

Dechlorination of Aromatic Chlorides in Aqueous System Catalyzed by Functionalized MontK10 Supported Palladium-tin

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Abstract: A novel bisupporter bimetal catalyst PVP-PdCl₂-SnCl₄/MontK10-PEG400, using for dehalogenation of insoluble aromatic halides in aqueous system, has shown high dechlorination activity and selectivity, without any organic solvent or phase transfer catalyst. The conversion of aromatic chlorides can reach 100%. The catalyst is easy to prepare and has good reusability.

Keywords: Dehalogenation in aqueous system, aromatic halides, MontK10, bisupporter, bimetal.

Aromatic chlorides are important chemicals widely applied in chemical industry. They intermix in industrial wastewater and daily wastewater, and pollute the water system. As known aromatic chlorides are teratogenic and carcinogenic substance and do harm to human beings. But only few studies on dechlorination of aromatic chlorides in aqueous system have been reported^{1,2} because most of aromatic chlorides are insoluble in water. In previous paper³ we described that MontK10 supported on bimetal can catalyze dechlorination of aromatic chlorides in aqueous system, but the phase transfer catalyst PEG400 in this reaction is difficult to recover and reuse.

In this paper we prepare a novel functionalized MontK10 supported on bimetal, establish a system PVP-PdCl₂-SnCl₄/MontK10-PEG400. The catalyst has shown high catalytic activity for dechlorination of aromatic chlorides in aqueous system in the presence of HCOONa as hydrogen donor (**Table 1**). The catalyst is easy to recover and efficient after reuse. For example, dechlorination of *m*-chlorotoluene under the same condition using the recovered catalyst for the five times, the conversion of *m*-chlorotoluene maintained over 60%. **Table 1** exhibits the synergic effects of catalytic dehalogenation. The conversion is obviously different among various combinations of two metals in catalyst. To compare supported monometal Pd²⁺(or Sn⁴⁺) catalyst, bimetal system of Pd²⁺ with second metallic ion Ni²⁺, Zn²⁺, Mn²⁺, Fe³⁺, Cu²⁺, Fe²⁺, Co²⁺, Sn⁴⁺ or Cr³⁺ can remarkably enhance the dehalogenation action, but Pd²⁺ with other second metallic ion decreased the catalytic activity. It seems that the bimetal catalytic system of palladium favored to combine with the fourth period metals in periodic table of elements for enhancing dehalogenation effects.

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Table 1 Effect of various palladium-based bimetallic systems on catalytic activities ^a

Catalyst	Conversion ^b (%)	Yield ^b (%)
PVP-SnCl ₄ /MontK10-PEG400	69.5	41.8
PVP-PdCl ₂ /MontK10-PEG400	78.5	44.2
PVP-PdCl ₂ -ZnCl ₂ /MontK10-PEG400	100	40.1
PVP-PdCl ₂ -CrCl ₃ /MontK10-PEG400	100	58.6
PVP-PdCl ₂ -FeCl ₃ /MontK10-PEG400	100	46.7
PVP-PdCl ₂ -CuCl ₂ /MontK10-PEG400	100	56.8
PVP-PdCl ₂ -MnCl ₂ /MontK10-PEG400	100	61.6
PVP-PdCl ₂ -FeCl ₂ /MontK10-PEG400	100	71.4
PVP-PdCl ₂ -SnCl ₄ /MontK10-PEG400	100	77.5
PVP-PdCl ₂ -CoCl ₂ /MontK10-PEG400	100	62.1
PVP-PdCl ₂ -NiCl ₂ /MontK10-PEG400	97.6	58.1
PVP-PdCl ₂ -AgNO ₃ /MontK10-PEG400	69.8	43.8
PVP-PdCl ₂ -SnCl ₂ /MontK10-PEG400	66.3	42.7
PVP-PdCl ₂ -CdSO ₄ /MontK10-PEG400	36.7	19.4
PVP-PdCl ₂ -PbCl ₂ /MontK10-PEG400	35.5	23.2
PVP-PdCl ₂ -HgCl ₂ /MontK10-PEG400	25.6	16.1

a, Reaction condition: catalyst 0.23g (Pd:7.24 × 10⁻⁶mol); Pd:M=4:1(mole ratio); *m*-chlorotoluene 3.4 × 10⁻³mol; HCOONa 7.2 × 10⁻³mol; Water 5 mL; reaction temperature 80°C; reaction time 4 h.

b, GC yield.

Various substrates lead to various catalytic dehalogenation effects under the same condition. The results are listed in **Table 2**.

Table 2 Activity for dehalogenation of different aromatic halides in water

Substrate	Time (h)	Conversion (%)	Yield(%)	
			Dehalogenation product ^a	Other product ^b
<i>o</i> -Chlorotoluene	4	100	Toluene(72.6)	2,2'-Dimethyldiphenyl(2.4)
<i>m</i> -Chlorotoluene	4	100	Toluene(77.5)	3,3'-Dimethyldiphenyl(2.5)
<i>p</i> -Chlorotoluene	4	100	Toluene(64.7)	4,4'-Dimethyldiphenyl(2.9)
<i>o</i> -Dichlorobenzene	4	100	Benzene(47.9)	Biphenyl(1.8)
<i>m</i> -Dichlorobenzene	4	100	Benzene(47.6)	Biphenyl(1.6)
<i>p</i> -Dichlorobenzene	4	100	Benzene(57.9)	Biphenyl(2.3)
<i>p</i> -Chloroacetophenone	4	100	Acetophenone(90.9)	4,4'-Diacetyldiphenyl(3.3)
<i>p</i> -Chlorobenzoic acid	4	100	Benzoic acid(68.7)	
Fluorobenzene	4	0		
Chlorobenzene	4	86.5	Benzene(57.4)	Biphenyl(2.2)
Bromobenzene	4	63.5	Benzene(44.8)	Biphenyl(4.8)
Iodobenzene	4	38.3	Benzene(23.1)	Biphenyl(3.4)

The reaction conditions are the same as **Table 1**. a.GC yield b. Separation yield

The data in **Table 2** show that PVP-PdCl₂-SnCl₄/MontK10-PEG400 reveals high catalytic dechlorination activity, substituted benzenes are completely converted in four hours, so do the other phenyl halides, except fluorobenzene. But monochlorobenzene without other substitutes can not be completely converted. Moreover, a small amount

of coupling products are found in reaction.

We also found that the catalytic activity varied with the change of Pd/Sn molar ratio in catalyst (see **Table 3**). Under the same condition, the catalytic activity of PVP-Pd /MontK10-PEG400 or PVP-Sn/MontK10-PEG400 is lower than that of PVP-Pd-Sn/MontK10-PEG400. The catalytic activity is increased to maximum as the molar ratio of Pd/Sn increased to 4/1.

Table 3 The effect of Pd/Sn molar ratio on the catalytic activity

Pd/Sn(mol ratio)	0	1:1	2:1	4:1	6:1	8:1	∞
Conversion(%)	69.5	86.2	93.5	100	100	100	78.5
Yield(%)	41.8	49.1	66.9	77.5	73.2	68.3	44.2

The reaction conditions are the same as **Table 1** except for Pd/Sn

The synergic effects of bimetal and the conjunct action of bisupporter PVP, MontK10-PEG400, give PVP-Pd-Sn/MontK10-PEG400(A) excellent capability of dehalogenation in aqueous system. Experimental results have proved that catalyst(A) shows an obvious dechlorination activity compared with other types of catalyst under the same condition. The results are listed in **Table 4**.

Table 4 Activity for dehalogenation over different catalysts

Catalyst	Conversion(%)	Yield(%)
PVP-PdCl ₂ -SnCl ₄ /MontK10	47.3	31.1
PVP-PdCl ₂ -SnCl ₄ /MontK10-PEG400	100	77.5
PVP-PdCl ₂ -SnCl ₄ /MontK10+PEG400	100	55.2
PVP-PdCl ₂ /MontK10-PEG400	78.5	44.2
PVP -SnCl ₄ /MontK10-PEG400	69.5	41.8

Reaction condition: Pd 7.24×10^{-6} mol; *m*-chlorotoluene 3.4×10^{-3} mol; HCOONa 7.2×10^{-3} mol; Water 5 mL; 80°C; 4 h

References

1. J. B. Hoke, *Appl. Catal. B*, **1992**, *1*, 285.
2. D. C. Jang, *Tetrahedron lett.*, **1996**, *37*, 5367.
3. X. L. Zhen, J. R. Han, R. H. Kang, X. M. Ouyang, *Chin. Chem. Lett.*, **2001**, *12* (4), 287.

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