

## PVP-Supported Palladium-Cadmium Bimetallic Catalyst for the Hydrogen Transfer Dechlorination of Aryl Chlorides

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**Abstract:** PVP-supported bimetallic catalyst, PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub>, exhibits extremely high catalytic activity for the hydrogen transfer dechlorination of aryl chlorides in neutral environment. The yields of dechlorination products are high under mild reaction conditions and the operation is simple.

**Keywords:** Bimetallic catalyst, aryl chlorides, hydrogen transfer dechlorination.

Supported bimetallic catalysts, due to their high selectivity and catalytic activity, have been widely applied to the hydrogenation of nitro-compounds<sup>1</sup> and esters<sup>2</sup>, the carbonylation of allyl halides<sup>3</sup> and the catalytic hydrodehalogenation of aromatic halides<sup>4,5</sup>. Liao and others utilized PVP[PVP=poly-(N-vinyl-2-pyrrolidone)]-supported palladium-ruthenium<sup>4</sup> and palladium-cobalt<sup>5</sup> bimetallic catalysts, in the presence of dihydrogen, to catalyze the hydrodechlorination of aryl chlorides. Although these reactions had high catalytic activity, the operation was rather complicated. In this paper, we reported an effective catalytic hydrogen transfer dechlorination of aryl chlorides in neutral environment, using PVP-supported bimetallic PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub> as catalyst, sodium formate as hydrogen donor. Except nitro chlorides, the catalyst showed very high activity and selectivity for the dechlorination of other chlorinated aromatics. Besides, the operation was very simple.

Under other identical conditions, as compared with PVP-supported monometallic catalyst, PVP-supported palladium-cadmium bimetallic catalyst exhibited much higher catalytic activity for the hydrogen transfer dechlorination of aryl chlorides. The yields of dechlorination products were remarkably increased, while the coupling by-products obviously decreased. Especially for the dechlorination of chlorobenzene and p-chloroacetophenone, the catalyst exhibited extremely high selectivity. By the analysis of TLC, no other side products were observed. The reaction almost quantitatively yielded the dechlorination products (see **Table 1**).

Experiment has proved that the monometallic catalyst PVP-CdCl<sub>2</sub> was not active for this reaction under the same reaction conditions. These results reveal that the high catalytic activity of PVP-supported palladium-cadmium bimetallic catalyst might be attributed to the synergistic effect of palladium species and cadmium species. It can also be seen from **Table 1** that for the isomeric *o*-, *m*- and *p*-chlorotoluenes, the order of both reaction rates and dechlorination product yields was *p*>*m*>*o*. The greater steric hindrance of an *o*-methyl than that of a *m*-methyl or *p*-methyl might lead to a decreased dechlorination rate for the substitution reaction of *o*-chlorotoluene.

**Table 1.** Hydrogen Transfer Dechlorination of Aryl Chlorides Catalyzed by PVP-PdCl<sub>2</sub> and PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub><sup>a</sup>

Substrate	Catalyst	Reaction Time (min)	Conversion <sup>b</sup> (%)	Yield (%) <sup>c</sup>	
				Dechlorination product	Other product
Chlorobenzene	PVP-PdCl <sub>2</sub>	240	54.1	benzene(37.4)	Biphenyl <sup>c</sup> (3.6)
<i>o</i> -Chlorotoluene	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	50	100	benzene(99.6)	
	PVP-PdCl <sub>2</sub>	240	49.4	toluene(30.6)	3,3'-dimethyldiphenyl <sup>c</sup> (4.1)
<i>m</i> -Chlorotoluene	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	40	100	toluene(97.9)	3,3'-dimethyldiphenyl <sup>c</sup> (0.02)
	PVP-PdCl <sub>2</sub>	240	49.4	toluene(30.6)	3,3'-dimethyldiphenyl <sup>c</sup> (4.1)
<i>p</i> -Chlorotoluene	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	40	100	toluene(97.9)	3,3'-dimethyldiphenyl <sup>c</sup> (0.02)
	PVP-PdCl <sub>2</sub>	240	56.3	toluene(32.3)	4,4'-dimethyldiphenyl <sup>c</sup> (7.8)
<i>p</i> -Chloroaniline	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	30	100	toluene(98.6)	4,4'-dimethyldiphenyl <sup>c</sup> (0.02)
	PVP-PdCl <sub>2</sub>	240	26.4	aniline(3.6)	4,4'-diaminodiphenyl <sup>c</sup> (10.2)
<i>p</i> -Chloroacetophenone	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	30	100	aniline(89.5)	4,4'-diaminodiphenyl <sup>c</sup> (1.8)
	PVP-PdCl <sub>2</sub>	240	51.8	acetophenone (41.0)	4,4'-diacetyldiphenyl <sup>c</sup> (2.1)
<i>p</i> -Chloronitrobenzene	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	60	100	acetophenone (99.8)	
	PVP-PdCl <sub>2</sub>	240	35.6	nitrobenzene (5.2)	4,4'-dinitrodiphenyl <sup>c</sup> (13.6)
	PVP-PdCl <sub>2</sub> -CdCl <sub>2</sub>	120	100	nitrobenzene (6.1)	Aniline <sup>b</sup> (18.8); 4-amino-4'-nitrodiphenyl <sup>c</sup> (38.2); 4,4'-diaminodiphenyl <sup>c</sup> (2.7)

Reaction conditions and notes:

a. 78<sup>o</sup>C; ethanol, 5 ml; HCOONa, 4.0 × 10<sup>-3</sup> mol; catalyst, PVP-PdCl<sub>2</sub>, 5.1 × 10<sup>-6</sup> mol Pd, PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub>, 5.1 × 10<sup>6</sup> mol Pd, Pd/Cd=1/0.13 (molar ratio); substrate, 2.1 × 10<sup>-3</sup>mol; H<sub>2</sub>O, 24 μl.

b. Conversion and yield are based on the data of GC analysis.

c. Separation yields.

During the reaction process, we also found that the Pd/Cd ratio had great influence on the catalytic activity. In the case of maintaining the amount of Pd metal, we changed the Pd/Cd molar ratio. The experimental results showed that the optimum catalytic activity can be obtained with a Pd/Cd molar ratio of about 1/0.13 (See **Table 2**).

**Table 2.** Influence of Pd/Cd Molar Ratio in PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub> on the Catalytic Activity

Pd/Cd (molar ratio)	0	1/1	1/0.7	1/0.5	1/0.25	1/0.13	1/0.1	1/0.06	1/0
Yield of acetophenone(%) (GC)	0	3.1	22.0	76.4	95.5	98.6	94.2	86.6	23.5

Reaction Conditions:

78<sup>0</sup>C; 90 min; ethanol, 5 ml; HCOONa, 4.0 × 10<sup>-3</sup> mol; catalyst, PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub>, 5.1 × 10<sup>-6</sup> mol Pd, *p*-Chloroacetophenone, 2.1 × 10<sup>-3</sup> mol.

Moreover, we also found that the content of water in reaction system greatly influenced the catalytic activity (see **Table 3**). When the system contained about 24 μl H<sub>2</sub>O [ H<sub>2</sub>O / Substrate = 1 /16 (molar ratio)], the dechlorination product yields reached the highest value.

**Table 3.** Influence of the Content of H<sub>2</sub>O in Reaction System on the Catalytic Activity

Content of H <sub>2</sub> O (μl)	9	14	19	24	29	39	49
Yield of acetophenone (%) (GC)	70.8	72.4	86.3	99.8	91.4	42.3	9.19

Reaction Conditions:

78<sup>0</sup>C; 60 min; ethanol, 5 ml; HCOONa, 4.0 × 10<sup>-3</sup> mol; catalyst, PVP-PdCl<sub>2</sub>-CdCl<sub>2</sub>, 5.1 × 10<sup>-6</sup> mol Pd, Pd/Cd=1/0.13 (molar ratio); *p*-Chloroacetophenone, 2.1 × 10<sup>-3</sup> mol.

If the reaction system contained either more or less than about 24 μl H<sub>2</sub>O, the reaction rates would be markedly decreased. The reaction hardly happened especially when large amount of water existed. The author believed that the existence of appropriate amount of water contributes to the solubility of sodium formate in ethanol, and also the decrease of the dissociation energy of C-Cl bond, which accelerated the hydrogen transfer dechlorination. The existence of large amount of water is unfavorable to the solubility of substrate halobenzene in ethanol, which lead to the remarkable decrease of reaction rate.

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