na_2SO_4 , (\times) NaNO_3 .

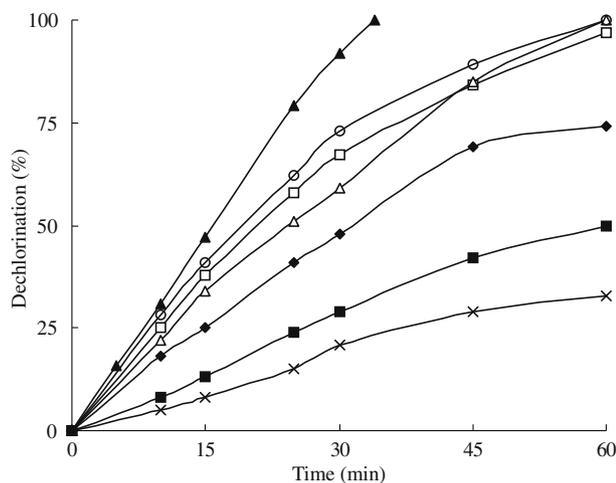


Fig. 2. The effects of transitional metal ions in water (▲) H₂O, (○) Fe(NO₃)₃, (◻) NiCl₂, (△) FeCl₂, (◆) CuCl₂, (■) Zn(NO₃)₂, (×) Pb(NO₃)₂.

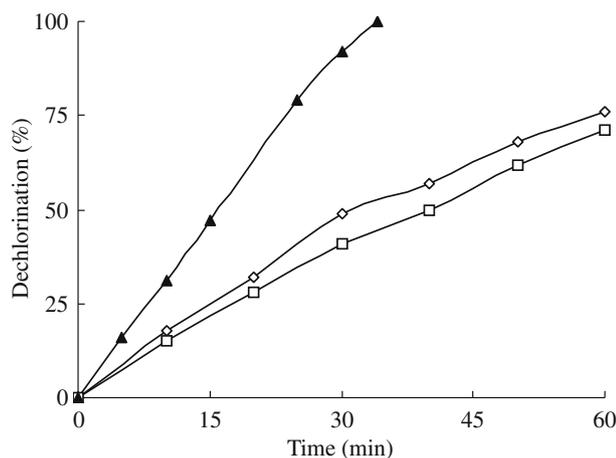


Fig. 3. The effects of trace amount of Cu²⁺ and Zn²⁺ on the hydrodechlorination of 4-CP (▲) H₂O, (◇) 50 ppm CuCl₂, (◻) 50 ppm Zn(NO₃)₂.

that the presences of transitional metal ions were disadvantageous to the dechlorination of 4-CP. Adding 0.03 g CuCl₂, Pb(NO₃)₂ or Zn(NO₃)₂ to the reaction system respectively, only about 75%, 50% and 35% 4-CP were hydrogenated after 60 min, however 4-CP was completely reacted just within 35 min when they were not present in water. Compared with CuCl₂, Pb(NO₃)₂ or Zn(NO₃)₂, the effects of NiCl₂, FeCl₂ or Fe(NO₃)₃ were weak, but the complete reactions still needed about 60 min.

In addition, even though the trace of amount (50 ppm) of Cu²⁺ or Zn²⁺ was present in water, the effects on the hydrodechlorination of 4-CP were considerably remarkable (Fig. 3). Both of the conversions of 4-CP were no more than 80% in 60 min.

All results mentioned above demonstrated that transitional metal ions inhibited the activity of the catalyst and decreased the rate of the dechlorination reaction. It was possibly due to the adsorption of transitional metal ions on the active sites of Pd/C to lead to the catalyst to poison. Maxted [30] had ever reported the poisoning of the metallic catalysts in detail. The authors claimed that the toxicity or nontoxicity of a metallic ion connected with its *d*-orbitals and *d*-electrons. Heavy metal ions, such as Fe²⁺, Fe³⁺,

Co²⁺, Ni²⁺, Pb²⁺, Mn²⁺, Cu²⁺, Cu⁺, Ag⁺ and Zn²⁺ etc., are highly toxic to the Pd and Pt catalysts because their *d*-electrons are taking part in the intermetallic bonds between the toxic metal and the catalyst. The lighter metal ions, such as Li⁺, Na⁺, K⁺, Rb⁺, Mg²⁺, Ca²⁺ and Al³⁺ etc., are not poisonous because they have no *d*-electron to form the bond between the metal and the catalyst.

4. Conclusions

In this work, we report the influences of soluble inorganic salts or ions on the hydrodechlorination of 4-CP in aqueous solutions using a palladium–carbon catalyst.

The presences of high concentrations of basic metal ions (Na⁺, K⁺) and alkali earth metal ions (Mg²⁺, Ca²⁺) did not effect the dechlorination reactions. But, some transitional metal ions, such as Fe²⁺, Cu²⁺, Pb²⁺, Zn²⁺ and Ni²⁺, could reduce the activity of Pd/C and even led Pd/C to deactivate, which possibly resulted from the ionic adsorption on the active sites or the deposition in metallic form on the surface of the catalyst. Some negative ions, such as Cl[−], Br[−], CO₃^{2−}, HCO₃[−], SO₄^{2−} and NO₃[−], did not inhibit the activity of the catalyst in aqueous solutions; however, I[−] had some disadvantageous influences on the hydrodechlorination of 4-CP.

These results are of considerable significance in actual hydro-treatment of industrial chlorinated organic wastewaters with Pd/C.

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References

- [1] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 102 (2002) 4009.
- [2] J.B. Hoke, G.A. Gramiccioni, E.N. Balko, Appl. Catal. B: Environ. 1 (1992) 285.
- [3] M.A. Keane, R. Larsson, Catal. Commun. 9 (2008) 333.
- [4] S. Zinovyev, A. Shelepchikov, P. Tundo, Appl. Catal. B: Environ. 72 (2007) 289.
- [5] E. Lopez, S. Ordonez, F.V. Diez, Appl. Catal. B: Environ. 62 (2006) 57.
- [6] J.M. Moreno, M.A. Aramendia, A. Marinas, J.M. Marinas, F.J. Urbano, Appl. Catal. B: Environ. 76 (2007) 34.
- [7] P. Tundo, A. Perosa, M. Selva, S. Zinovyev, Appl. Catal. B: Environ. 32 (2001) L1.
- [8] Y. Ukisu, T. Miyadera, Appl. Catal. B: Environ. 40 (2003) 141.
- [9] C. Schueth, M. Reinhard, Appl. Catal. B: Environ. 18 (1998) 215.
- [10] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodríguez, Appl. Catal. B: Environ. 78 (2008) 259.
- [11] F. Murena, F. Gioia, Appl. Catal. B: Environ. 38 (2002) 39.
- [12] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A 173 (2001) 329.
- [13] M.A. Keane, J. Chem. Technol. Biotechnol. 80 (2005) 1211.
- [14] C.H. Xia, Y. Liu, J.B. Yu, W. Qin, J. Xu, X.M. Liang, Catal. Commun. 10 (2009) 456.
- [15] C.H. Xia, J. Xu, W.Z. Wu, X.M. Liang, Catal. Commun. 5 (2004) 383.
- [16] Z.J. Yang, C.H. Xia, Q. Zhang, J.P. Chen, W.Z. Wu, X.M. Liang, Waste Manage. 27 (2007) 588.
- [17] Z.J. Yang, C.H. Xia, Q. Zhang, J.P. Chen, W.Z. Wu, X.M. Liang, A. Kettrup, Fresenius Environ. Bull. 15 (2006) 86.
- [18] C.H. Xia, J. Xu, W.Z. Wu, Q. Luo, J.P. Chen, Q. Zhang, X.M. Liang, Appl. Catal. B: Environ. 45 (2003) 281.
- [19] F. Zhang, J.P. Chen, H. Zhang, Y.W. Ni, X.M. Liang, Chemosphere 68 (2007) 1716.
- [20] P.D. Vaidya, V.V. Mahajani, Appl. Catal. B: Environ. 51 (2004) 21.
- [21] M.A. Aramendia, R. Burch, I.M. Garcia, A. Marinas, J.M. Marinas, B.W.L. Southward, F.J. Urbano, Appl. Catal. B: Environ. 31 (2001) 163.
- [22] Y. Ukisu, S. Kameoka, T. Miyadera, Appl. Catal. B: Environ. 27 (2000) 97.
- [23] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, F. Lafont, A. Marinas, J.M. Marinas, F.J. Urbano, J. Mol. Catal. A 184 (2002) 237.
- [24] G. Del Angel, J.L. Benitez, J. Mol. Catal. A 165 (2001) 9.
- [25] B. Coq, G. Ferrat, F. Figueras, J. Catal. 101 (1986) 434.
- [26] S.S. Zinovyev, A. Perosa, P. Tundo, J. Catal. 226 (2004) 9.
- [27] K. Mackenzie, H. Frenzel, F.D. Kopinke, Appl. Catal. B: Environ. 63 (2006) 161.
- [28] C. Schueth, S. Disser, F. Schueth, M. Reinhard, Appl. Catal. B: Environ. 28 (2000) 147.
- [29] C.G. Schreier, M. Reinhard, Chemosphere 31 (1995) 3475.
- [30] E.B. Maxted, Adv. Catal. 3 (1951) 129.