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HIGHLY ACTIVE POLYMER-SUPPORTED PALLADIUM-COBALT CATALYSTS FOR THE HYDRODECHLORINATION OF ORGANIC CHLORIDES

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Abstract: Polymer-supported catalyst, PVP-PdCl₂-Co(OAc)₂, exhibits very high catalytic activity for the hydrodechlorination of organic chlorides, especially polychlorobiphenyls, under mild conditions.

The reduction of organic halides to the corresponding hydrocarbons plays an important role in organic synthesis and environmental decontamination. Although reductive dehalogenation of organic halides by means of metal hydrides, formic acid (or its salt), alcohols or other reducing agents is a well-known and widely applied reaction,¹⁻⁸ the catalytic hydrodechlorination of organic chlorides with dihydrogen as the hydrogen donor under mild conditions is still a difficult task,

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especially polychlorobiphenyls. In this communication, we report that the polymersupported palladium-cobalt catalysts show very high catalytic active for the hydrodechlorination of organic chlorides under mild conditions. High conversion (>99.9%) can be obtained in a short reaction time, even for polychlorobiphenyls (PCBs).

is known that palladium catalysts are usually It active for the hydrodehalogenation of organic halides in heterogeneous or homogeneous catalysis.9-11 It can be seen from the experimental results shown in Table 1 that the monometallic catalyst PVP-PdCl₂ [PVP = poly(N-vinyl-2-pyrrolidone)] already shows a high catalytic activity in the presence of a base (base/Cl = 1.0). Bi or multimetallic catalysts are new topic in homogenous and polymer-supported catalysis which have been extensively studied in recent years¹²⁻¹⁴ In this communication, very active polymer-supported bimetallic catalyst is presented which is obtained simply by adding a second transition metal component to the monometallic catalyst PVP-PdCl₂. Among the transition metal compounds tested, only cobalt compound exhibits a synergic effect which leads to a further increase in the activity of the polymer-supported monometallic palladium catalyst. Only 27 min are required to complete the hydrodechlorination of chlorobenzene under the reaction conditions listed in Table 1. However, PVP-CoCl₂ and PVP-Co(OAc)₂ are not catalytic active for the hydrodechlorination of chlorobenzene under the same reaction conditions. The Pd/Co ratio influences the catalytic activity of the polymer-supported bimetallic catalyst. A Pd/Co ratio of 1/1 is suitable for the hydrodechlorination of chlorobenzene. Table 2 lists the results of the

Catalyst	TOFmax ^b	Reaction	Conversion ^C	
	(min ⁻¹)	time (min)	(%)	
PVP-PdCl ₂	96	37	100	
PVP-PdCl ₂ -FeCl ₃	94	38	100	
PVP-PdCl2-NiCl2	88	40	97	
PVP-PdCl ₂ -Ni(OAc) ₂	65	45	96	
PVP-PdCl2-RuCl3	45	180	97	
PVPPdCl2CuCl2	34	180	44	
PVP-Co(OAc)2	nil	60	nil	
PVP-CoCl2	nil	60	nil	
PVP-PdCl2-CoCl2	127	30	100	
PVP-PdCl2-Co(OAc)2	128	27	100	
PVP-PdCl2-0.5Co(OAc)2	99	32	100	
PVP-PdCl2-2Co(OAc)2	98	35	100	

Table 1 Hydrodechlorination of chlorobenzene^a

^a65 °C, 0.1 MPa H₂, absolute ethanol (14 ml), NaOAc (4 mmol), chlorobenzene (4 mmol), catalyst (4×10^{-3} mmol Pd). ^bMaximum turnover frequency (mol H₂/mol Pd'min) calculated from the amount of dihydrogen uptake. ^cConversion based on the data of GC analysis and benzene was the only product in all cases.

Substrate	TOFmax ^b	Reactiom	Conversion ^c	Productd
	(min ⁻¹)	time (min)	(%)	(%)
Chlorobenzene ¹⁵	128	27	100	benzene(100)
p-Chlorotoluene	70	55	100	toluene(100)
m-Chlorotoluene	68	52	100	toluene(100)
p-Chlorobenzonitrile	145	23	100	benzonitrile(100)
o-Dichlorobenzene	61	85	100	benzene(100)
m-Dichlorobenzene	58	100	100	benzene(100)
p-Dichlorobenzene	65	100	100	benzene(100)
3,4-Dichlorotoluene	32	122	100	toluenc(100)
1,2,4-Trichlorobenzene	56	118	100	benzene(100)
Perchlorobenzene	42	192	100	benzene(100)
Benzyl chloride	129	20	100	tolucne(100)
Polychlorobiphycnyls ^e	14	227	99.9	mainly biphcnyl

Table 2 Hydrodechlorination of organic chlorides catalyzed by PVP-PdCl₂-Co(OAc)₂^a

^a65°C, 0.1 MPa H₂, absolute ethanol (14 ml), NaOAc (4 mmol), Cl/Pd = 1000, catalyst (4×10⁻³ mmol Pd), Pd/Co = 1. ^bCalculated from the amount of dihydrogen uptake. ^cConversion based on the data of GC analysis. ^d Determined by GC analysis. ^eThe chlorine content in the PCBs is 60 percent (w/w). hydrodechlorination of some organic chlorides catalyzed by the bimetallic catalyst PVP-PdCl2-Co(OAc)2. Chlorobenzenes bearing different functional groups are successfully hydrodechlorinated, among which electron-withdrawing groups can promote the hydrodechlorination. It is worthwhile to note that the isomeric o-, m- and p-dichlorobenzenes can be successfully hydrodechlorinated to give the product benzene in 100% yield, and the different steric hindrances of the two chlorine atoms do not result in significant differences in the reaction rate. It is important that 1,2,4-trichlorobenzene and perchlorobenzene can be completely hydrodechlorinated to benzene in 118 and 192 min. It reveals that this bimetallic catalyst should be a good catalyst for the effective removal of highly toxic polychlorobiphenyls, an environmental contaminant, which is a difficult task by the usual catalytic hydrodechlorination with dihydrogen as the hydrogen donor under mild conditions. Result of the hydrodechlorination of polychlorobiphenyls shows that the bimetallic catalyst is very effective for the elimination of these highly toxic polychlorobiphenyls. A conversion of 99.9% can be obtained in 227 min. The selectivity of this catalyst is high with no biaryl formation or aromatic ring hydrogenation observed in all cases.

In summary, the bimetallic catalyst, PVP-PdCl₂-Co(OAc)₂ (or CoCl₂), exhibits very high catalytic activity for the hydrodechlorination of aromatic chlorides, which is important in organic synthesis.

Experimental Section

General: High purity dihydrogen (>99.9%) was used for the catalytic experiments.

Absolute ethanol was dried through 5A molecular sieves prior to use. PVP (BASF, purity > 95%) and other reagents were used without further purification. Chemical analyses of the products were performed by GC (Shangfen GC 102, 2 m DEGS column), The conversion and halide contents of the solution of PCBs were analyzed by GC with 2 m column packed with SE30 at 200°C and with an electron capture detector. Reagent and products were identified by comparison with authentic samples.

Preparation of catalysts: To a mixture of 1 ml of 5 mol dm⁻³ HCl and 0.056 g (0.31 mmol) of PdCl₂, 75 ml of absolute ethanol and 0.724 g of PVP were added. After stirring at room temperature for 48 h, a red-brown solution was obtained (the catalyst PVP-PdCl₂, 4×10^{-3} mmol Pd ml⁻¹, N/Pd=20). To the monometallic catalyst, a second transition metal compound (*e.g.* FeCl₃·6H₂O, CoCl₂·6H₂O, Co(OAc)₂·4H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O, Ni(OAc)₂·4H₂O, or RuCl₃·3H₂O) was added, then stirred at room temperature for 24 h, to yield the polymer-supported bimetallic catalyst (PVP-PdCl₂-mMX, 4×10^{-3} mmol Pd ml⁻¹, N/Pd = 20, M/Pd = m).

General procedure for hydrodechlorination: A 65 ml three necked and jacketed bottle fitted with a silicon rubber septum was first charged with 4 mmol of base, evacuated and connected to a constant pressure gas burette containing dihydrogen. Then 14 ml of absolute ethanol and 1 ml of the catalyst solution $(4 \times 10^{-3} \text{ mmol Pd})$ was introduced through the silicon rubber septum via a syringe successively. After the catalyst was reduced in situ for 15 min, the substrate (Cl/Pd=1000) was added.

POLYMER-SUPPORTED CATALYST

Samples were removed via a syringe for GC analysis at the given time. The reaction was monitored by the dihydrogen uptake.

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