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Highly Active Polymer Anchored Palladium Catalyst for the Hydrodehalogenation of Organic Halides under Mild Conditions

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Abstract: Palladium anchored on poly(N-vinyl-2-pyrrolidone) (PVP-$PdCl_2$) exhibits very high catalytic activity for the hydrodehalogenation of organic halides under atmospheric pressure in the presence of a base.

The dehalogenation of organic halides is a useful process in organic synthesis. Recently attention has been focused on the catalytic hydrodehalogenation principally because the simplicity and rapidity of this reaction render it as the most attractive alternative for the elimination of halogenated environmental contaminants. The typical hydrogen donors reported in the literature for the homogeneous catalytic hydrodehalogenation are metal hydrides,[1-6] formic acid (or its salts),[7-10] alcohols,[10-15] and others.[16,17] Although dihydrogen has been widely employed in the heterogeneous catalytic systems [18-21], it has seldom been used in the homogeneous catalytic hydrodehalogenation except some cases in recent works [15,22,23]. Here we report a very active soluble catalyst for the hydrodehalogenation of organic halides using dihydrogen as the hydrogen donor in the presence of a base. This catalyst is prepared by anchoring palladium dichloride on poly(N-vinyl-2-pyrrolidone)[24]. If the polymer is omitted, $PdCl_2$ itself exhibits only a very low activity [25].

The hydrodehalogenation was carried out under atmospheric pressure of dihydrogen and at 65°C in absolute ethanol. Under these conditions, the PVP-$PdCl_2$ catalyst exhibited only very low activity for the hydrodechlorination of chlorobenzene. The maximum turnover frequency (TOF) was only 0.18 min^{-1}. This is partly due to the formation of the hydrogen chloride which causes a gradual decrease of the partial pressure of dihydrogen in the reactor. If a base is stoichiometrically added to the reaction system directly, the PVP-$PdCl_2$ catalyst will exhibit a higher or even very high activity for the hydrodechlorination of chlorobenzene. The results of the hydrodechlorination in the presence of different bases are summarized in Table 1. The catalyst activity is closely related to the base strength, that means a stronger base is corresponding to a more active catalyst system. For example, PVP-$PdCl_2$ is the most active one in the presence of KOH and in this case the maximum TOF can reach 100 min^{-1}. On the other hand, the $Mg(OH)_2$ system gives only a maximum TOF of 3.7 min^{-1}. It is obvious that the function of the base is not only to neutralize

Table 1.
Effect of bases on the hydrodechlorination of chlorobenzene catalyzed by PVP-PdCl$_2$

Base	PhCl/Pd (mol ratio)	Maximum TOF [a] (mol PhCl/mol Pd-min)	Conversion [b] (%)
KOH	900	100	80 (1), 80 (6)
NaOH	900	94	100 (2)
NaOAc	900	50	100 (6)
Na$_2$CO$_3$	300	16	100 (3)
Ca(OH)$_2$	300	3.9	100 (6)
Mg(OH)$_2$	300	3.7	100 (8)

a). Calculated from the amount of dihydrogen uptake. b). The conversion based on the data of GC analysis at the time indicated in parentheses (in h).
Reaction conditions: 65 °C, normal pressure, 20 ml absolute ethanol, 5mmol base (2.5mmol for Mg(OH)$_2$ and Ca(OH)$_2$), 5 mmol chlorobenzene.

Table 2.
Hydrodehalogenation of some organic halides catalyzed by PVP-PdCl$_2$

Organic halide	Maximum TOF [a] (mol PhCl/mol Pd-min)	Conversion [b] (%)	Product (mol %)
Chlorobenzene	92	77.5(1), 100(2)	benzene(100)
Bromobenzene	108	92.5(1), 100(2)	benzene(100)
Iodobenzene	no H$_2$ uptake	100(1)	benzene(100)
m-Dichlorobenzene	59	94.8(1)	benzene(98.7), chlorobenzene(1.3)
		100(2)	benzene(100)
p-Dichlorobenzene	44	71.8(2)	benzene(95.8), chlorobenzene(4.2)
		100(6)	benzene(100)
1,2,4-Trichlorobenzene	45	54.0(1)	benzene(5.0), chlorobenzene(8.5), p-dichlorobenzene(9.3), m-dichlorobenzene(16.3), o-dichlorobenzene(60.9)
		58.5(3)	benzene(7.0), chlorobenzene(7.3), p-dichlorobenzene(8.8), m-dichlorobenzene(15.9), o-dichlorobenzene(61.0)
Benzyl chloride	86	94.3(1)	toluene(100)
Chloro-cyclohexane	12	4.2(1)	cyclohexane(100)

a).Calculated from the amount of dihydrogen uptake. b). The conversion based on the data of GC analysis at the time indicated in parentheses (in h).
Reaction conditions: 65 °C, normal pressure, 15 ml absolute ethanol, 5 mmol NaOH, Pd: 5 × 10^{-3} mmol, X/Pd = 1000.

the hydrogen chloride formed but also to intervene the catalytic cycle in someway.[12] Although the catalyst system with KOH exhibits high initial activity, its stability is poor. The reaction stops in 1 h with a chlorobenzene conversion of 80% with this system. NaOH is the most suitable base for the reaction, with which the reaction rate is fast and the catalyst is stable. Systems with

NaOAc, Na_2CO_3, $Mg(OH)_2$ and $Ca(OH)_2$ also give 100% conversion of chlorobenzene but they take longer time to complete the reaction. Moreover, benzene is the only product for all of these catalytic reactions. No other by-products such as biphenyl have been found by GC analysis.

It is noteworthy that dihydrogen is not the only hydrogen source for the strong base systems, because the conversion of chlorobenzene calculated from the data of GC analysis is higher than that from the dihydrogen uptake measured during the reaction. For example, the conversions of chlorobenzene in the case of the catalyst system with KOH in ethanol at 40 min are 77% and 65% based on GC analysis and dihydrogen uptake, respectively. These results indicate that in addition of dihydrogen, ethanol also plays a role as a hydrogen donor.[15] However, the conversions of chlorobenzene based on GC analysis and dihydrogen uptake are almost the same when a weak base is used. For example, in the case of the catalyst system with $Mg(OH)_2$ the conversions based on both methods are 82.0% and 81.8% respectively at 250 min.

Besides chlorobenzene, other aryl halides, such as bromobenzene, m-dichlorobenzene, p-dichlorobenzene, 1,2,4-trichlorobenzene and benzyl chloride, can also be hydrodehalogenated with high conversion over the PVP-$PdCl_2$ catalyst in the presence of a base (Table 2). Iodobenzene is different from the other halogenated substrates as it can be readily converted to benzene without any uptake of dihydrogen. In this case the solvent itself is the only hydrogen source. The reaction of chloro-cyclohexane is slow and the conversion is low.

The choice of solvent for the hydrodechlorination using the polymer-anchored palladium catalyst is rather specific. The data listed in Table 3 demonstrate that only alcohols are the suitable ones, among which, ethanol or iso-propanol is the best solvent. Ethanol containing only 5% H_2O retards the reaction obviously.

Table 3.
Effect of solvents on the hydrodechlorination of chlorobenzene

Solvent	Maximum TOF [a] (mol PhCl/mol Pd·min)	Conversion [b] (%)
Methanol[c]	15	63.9 (1), 97.9 (5)
Absolute ethanol	94	100 (2)
95% ethanol	10	10.5 (1), 19.1 (2)
n-Propanol	59	94.1 (1), 94.2 (2)
iso-Propanol	88	88.9 (1), 99.0 (3)
n-Butanol	2	2.7 (2)
Dioxane	0	0 (1)
Toluene	2	3.0 (2)
Acetone[d]	1	1.2 (1)

a). Calculated from the dihydrogen uptake. b). The conversion at the time indicated in parentheses (in h). c). 60°C. d). 50°C.
Reaction conditions: PhCl/Pd = 900 (mole ratio), base 5 mmol NaOH, solvent 20 ml, the others are the same as those in Table 1.

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24. PVP-$PdCl_2$ catalyst was prepared as follows: PVP (1.14 g, BASF, K= 27-33) was dissolved in absolute ethanol (141 ml) and then the $[PdCl_4]^{2-}$-H_2O solution (9 ml, 0.057 M) was added. The mixture was stirred at room temperature for 48 h. In our experiments, 1-3 mL of this solution were used directly as catalyst.
25. $PdCl_2$ gives a chlorobenzene conversion of 3.8% in 2 h under the reaction conditions shown in Table 1 in the presence of NaOH.

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