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Dehalogenation of Aryl Halides Catalyzed by MontK10 Immobilized PVP-Pd-Sn Catalyst in Aqueous System

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Abstract: A series of PVP-Pd-Sn/MontK10 catalysts were prepared by immobilization of PVP[poly(N-vinyl-2-pyrrolidone)] supported bimetallic catalyst using MontK10 as carrier. This catalyst has good catalytic activity for hydrogen transfer dehalogenation of aryl halides. The catalytic reaction was carried out in aqueous system in the presence of phase transfer catalyst and sodium formate as hydrogen source. The catalyst with loading Pd 0.19wt% and molar ratio of Pd/Sn 8:1 gives the highest activity and good stability. This catalyst is more reducible with $NaBH_4$. It is also found that the catalyst is easily separated from the reaction system.

Keywords: Phase transfer catalyst, aryl halide, dehalogenation, MontK10.

Catalytic dehalogenation of organic halides is of great value to the organic synthesis and for the preventing of environmental pollution. Although, in recent years, there are many reports describing dehalogenation of organic halides in the literature[1,2,3], most of them were carried out in the organic system,only few examples[4,5] of dehalogenation were carried out in aqueous system. The toxic aryl halides may contaminate and harm human being seriously through food chain. Therefore, it is of utmost importance to seek effective methods for removing these contaminants not only from groundwater but also from industrial effluents and waste streams.

It was reported that bimetal synergistic action could greatly enhance the activities of the catalysts in the reduction reactions[6]. PVP-supported bimetallic catalyst [PVP = poly (N-vinyl-2-pyrrolidone)] also exhibited high catalytic activity and selectivity for dechlorination of aryl chloride[1], but the catalytic dehalogenation reaction needed to carry out in organic systems, and the catalyst was difficult to be recovered. In addition, the catalyst would lose activity if the reaction occurred in water. In this paper, the novel dually supported bimetallic catalyst PVP-Pd-Sn/MontK10 is reported. It is prepared by adsorption and bonding MontK10 with PVP-Pd-Sn complex, which was prepared following the literature[1]. In the presence of a small amount of phase transfer catalysts PEG-400 and HCOONa as hydrogen donors. This catalyst exhibits much better activity for hydrogen transfer dehalogenation of aryl halides in aqueous system, comparing with PVP supported bimetallic (or monometallic) and the PVP and MontK10 dually supported mono-metallic catalyst (see **Table 1, 2**).

Table 1 Hydrogen transfer dechlorination of o-chlorotoluene catalyzed by different catalysts in aqueous system[a]

Catalyst [c]	Yield [b]
PVP-$PdCl_2$	0
PVP-$PdCl_2$-$SnCl_4$	0
PVP-$PdCl_2$/MontK10	28.6
PVP-$PdCl_2$-$SnCl_4$/MontK10	47.1
PVP-$SnCl_4$/MontK10	0

Reaction condition and notes:

a. Catalysts, 5.5×10^{-6} mol Pd, Pd/Sn = 8:1; o-chlorotoluene 13.2 mmol; HCOONa 14.7 mmol; PEG-400 2.5 mmol; water 10 ML; refluxing temperature

b. GC yield.

c. The catalyst is used in dehalogenation reaction after being reduced

The reason is that polar surface of MontK10 makes the bimetallic compound of PVP homoadsorbed, which consist of organic micro circumstance with reactant, under the phase transfer action of PEG, dehalogenation reaction is accelerated. The PVP and MontK10 dually supported bimetallic catalyst is easily prepared and recovered. When the catalyst was reused after 6 times, the conversion of substrates can still reach more than 50%.

Table 2 Dehalogenation of aryl halides catalyzed by PVP-Pd-Sn/MontK10 in aqueous system[a]

Substrate	Time (h)	Conversion (%)	yield(%) [b]	
			dehatogenation product	other product [c]
P-chloroaniline	4.5	100	aniline (82.6)	4,4'-diaminodiphenyl(0.3)
o-chloroaniline	4.5	100	aniline (74.2)	
m-chloroaniline	4.5	100	aniline(55.5)	3.3'-diaminodiphenyl(0.15)
p-chlorotoluene	4.5	100	toluene(64.1)	4.4'-dimethyldiphenyl (1.5)
o-chlorotoluene	4.5	100	toluene(65.6)	
m-chlorotoluene	4.5	100	toluene(50.2)	3.3'-dimethyldiphenyl(0.9)
p-chloroacetophenone	16	100	acetophenon(73.9)	4.4'-diacetyldiphenyl(6.4)
Fluorobenzene	16	0		
Chlorobenzene	16	76.7	benzene(40.4)	diphenyl(0.35)
Bromobenzene	16	51.8	benzene(29.5)	diphenyl(0.5)
Iodobenzene	16	0		

Reaction condition and notes:

a. Catalyst 0.620 g (Pdwt%=0.19%), substrate 13.2 mmol, PEG-400 2.5 mmol, HCOONa 36.9 mmol, water 10 ML, refluxing temperature.

b. GC yield,

c. Separation yield.

Table 2 shows the relatively high catalytic activity and selectivity for dechlorination and debromination of the PVP-Pd-Sn/MontK10 catalyst system. Electron-donating group substituted chlorobenzene can be completely dechloried in 4.5 h, chlorobenzene, bromobenzene and electron-withdrawing group substituted chlorobenzenes can be completely converted through a long time, flurobenzene and iodobenzene do not react at all. Meantime, a small amount of coupling products are often produced besides dehalogenated products.

Pd/Sn molar ratio has great influence on the catalytic activity (**Table 3**). PVP-Sn/MontK10 has no catalytic activity on reaction. PVP-Pd/MontK10 exhibits somewhat activity, but the activity lower than PVP-Pd-Sn/MontK10 (**Table 1**). It is concluded that Pd is a necessary metal in this catalytic system, and Pd and Sn have synergistic action on the catalytic activity. The yield is markedly increased as the molar ratio of Pd/Sn increases, the best molar ratio is 8:1, when Pd/Sn ratio is increased further, the yield of dehalogenation product decreases.

Table 3 The effect of Pd/Sn Molar ratio on the catalytic activity [a]

Pd/Sn(mol)	0	2:1	4:1	6:1	8:1	10:1
Yield(%)[b]	0	27.6	33.2	52.8	78.1	54.8

a. The reaction conditions are the same as **Table 2** except for Pd/Sn, b. GC yield

Adding appropriate phase transfer catalysts in the reaction system can greatly promote the dehalogenation reaction (see **Table 4**).

Table 4 The effect of phase transfer catalyst on dehalogenation reaction[a]

Phase transfer catalyst	0	PEG-200	PEG-400	PEG-600	PEG-800	PEG-1000	$(NH_3)_4$ NI	CTAB	BETA
Yield [b] （%）	36.3	48.0	78.1	73.2	66.7	62.7	1.8	7.4	48.5

a. The reaction conditions are the same as in **Table 2** except for phase transfer catalyst.
b. GC yield

As **Table 4** shows that PEG-400 is the best phase transfer catalyst in catalytic dehalogenation reaction. Probably, the reason is that chain length of the PEG-400 is suitable for dissolving PEG-400 both in water and organic solvents. In the water phase PEG complexes with Na^+ in HCOONa and forms ion pair with $HCOO^-$. The ion pair enters into the organic micro circumstance which consists of adsorbed PVP MontK10 and aromatic halides. As a result, the dehalogenation reaction is accelerated.

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