A novel silica-polyglycol supported polymer-anchored bimetallic palladium-based catalyst for dechlorination of aromatic chlorides in water

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Abstract

A new type of combined heterogeneous catalyst, PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600, was prepared by reaction of silica gel functionalized by polyethylene glycol (PEG) with average molecular weight 600 as a carrier system with phase transfer properties, with polyvinylpyrrolidone (PVP)-anchored PdCl$_2$ and CuCl$_2$ complex, and characterized by IR, XPS and TEM. The catalyst, in which the Pd/Cu molar ratio is 2/1, has shown good activity and selectivity for dechlorination of aromatic chlorides in water. In the presence of HCOONa as hydrogen donor and basic media, conversion in the dechlorination of *p*-chlorotoluene can reach 96.6% at 80°C only for 2.5 h. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer-anchored bimetallic complex; Supported phase transfer catalyst; Dehalogenation; Wastewater; Aromatic halide

1. Introduction

For a long time, dehalogenation has received extensive attention in synthetic reactions and the treatment of contaminants with organic halides. Catalysts have been demonstrated to play important roles in the dehalogenation. A lot of catalytic systems showed good activities or high selectivities for the dehalogenation [1] in the organic phase, among which palladium-based systems are the most commonly used. Recently it was reported that polymer-anchored monometallic or bimetallic palladium-based catalysts [2] are the efficient homogeneous catalytic dehalogenation systems in which the bimetallic synergic effect [3] can enhance reaction rates and selectivity.

However, these homogeneous catalysts are difficult to recover and reuse.

In the recent years, dechlorination in water has attracted much attention due to pollution problems of organic halides in water system. Various metal particles and bimetallic system have been employed to investigate the aqueous dechlorination [4–6]. Recent efforts have concentrated on the use of zero-valence iron [7–9] and palladized iron [10–12] for the dechlorination of chlorinated organic compounds from effluents. Results showed that they could effectively or rapidly and completely reduce low weight halogenated hydrocarbons to hydrocarbons in water. However, only few reports are concerned with the dehalogenation of aromatic halides in water because of their very low solubility.

According to immobilized homogeneous transition metal complex catalysts offering the advantage over

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their homogeneous counterparts of easy separation from the reactant and product solution [13], and the necessity of the dehalogenation in water of aromatic halides, in the present study, we describe a new combined heterogeneous catalyst with phase transfer properties that is composed of the polyvinylpyrroli-done (PVP)-anchored $PdCl_2$ and $CuCl_2$ complex, PVP-$PdCl_2$-$CuCl_2$, supported on silica gel function-alized by phase transfer catalyst polyethylene glycol (PEG) with molecular weight 600, SiO_2-PEG600. The catalytic activities of the resulting catalyst for the dehalogenation of the aromatic halides in water and its characterization by IR, XPS and TEM are reported.

2. Experimental

2.1. Instrumentation

XPS spectra were recorded by a Kratos XSAM800 multifunctional surface analysis apparatus using Al Kα (1486.6 eV) as the exciting source and $C\,1s = 285.0$ eV as internal standard; IR spectra were ob-tained on a Perkin-Elmer 1730 infrared spectropho-tometer in potassium bromide disks; Carbon analysis was recorded on Hitachi MT-3 elemental analysis; The amount of Pd and Cu per gram catalyst was determined by atomic absorption spectrometry (Hi-tachi 180-30). The products were quantified by GC (a 102G chromatographic instrument with a $2\,m \times 3\,mm$ column coated with 20% SE-30). By-products were separated by column chromatography and identified by IR, ^1H NMR (FX-90Q spectrometer) and MS (GCMS-QP1000).

2.2. Materials

PVP were purchased from BASF, silica gel H was 10–40 μm in particle diameter. Other chemicals (PC) were used as received without further purification.

2.3. Preparation of a novel catalyst

A carrier system with phase transfer properties, SiO_2-PEG600, was prepared by immobilization of phase transfer catalysts onto oxides to simplify, by filtration, the separation and recovery process. The polyethylene glycol with average molecular weight 600 (PEG600), as a phase transfer catalyst, was heated in fluxing toluene for 3 h with silica gel with continuous removal of the water–toluene azeotrope. After filtering, the white powder was soxhlet extracted 12 h with toluene and dried under vacuum. Carbon analysis of the product (SiO_2-PEG600) indicated the degree of functionalization to be 0.28 mmol of glycol per gram of support.

In a 250 ml flask, 0.037 g of $PdCl_2$ was dissolved in 0.5 ml of 5 M HCl, then 100 ml of absolute ethanol and 0.56 g of PVP were added to give the red-brown PVP-$PdCl_2$ solution. After the mixture was stirred at room temperature for 48 h, the second compound cupric chloride was added to the mixture and con-tinuously stirred at room temperature for another 48 h. Finally, preparation of the soluble polymer-anchored bimetallic catalyst PVP-$PdCl_2$-$CuCl_2$ was accomplished.

20 ml of PVP-$PdCl_2$-$CuCl_2$ solution (or PVP-$PdCl_2$ solution) was added to a 30 ml flask containing 1 g of SiO_2-PEG600 (or SiO_2) and the mixture was stirred at room temperature for 48 h. After filtrating and drying at room temperature, we finally obtained the novel cat-alyst PVP-$PdCl_2$-$CuCl_2$/SiO_2-PEG600 with pale pink color and other catalysts like PVP-$PdCl_2$-$CuCl_2$/SiO_2 and PVP-$PdCl_2$/SiO_2-PEG600.

2.4. General procedure for dehalogenation in water

In a typical run, the flask was successively loaded with 0.23 g of the catalyst (Pd: 6.28×10^{-6} mol), 7.2 mmol of the sodium formate, 3.4 mmol of the aryl chloride and 2.5 ml of sodium hydroxide solution (pH = 11.7). The mixture was stirred at 80°C for 2.5 h by magnetic stirring. After the reaction was stopped, the reaction mixture was fully extracted with ethyl ether. The yield and the conversion of dehalogenation were quantified by GC analysis for the combined or-ganic extracts. The products with high boiling point were separated by column chromatography and then quantified by weight.

3. Results and discussion

By tests of various bimetallic systems, PEG with the different molecular weight, the molar ratio of Pd

Table 1
Effect of different carriers on catalytic activity of the catalysts[a]

No	Catalyst	Conversion (%)	Yield (%)
1	PVP-PdCl$_2$	13.2	10.5
2	PVP-PdCl$_2$-CuCl$_2$	16.3	14.7
3	PdCl$_2$-CuCl$_2$/SiO$_2$	10.4	0.5
4	PVP-PdCl$_2$-CuCl$_2$/SiO$_2$	57.4	25.3
5	PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600	92.1	50.8
6	PVP-PdCl$_2$/SiO$_2$-PEG600	64.8	44.6

[a] Reaction conditions: the used catalysts all contained 4.44×10^{-6} mol of palladium; 3.4 mmol p-chlorotoluene; 7.5 mmol sodium formate; 5 ml water; 100°C; 4 h.

to Cu and inorganic carriers, we finally established a novel active catalyst PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 (Pd:Cu = 2:1, molar ratio) for the dehalogenation of aromatic halides in water. The data listed in Table 1 reveal that, of all the catalysts, PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 (no. 5) is the most efficient. Its activity for p-chlorotulene dechlorination in water is substantially higher than those of the separate homogeneous catalysts (nos. 1, 2) and the separate heterogeneous catalysts (nos. 3, 4, 6). The catalyst with polymer PVP carrier (no. 4) exhibits dramatically higher than that without PVP (no. 3). It is preliminarily followed that the polymer PVP can make metal particles homodisperse at the surface and so increase the activity of the catalyst. By the comparison of nos. 4 and 5, we found the greatly increase of the conversion of the dechlorination in no. 5. It is interpreted that, as expected, immobilized phase transfer catalysis effect on the dechlorination reaction occurred in two-phase system. In addition, from the experimental results in nos. 5 and 6, we can see the synergic effect of the bimetallic system. The addition of the second metallic salts cupric chloride to the catalytic system improved the activity of the catalyst (no. 6). In general, the designed novel catalyst PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 first successfully showed good activity for the dechlorination of insoluble p-chlorotoluene in water. In order to study the structure of the new catalyst and further confirm the influence of each component in the catalyst, we characterized some catalysts such as PVP-PdCl$_2$/SiO$_2$-PEG600, PVP-PdCl$_2$-CuCl$_2$/SiO$_2$ and PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600, etc. by IR, XPS and TEM, etc.
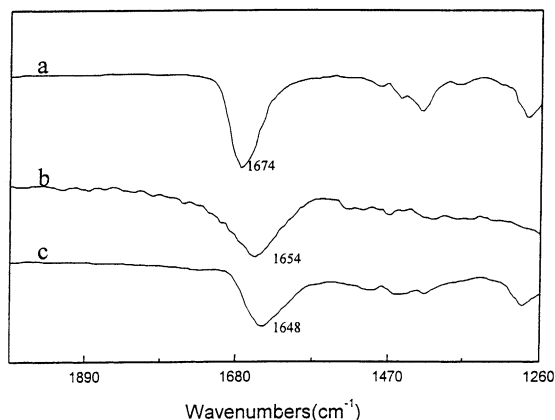

Fig. 1. IR spectra of the catalysts: (a) PVP; (b) PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600; (c) PVP-PdCl$_2$-CuCl$_2$.

Infrared spectra of the PVP-PdCl$_2$ complex and PVP-PdCl$_2$-CdCl$_2$ complex have been reported [2], in which the changes of $\upsilon_{C=O}$ value in PVP suggested that the oxygen atom of carbonyl group in PVP made complexion not only with palladium ion but with the second metal ion. IR study also showed that the structure of the tethered PVP-PdCl$_2$-CuCl$_2$ complex is the same as that of the free complex. When the PVP-PdCl$_2$-CuCl$_2$ complex was supported on the SiO$_2$-PEG600, the same conclusions can be obtained. The IR spectra are shown in Fig. 1.

Furthermore, we measured the XPS for the catalysts PVP-PdCl$_2$/SiO$_2$-PEG600, PVP-PdCl$_2$-CuCl$_2$/SiO$_2$ and PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 to verify the
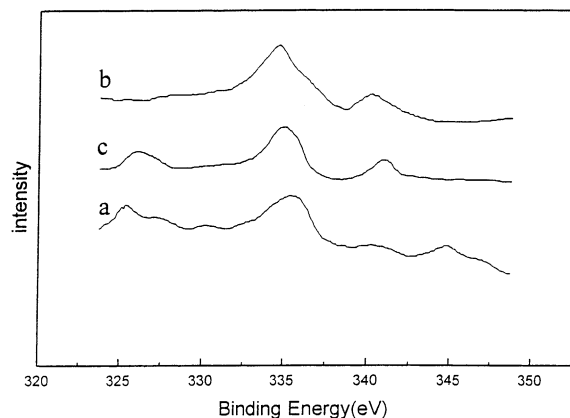
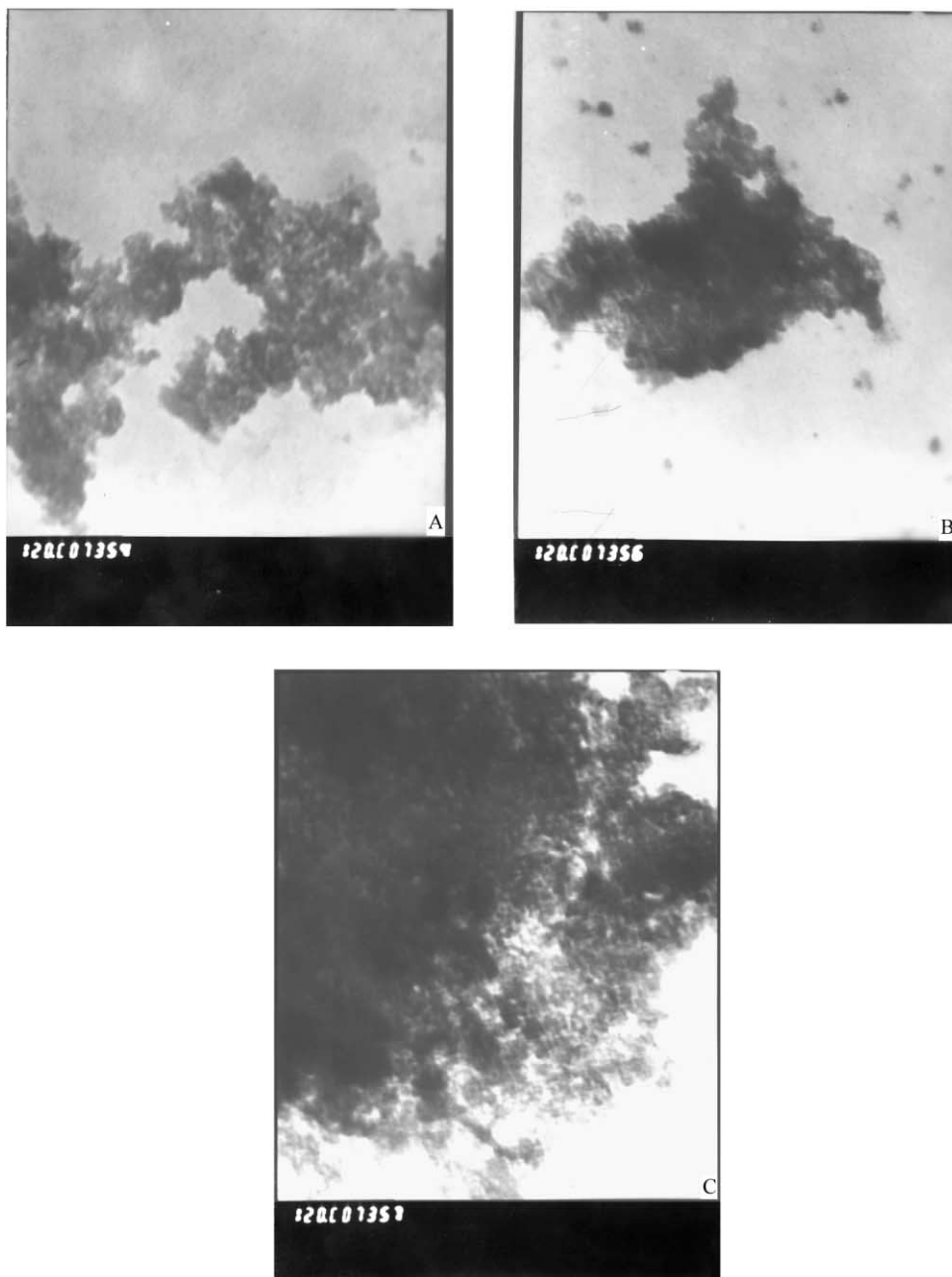Fig. 2. XPS spectra of the catalysts: (a) PVP-PdCl$_2$/SiO$_2$-PEG600; (b) PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600; (c) PVP-PdCl$_2$-CuCl$_2$/SiO$_2$.

Fig. 3. The TEM photograph of PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 (A), PVP-PdCl$_2$-CuCl$_2$/SiO$_2$ (B), and PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 (C).

synergic effect between the metal particles. Because the amount of Cu in the catalysts is relatively small, there is no information of copper ion in the XPS spectra. The results of XPS experiments were shown in Fig. 2. It is known that the binding energy of $Pd^o3d_{5/2}$ is 335.0 eV. Curve (a) indicated that the $Pd3d_{5/2}$ peak observed in the $PVP-PdCl_2/SiO_2-PEG600$ catalyst appeared to be centered at 336.9 eV. The addition of $CuCl_2$ decreased the oxidation state of palladium ion in the catalyst, as evidenced by the shift of the binding energy of $Pd3d_{5/2}$ towards lower energies (335.7 eV) as shown in curve (b). The data showed that the electrons in copper ions partly fluxed towards palladium ions and hence confirmed the certain synergic effect between palladium ions and copper ions. Compared with the $Pd3d_{5/2}$ peak of the catalyst (b), that of the catalyst $PVP-PdCl_2-CuCl_2/SiO_2$ (c) showed a 1.0 eV shift towards higher energy. This result suggests that, to some degree, coordination of the oxygen atom in phase transfer catalyst PEG with metallic ions occurred.

The TEM analyses were performed for $PVP-PdCl_2-CuCl_2/SiO_2-PEG600$ (A), $PVP-PdCl_2-CuCl_2/SiO_2$ (B) and $PdCl_2-CuCl_2/SiO_2-PEG600$ (C). As shown in Fig. 3. A appeared to show three-dimensional globular forms (BET surface area, 228.7 $m^2 g^{-1}$) and was homodisperse. Compared with A, B without PEG chain exhibited the agglomerates of globles and at the same time BET surface area dropped to 177.1 $m^2 g^{-1}$. These results demonstrated that the immobilized PEG chain in the catalyst A could make metal particles more homodisperse at the surface and so increase the surface area. In line with the conclusions of XPS, this
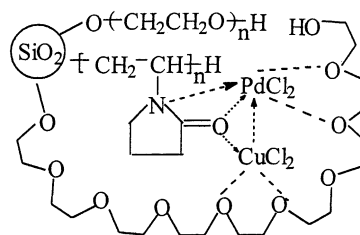

Fig. 4. The structure representation of the catalyst $PVP-PdCl_2-CuCl_2/SiO_2-PEG600$.

also showed that PEG chain participated in complexion with bimetallic ions. To bimetallic system without PVP carrier C, its TEM photograph showed there were some metallic agglomerates with different sizes and the distribution was not homogeneous. In addition, the surface area (92.6 $m^2 g^{-1}$) was also greatly decreased compared to A. This revealed that polymer PVP could evenly distribute metallic particles throughout the catalyst surface. Based on the above characterization data, a possible structure for the $PVP-PdCl_2-CuCl_2/SiO_2-PEG600$ catalyst is shown in Fig. 4.

On the other hand, we studied the activities and selectivities of the novel catalyst, $PVP-PdCl_2-CuCl_2/SiO_2-PEG600$, for various aromatic halides in water. Results are summarized in Table 2.

The catalyst has been found to catalyze selectively the dechlorination of organic chlorides in water and shows no activity for defluorination due to the high bond energy of C–F bond. Additionally, it also shows low catalytic activities in the dehalogenation of

Table 2
Activities on dehalogenation of aromatic halides in water by $PVP-PdCl_2-CuCl_2/SiO_2-PEG600$

No.	Substrate	Conversion (%)	Yield (%)	
			Products	By-products
1	Fluorobenzene	0.0		
2	Chlorobenzene	91.5	Benzene (44.4)	Biphenyl (2.0)
3	Bromobenzene	34.1	Benzene (14.5)	Biphenyl (1.2)
4	Iodobenzene	43.0	Benzene (18.6)	Biphenyl (6.8)
5	o-Chlorotoluene	78.6	Toluene (68.5)	2,2′-Dimethyldiphenyl (0.1)
6	m-Chlorotoluene	62.9	Toluene (41.2)	3,3′-Dimethyldiphenyl (0.2)
7	p-Chlorotoluene	96.6	Toluene (68.5)	4,4′-Dimethyldiphenyl (0.4)
8	p-Dichlorobenzene	86.2	Benzene (38.1)	Chlorobenzene (8.4) biphenyl (0.5)
9	p-Chloroaniline	85.3	Aniline (55.9)	4,4′-Diaminodiphenyl (1.2)
10	p-Chloroacetophenone	92.0	Acetophenone (85.8)	4,4′-Diacetyldiphenyl (2.3)

Table 3
Stability studies of the catalyst PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600 on the dechlorination of the p-chloroacetophenone[a]

Number of reuses	Conversion (%)	Amount of Pd (10^{-5} mol g^{-1} cat^{-1})
0	92.0	2.73
1	72.0	2.63
2	72.5	2.57
3	73.0	2.38
4	73.5	2.35
5	72.0	2.30

[a] Reaction conditions are the same as the general process except the catalyst is recycle.

bromobenzene and iodobenzene. This may be explained by the HSAB principles. During the course of the oxidation-addition of halides and Pd^o resulted from the reduction of the catalyst by HCOONa, I$^-$ and Br$^-$, which are both soft bases, are easy to combine with Pd^o, which is a soft acid, so that Pd–I and Pd–Br bond are very strong and not easily broken that results in the toxication of the catalyst. But Cl$^-$ belongs to the hard base and readily cleavages from the addiction product PhPdX. Results also indicate that there are some by-products like biphenyl compounds besides primary dehalogenative products (Table 2). The catalyst is an efficient catalyst on the dehalogenation of aryl chlorides not only with electron-withdrawing group but also with electron-donating group.

The experiments of reusability were done under similar reaction conditions. The results shown in Table 3 indicated that after one cycle, conversion of the p-chloroacetophenone decreased remarkably and then kept at the 70% or so. The reason is that in the preparation of the catalyst, a small part of PdCl$_2$-CuCl$_2$, with not complexing with PVP, was directly absorbed on the SiO$_2$-PEG600 and was apt to leach from the catalyst under the strong stirring when the dehalogenation carried out. Therefore, the conversion after the first run remarkably decreased because of the loss of the active metals. In the following cycles, because the large part of PdCl$_2$-CuCl$_2$ that complexed with PVP and PEG did not readily come off, the conversion of the p-chloroacetophenone was at the same level. We can also explain these results from the decreasing tendency of the amount of Pd in the catalyst versus the numbers of cycles. Except for the remarkably decrease in the first cycle, the amount of

Pd in the catalyst has decreased only slightly. In short, the novel catalyst PVP-PdCl$_2$-CuCl$_2$/ SiO$_2$-PEG600 exhibits a good stability and recyclability.

4. Conclusions

We prepared a novel catalyst PVP-PdCl$_2$-CuCl$_2$/ SiO$_2$-PEG600 (Pd:Cu = 2:1, molar ratio) by a simple procedure, which indicates the good activities and selectivities for dechlorination in water of insoluble aromatic chlorides. The polymer PVP-anchored bimetallic complex component is necessary for the high catalytic dechlorination activity of the new catalyst. Immobilized PEG600 on one side contributes to the performing of the reaction in two-phase systems, and on the other side can be separated and recycled. The carrier SiO$_2$ is an important component for the separation and recovery process of the whole combined catalyst PVP-PdCl$_2$-CuCl$_2$/SiO$_2$-PEG600. Although further studies in other aspects of the new catalyst still need, the preliminary work have shown that combinations of tethered complexes and supported phase transfer catalysts offer opportunities for the creation of highly active catalysts.

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