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Complete Hydrodechlorination of DDT and Its Derivatives Using a Hydroxyapatite-supported Pd Nanoparticle Catalyst

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Complete hydrodechlorination of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and its derivatives 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (DDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD) was achieved using a hydroxyapatite-supported Pd nanoparticle catalyst (Pd^{0}HAP) in the presence of molecular hydrogen under mild reaction conditions. The catalytic activity of Pd^{0}HAP was significantly higher than those of previously reported Pd catalysts.

Chlorinated organic compounds are manufactured on a large scale and used in a variety of chemical industries. However, they have an often fatal impact on the environment and living organisms.[1] The most infamous of these compounds, 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT), was widely adopted as a pesticide and insecticide, particularly for the elimination of mosquitoes in malaria-infested areas of the world, due to its high effectiveness and low cost. Nowadays, many countries have prohibited the use of DDT because of its toxicity and chemical stability, which lead to water pollution and soil contamination.[2]

Much attention has been given to the disposal of large quantities of DDT, and many approaches to complete dechlorination of DDT—including photochemical,[3] electro-chemical,[4] biochemical,[5] and mechanochemical[6] reactions—have been developed. However, most of these processes require severe conditions and special equipment. In order to achieve the disposal of DDT using green and sustainable technology, the development of an efficient catalytic system for decomposition of DDT under mild conditions is desirable.

Catalytic hydrodechlorination using molecular hydrogen is one of the most promising and greenest methodologies for decomposition of DDT without the formation of persistent organic pollutants such as dioxins and PCBs.[7] Hydrodechlorination of DDT using Pd catalysts has been studied for many years,[8] however previously reported catalyst systems suffered from low activity, and complete dechlorination of DDT was not achieved.

We recently developed novel heterogeneous catalysts using hydroxyapatite (HAP),[9] $Ca_{10}(PO_4)_6(OH)_2$, as a macroligand for catalytically active species in various environmentally benign organic transformations.[10] In particular, the HAP-bound Pd nanoparticle catalyst (Pd^{0}HAP)[11a] and magnetically functionalized Pd^{0}HAP–γ-Fe_2O_3[11b] acted as efficient heterogeneous catalysts for complete hydrodechlorination of aryl chlorides and benzyl chlorides under atmospheric pressure of molecular hydrogen. In this paper, we demonstrate complete dechlorination of DDT and its derivatives catalyzed by Pd^{0}HAP using molecular hydrogen.

The HAP-supported Pd(II) complex (Pd^{II}HAP) was synthesized according to a procedure described in a previous paper.[12] Powdered HAP was stirred in an acetone solution of $PdCl_2(PhCN)_2$ at room temperature for 3 h, and the resulting slurry was filtered, washed with acetone and dried under vacuum, affording Pd^{II}HAP (2.01 g, Pd content: 0.02 mmol g^{-1}) as a pale yellow powder. Characterization of Pd^{II}HAP by elemental analysis, XPS, EDX, and Pd K-edge XAFS showed that a monomeric $PdCl_2$ species was grafted by chemisorption onto the HAP surface. Next, the HAP-supported Pd nanoparticle catalyst Pd^{0}HAP was prepared as follows: Pd^{II}HAP (0.2 g) was placed in a stainless steel autoclave with a glass lining (100 mL) and reduced with H_2 (1 atm) in the presence of Cs_2CO_3 (1.5 mmol) and 2-propanol (6 mL) at 60 °C for 30 min to form a gray powder. For analysis, the Pd^{0}HAP catalyst was separated by filtration and characterized by field-emission scanning electron microscopy (FE-SEM). Figure 1a shows the formation of Pd nanoparticles with a mean diameter (d) of 4 nm and a narrow size distribution (standard deviation: $\sigma = 0.30$ nm, $\sigma/d = 7.5\%$) on the HAP surface.

For the hydrodechlorination reaction, DDT (0.2 mmol) was added and the vessel was repressurized with H_2. The results obtained are shown in Table 1. After 10 h, the completely dechlorinated product 1,1-diphenylethane (**1**) was obtained in quantitative yield.[13] The reaction rate increased with increasing H_2 pressure (Entries 1–4); complete dechlorination to **1** was achieved in 1 h under 10 atm of H_2 (Entry 4). When the reaction was carried out without Cs_2CO_3, **1** was obtained in extremely low yield (Entry 5), and in the absence of the Pd^{0}HAP catalyst, DDT was not converted at all (Entry 6). Various bases were screened as acceptors of HCl generated in the hydrodechlorination reaction: the use of Na_2CO_3, K_2CO_3, and triethylamine resulted in low yields of **1** (Entries 7–9). Among the various solvents examined, 2-propanol was found to be optimal, and DMF also provided a good yield of **1** (Entries 4 and 10). In contrast, low yields of **1** were obtained using other solvents such

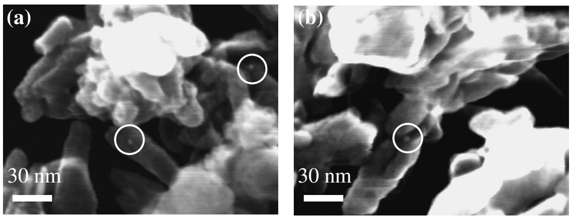
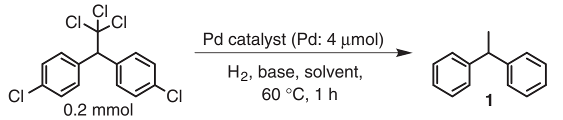


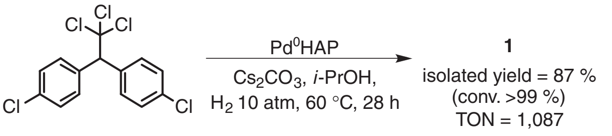
Figure 1. FE-SEM photographs of Pd nanoparticles on Pd^{0}HAP (a) after pretreatment with H_2 and (b) after hydrodechlorination of DDT.

Table 1. Dechlorination of DDT under various conditions[a]



Entry	H$_2$ /atm	Base	Solvent	Time /h	Conv. /%[b]	Yield of **1**/%[b]
1	1	Cs_2CO_3	*i*-PrOH	10	>99	>99
2	4	Cs_2CO_3	*i*-PrOH	5	>99	>99
3	7	Cs_2CO_3	*i*-PrOH	2	>99	>99
4	10	Cs_2CO_3	*i*-PrOH	1	>99	>99
5	10	None	*i*-PrOH	1	99	4
6[c]	10	Cs_2CO_3	*i*-PrOH	1	0	0
7	10	Na_2CO_3	*i*-PrOH	1	99	54
8	10	K_2CO_3	*i*-PrOH	1	>99	85
9[d]	10	NEt_3	*i*-PrOH	1	>99	32
10	10	Cs_2CO_3	DMF	1	>99	72
11	10	Cs_2CO_3	MeOH	1	16	<1
12	10	Cs_2CO_3	EtOH	1	76	3
13	10	Cs_2CO_3	Me-*c*-Hex[e]	1	74	4
14	10	Cs_2CO_3	Anisole	1	31	2
15[f]	10	Cs_2CO_3	*i*-PrOH	1	>99	19
16[g]	10	Cs_2CO_3	*i*-PrOH	1	>99	16

[a] Base (1.5 mmol), solvent (6 mL). [b] Determined by GC using an internal standard. [c] Without Pd^{0}HAP catalyst. [d] NEt_3 (3 mmol). [e] Methylcyclohexane. [f] 5 wt % Pd/C was used as a catalyst. [g] 5 wt % Pd/Al_2O_3 was used as a catalyst.

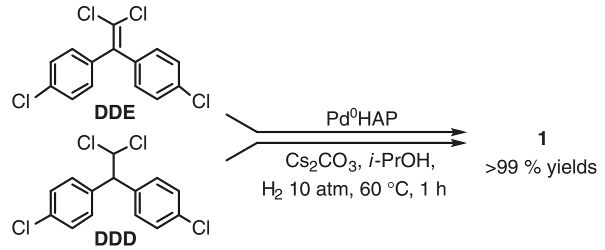


Scheme 1. Dechlorination of DDT using Pd^{0}HAP catalyst. Reaction conditions: DDT (1 mmol), Pd^{0}HAP (Pd: 4 μmol), Cs_2CO_3 (7.5 mmol), and *i*-PrOH (12 mL).

as methanol, ethanol, methylcyclohexane, and anisole (Entries 11–14). Notably, the catalytic activity of Pd^{0}HAP for complete dechlorination to **1** was significantly higher than those of commercially available heterogeneous Pd catalysts (Entries 15 and 16).[14]

As highlighted in Scheme 1, the Pd^{0}HAP catalyst (Pd: 0.08 mol % relative to chlorine) converted 0.35 g (1 mmol) of DDT to give **1** in 87% isolated yield (0.16 g) under 10 atm of H_2 at 60 °C for 28 h; the turnover number (TON, mol of Cl atoms removed per mol Pd content) reached 1087. This TON value was much greater than those of previously reported catalytic systems for dechlorination of DDT, such as 5 wt % Pd on carbon/KOH (TON = 175),[8a] 10 wt % Pd on carbon/NEt_3 (TON = 149),[8b] sol–gel entrapped Pd[Rh(cod)Cl]$_2$ (TON = 90),[8c] and 5 wt % Pd on carbon/NaOH (TON = 53).[8d] It can be seen that the surface-supported Pd nanoparticles react efficiently with bulky DDT molecules because of the nonporous structure of HAP.[15]

Moreover, the Pd^{0}HAP catalyst showed good reusability without significant loss of activity. Upon complete dechlorination of DDT, portions of DDT and Cs_2CO_3 were successively added to the resulting mixture and further treated under identical reaction conditions. The second dechlorination of DDT proceeded at a similar rate to the fresh reaction, affording a 92% yield of **1**. It was concluded that the Pd^{0}HAP-based catalytic hydrodechlorination system provided a simple and practical degradative treatment of DDT.



Scheme 2. Pd^{0}HAP-catalyzed dechlorination of DDT metabolites using H_2. Reaction conditions: DDE or DDD (0.25 mmol), Pd^{0}HAP (Pd: 4 μmol), Cs_2CO_3 (1.5 equiv relative to Cl atom), and *i*-PrOH (6 mL).

FE-SEM analysis of the spent Pd^{0}HAP catalyst showed that the average size of the Pd nanoparticles on the HAP surface was similar to that of the fresh catalyst, and there was no apparent aggregation (Figure 1b). Inductively coupled plasma (ICP) analysis confirmed that no palladium had leached into the 2-propanol solution after dechlorination of DDT (<0.1 ppm). These results reveal that the HAP support was effective in preventing both leaching and agglomeration of Pd nanoparticles, probably due to its strong adsorption capacity. This is consistent with the retention of high catalytic activity in the recycling experiments.

The Pd^{0}HAP catalyst was further applied to the dechlorination of the DDT derivatives 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (DDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD), which are known metabolites of DDT found in the environment (Scheme 2). These substrates, containing aliphatic sp^2 and sp^3 C–Cl bonds, respectively, gave **1** quantitatively in 1 h under the same reaction conditions. In addition, other chlorinated compounds containing sp^3 C–Cl bonds were successfully dechlorinated using the same catalytic system; for example, (2-chloroethyl)benzene and 1-(2-chloroethyl)naphthalene were dechlorinated to give ethylbenzene and 1-ethylnaphthalene in quantitative yield, respectively, in 12 h under the same reaction conditions.

In conclusion, the Pd^{0}HAP system served as an efficient heterogeneous catalyst for complete dechlorination of DDT and its derivatives. The catalytic methodology described here is a powerful candidate for a green disposal protocol for DDT as it has the following advantages: (1) a simple work-up procedure, (2) the use of molecular hydrogen as a clean hydrogen donor, (3) high catalytic performance with a TON of around 1000, and (4) reusability.

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13 Pretreatment of Pd^{II}HAP with H_2 to form Pd^0HAP was necessary for generating high catalytic activity in the dechlorination reaction of DDT. Without the pretreatment, **1** was obtained in 43% yield for 10 h under 1 atm of H_2, although the yield was improved slightly when the reaction time was prolonged (61% at 20 h).

14 Commercially available Pd/carbon and Pd/alumina also contain Pd nanoparticles (ca. 4 nm) (Wako Pure Chemicals); however, they have wider size distributions (Pd/carbon: $d = 4.3$ nm, $\sigma = 0.78$ nm, and $\sigma/d = 18.1\%$; Pd/alumina: $d = 4.4$ nm, $\sigma = 0.91$ nm, and $\sigma/d = 20.7\%$).

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