Rapid and Complete Hydrodechlorination of 2,4-Dichlorophenoxyacetic Acid Catalyzed by Pd/TiO_2 with H_2 in Deionized Water

Ichiro Yamanaka,* Koji Nishikawa, and Kiyoshi Otsuka
Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152-8552

(Received, January 15, 2001; CL-010037)

Pd/TiO_2 catalyzes rapid and complete hydrodechlorination of 2,4-dichlorophenoxyacetic acid dissolved in H_2O with H_2 to phenoxyacetic acid with a high turnover number of Pd at 303 K.

Detoxification and disposal of halogenated aromatics is one of the most serious problems in environmental chemistry. Many methods, oxidative decomposition and reductive deharogenation, were proposed and examined. However, most of the methods were operated under serious conditions, at higher temperature, under higher pressure and using expensive oxidants and reductants. These methods require much energy and cost for the detoxification. Therefore, a new method to detoxify halogenated aromatics is desired under mild conditions.[1–4]

A few catalysts (Pd/SiO_2, Pd/Al_2O_3, and Ru/carbon) were reported for the hydrodechlorination of chloroaromatics with H_2 under mild conditions.[1–3] Active hydrogen species generated on Pd or Ru was proposed to dechlorinate chloroaromatics. Thus, we considered that a hydrodechlorination activity of hydrogen species on the catalyst should be enhanced by the choice of a suitable support of Pd. We found Pd/TiO_2 catalyst to enable to perform rapid and complete hydrodechlorination of chloroaromatics.

Various Pd catalysts were prepared by a conventional impregnation method: i) impregnation of $PdCl_4^{-2}$ aq to supports, ii) drying at 373K and calcination for 2h at 573 K, iii) reduction with H_2 for 2h at 573 K. The amount of Pd loading was 1 wt%.

2,4-Dichlorophenoxyacetic acid (2,4-D) which is used as herbicides, was chosen as a typical model of chloroaromatics. Figure 1 shows catalytic activities for the hydrodechlorination of 2,4-D. The hydrodechlorination was started by bubbling H_2 (1 atm, 10 mL min^{-1}) into the aqueous solution of 2,4-D (2 mmol L^{-1}, 40 mL) with the catalyst (0.125 mmol L^{-1}) and stirring with a magnetic spin-bar. The reaction was continued for 30 min at 303 K. Products, phenoxyacetic acid (PAA), 2-chlorophenoxyacetic acid (2-Cl), and 4-chlorophenoxyacetic acid (4-Cl), were analyzed by HPLC. The Pd supported on carbon (carbon fiber, active carbon, and graphite), SiO_2 and Al_2O_3 reported previously[1–3] catalyzed the hydrodechlorination of 2,4-D with H_2 under this reaction condition. However, their yields of PAA, complete dechlorinated product, were not enough. Therefore, we have examined other oxides as the support of Pd. As shown in Figure 1, Pd supported on TiO_2 performed the highest catalytic activity for the hydrodechlorination. Of course, the TiO_2 without Pd was not active for the hydrodechlorination. On the other hand, the catalytic activity of TiO_2 supported Pt or Rh on which H_2 dissociative adsorbs was very low. A strong synergism of Pd and TiO_2 was observed for the hydrodechlorination. In addition, the Pd/TiO_2 catalyst showed the same catalytic activity for the hydrodechlorination in the dark. Thus, TiO_2 functioned as the support of Pd but not photo-catalyst.

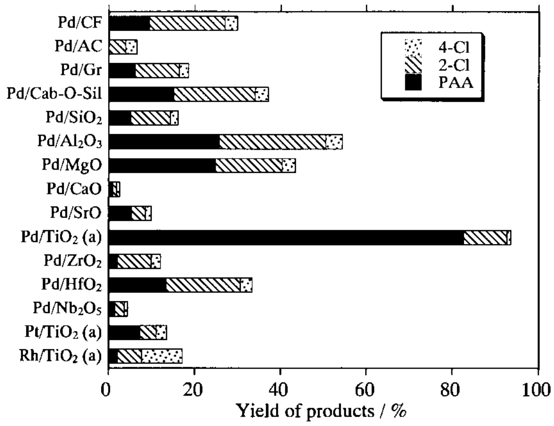

Figure 1. Hydrodechlorination of 2,4-D with H_2 catalyzed by various catalysts at 303 K. (a) TiO_2 supplied from Catalysis Society of Japan (JRC-TIO-4). Catalysts: Pd (1 wt%)/support (5 mg, 0.125 g L^{-1}), 2,4-D 2 mM, H_2 1 atm, reaction time 30 min.

This TiO_2 was supplied from Catalysis Society of Japan as a reference standard catalyst (JRC-TIO-4).[5] The structure of TIO-4 consists of a mixture of anatase and rutile crystals about 7:3 confirmed by XRD. To get information for the synergism of Pd and TiO_2, other three kinds of TiO_2 (anatase and rutile) supplied from Catalysis Society of Japan were examined as supports for the hydrodechlorination of 2,4-D with H_2 in Table 1. The reaction time was reduced to 30 to 10 min to compare significant catalytic activities. All kinds of TiO_2 supported Pd were active for the hydrodechlorination. Catalytic activities were Pd/TIO-4 > Pd/TIO-2 > Pd/TIO-3 > Pd/TIO-5. This order was not corresponding to the order of each surface area of TiO_2. This result proposed that the surface area of TiO_2 does not directly affect the catalytic activities.

Table 1. Effects of kinds of TiO_2 support for Pd on the hydrodechlorination of 2,4-D with H_2 at 303 K

Support for Pd	Crystal	S.A. m^2 g^{-1}	Product yield / % PAA	2-Cl	4-Cl	Conv. / %
TIO-4	anatase (+rutile)	49	37.6	23.0	4.1	64.7
TIO-2	anatase	18	19.6	26.2	4.2	50.0
TIO-3	rutile	40	10.1	11.7	2.9	24.7
TIO-5	rutile	3	7.4	9.1	2.4	18.9

Pd (1 wt%)/TiO_2 (0.125 g L^{-1}), 2,4-D 2 mM, H_2 1 atm, reaction time 10 min.

To get information for reaction scheme, kinetic experiments of the hydrodechlorination were studied. Turnover number for the hydrodechlorination (TON-Cl) was defined as the amount of Cl dechlorinated (mol) per Pd (mol) to evaluate the catalytic activity for the hydrodechlorination.

Copyright © 2001 The Chemical Society of Japan

First, time course of the hydrodechlorination of 2,4-D catalyzed by Pd (1 wt%)/TIO-4 (0.125 g L^{-1}) was carried out. The conversion of 2,4-D and the TON-Cl defined above smoothly increased with reaction time and attained 90% and 300 at 30 min, respectively. Major product was PAA (93.0% selectivity) and minor ones were 2-Cl (6.5) and 4-Cl (0.5) at 30 min. On the other hand, major product was 2-Cl at the early stage of the hydrodechlorination. The selectivity to PAA increased with reaction time, in contrast, the selectivity to 2-Cl- and 4-Cl decreased. When the selectivities to PAA, 2-Cl- and 4-Cl were extrapolated at 0 min, these selectivities were respectively estimated to 0, 80, and 20%. These results strongly suggested that the initial products were 2-Cl (80% selectivity) and 4-Cl (20%), and PAA was secondary dechlorinated product from the both primary ones. The initial product selectivities suggested that the hydrodechlorination rate at *p*-position of 2,4-D was faster than that at *o*-position. A steric hindrance and electronic withdrawing effect of the [-O–CH_2CO_2H] group of 2,4-D should reduce the hydrodechlorination rate at *o*-position.

Second, effects of concentrations of 2,4-D, H_2, and the Pd/TIO-4 catalyst on the hydrodechlorination were studied. Figure 2 shows the effects of the concentration of 2,4-D on the hydrodechlorination. To reduce the conversion of 2,4-D, reaction time and the concentration of the catalyst were reduced from 30 to 10 min and from 0.125 to 0.0125 g L^{-1}. The TON-Cl increased with increasing the concentration of 2,4-D and attained the maximum at 1 mM. The conversion of 2,4-D smoothly decreased with increasing the concentration. A higher concentration of 2,4-D (2 mM) is not favor for the effective hydrodechlorination.

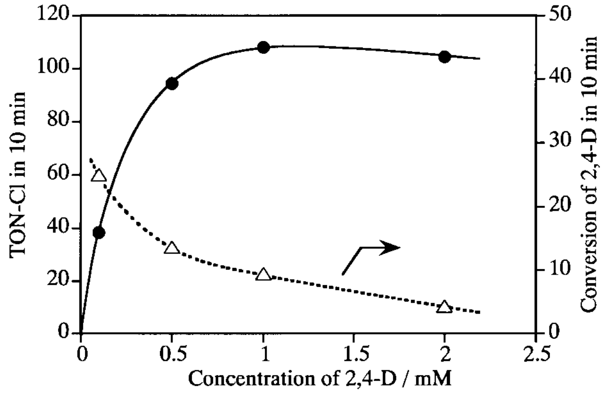

Figure 2. Effects of concentration of 2,4-D on the TON-Cl and the conversion of 2,4-D for the hydrodechlorination in 10 min at 303 K. Pd (1 wt%)/TIO-4 (0.0125 g L^{-1}), H_2 1atm.

In the case of the $P(H_2)$ dependence, the TON-Cl exponentially increased with raising $P(H_2)$ from 0 to 1 atm. This result proposed that the concentration of active hydrogen species on the Pd/TIO-4 exponentially increased with $P(H_2)$.

These experimental facts mentioned above strongly suggested that competitive adsorption of 2,4-D and hydrogen species on the catalysts should control the hydrodechlorination rate. At higher concentration of 2,4-D (>1 mM), adsorbed 2,4-D should depress the adsorption of H_2 and the formation of active hydrogen species on the catalyst.

As mentioned above, the catalytic activity of the Pd/TIO-4 decreased at a higher concentration of 2,4-D. In order to perform the complete dechlorination of 2,4-D, effect of the concentration of the Pd/TIO-4 catalyst on the hydrodechlorination with H_2 (1 atm) was studied, as shown in Figure 3. The conversion of 2,4-D exponentially increased with increasing the concentration of the catalyst below 0.125 g L^{-1} though the conversion of 2,4-D increased. The complete hydrodechlorination of 2,4-D with H_2 was performed at the concentration of 0.625 g L^{-1} within 10 min.

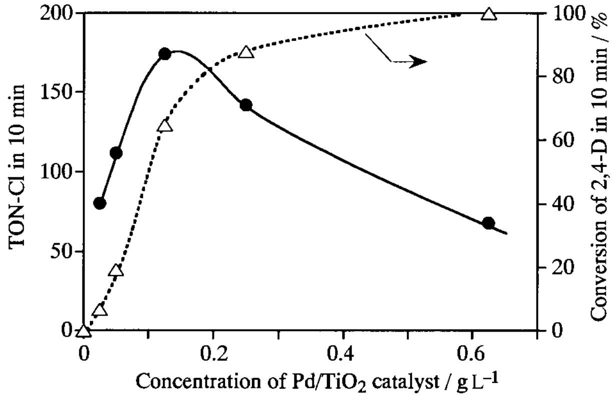

Figure 3. Effects of concentration of Pd (1wt%)/TIO-4 catalyst on the TON-Cl and the conversion of 2,4-D for the hydrodechlorination in 10 min at 303 K. 2,4-D 2mM, H_2 1atm.

The TON-Cl increased with increasing the concentration of catalyst and attained the maximum of 174 at 0.125 g L^{-1}. Decrease in TON-Cl above 0.250 g L^{-1} was due to the high conversion of 2,4-D. The Pd/TIO-4 catalyst effectively works at the higher concentration of the catalyst. When 5 wt% loading Pd/TIO-4 (1 mg), in place of 1 wt% loading Pd/TIO-4 (5 mg), was used for the hydrodechlorination, the TON-Cl was just 40. Though the amounts of Pd in the both catalysts were the same, the TON-Cl of 1 wt% loading Pd/TIO-4 catalyst was larger than 4 times of that of 5 wt% loading one. This result suggests that an interface of Pd and TiO_2 is essential for the generation of active hydrogen species. The data of the product selectivities versus the conversions of 2,4-D in the time course experiment and Figures 2 and 3, could be plotted on a smooth line. This fact proposed that the product distribution determined by the conversion of 2,4-D.

We can propose the model of the hydrodechlorination on Pd/TiO_2, as follows. Nature of the interface of Pd particle and the surface of TiO_2 controls the hydrodechlorination because the strong synergism of Pd and TiO_2 was observed. H_2 dissociatively adsorbs on the interface generating active hydrogen species and 2,4-D competitively adsorbs. The active hydrogen species successively dechlorinate 2,4-D to PAA through 2- or 4-Cl. The active hydrogen species is not simple hydrogen atom (H·) because hydrogenation of aromatic ring did not proceed.

As described so far, the Pd/TiO_2 catalyst has very unique catalytic ability for the hydrodechlorination with H_2. The Pd/TiO_2 catalyst is expected to show catalytic activity for the hydrodechlorination of other poisonous chloroorganic compounds under mild conditions.

References

1 J. B. Hoke, G.A. Gamiccioni, and E.N. Kalko, *Appl. Catal. B: Envir.*, **1**, 285 (1992).
2 C. Schüth and M. Reinhard, *Appl. Catal. B: Envir.*, **18,** 215 (1998).
3 V. Felis, C.D. Bellefon, P. Fouilloux, and D. Scweich, *Appl. Catal. B: Envir.*, **20**, 91 (1999).
4 Y.Ukis, S. Kameoka, T. Miyadera, *Appl. Catal. B: Envir.*, **27**, 97 (2000).
5 wwwsoc.nacis.ac.jp/catsj