Catalytic Hydrodechlorination of Chlorobenzene over PtPd Bimetallic Catalysts Synthesized by Microwave Method

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Abstract: A series of Pt-Pd bimetallic catalysts have been prepared by microwave method, and characterized by TEM and XPS. Hydrodechlorination of chlorobenzene was carried out over these supported catalysts. The effects of the kinds of catalysts and solvents on the catalytic activity were investigated. When the reaction temperature was 298 K and the hydrogen pressure was 0.1 MPa, Pt-Pd/C exhibited high conversion of 100% to monochlorobenzene and selectivity of 71.75% to cyclohexane. The Pt-Pd/C has high catalytic activity for a variety of organic hydrogenation reactions.

Keywords: Microwave method; Pt-Pd/C; hydrodechlorination; chlorobenzene; solvents

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1. INTRODUCTION

Chlorinated organic compounds are widely used as starting materials, intermediates and solvents, so chlorinated organic compounds have been used in large scales in chemical industry, agricultural chemistry, medical chemistry, electronic industries and constitute one of the most important classes of organic pollutants[1,2]. They are widespread environment contaminants, existing not only in various water effluents, waste oils, but also in atmosphere and soils. However, these compounds especially chloroarenes are harmful to many aspect of the environment and human life because of their acute toxicity, thermal stability, and strong bioaccumulation potential[3]. Many fundamental investigations have been done to clear these chlorinated organic compounds, or convert them to alternative materials which are environmentally acceptable. Catalytic hydrodechlorination (HDC) of organic compounds have recently been recognized as one of the promising routes with low energy demands proposed for remediation of chlorinated organic compounds[4].

Pt, Pd, Ru, Ni are the most commonly catalysts for HDC[5-10]. Babu et al.[11] synthesized a series of alumina-supported Pd catalysts for the HDC of chlorobenzene under ambient conditions. They found that catalysts with cationic palladium (Pd^{n+}) offered higher activity compared to those having metallic palladium (Pd^0), and that the larger particle size attained better stability. However, in most of the reactions, benzene was the main product, which is an environmental pollutant as well. Liu et al.[12] studied the HDC of chlorobenzene using PVP-stabilized platinum nanocatalysts. It showed a high selectivity nearly 100% to cyclohexane; however the activity was not satisfied. Liu et al.[13] synthesized a series of PVP-stabilized Pd, Pt, Pd–Pt nanocatalysts. They found that the maximum conversion of chlorobenzene (95.34%) was achieved using PVP–Pd/Pt = 1/1 catalytic system and the selectivity to cyclohexane increased slowly with increasing of platinum content in bimetallic nanocatalysts.

As a rapid and uniform heating method, microwave-assisted polyol process has been widely used in preparing metal particles[14,15]. The main advantages of microwave irradiation were discussed by Tsuji et al.[16]: the uniform heating of the solution leading to a more homogeneous nucleation and shorter crystallization time. Berry et al.[17] synthesized a series of alumina-supported Pd–Fe mono- and bimetallic catalysts by

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microwave irradiation and by conventional calcination methods. HDC of chlorobenzene was carried out on these catalysts. Catalysts prepared by microwave irradiation give higher chlorobenzene conversion compared to those obtained over conventionally heated catalysts under all the experimental conditions used in the present study.

In this paper, actived carbons supported Pt-Pd mono- and bimetallic catalysts were made by microwave method. Those supported nanocatalysts were used to HDC of chlorobenzene and hydrogenation of other organics. We investigated the kinds of catalysts and the solvents effect on the reaction.

2. EXPERIMENTAL

2.1. Materials and Instruments

Hydrogen hexachloroplatinate (IV) hexahydrate (H_2PtCl_6 $6H_2O$) was purchase from Beijing Chemicals Co. Palladium chloride ($PdCl_2$) was purchase from Tianjin Chemicals Co. Hydrogen (H_2) with a purity of 99.999% was generated by an extra-pure hydrogen generator HA-300. Other reagents were of analytical grade purity and were used as received (Beijing Chemicals Co.)
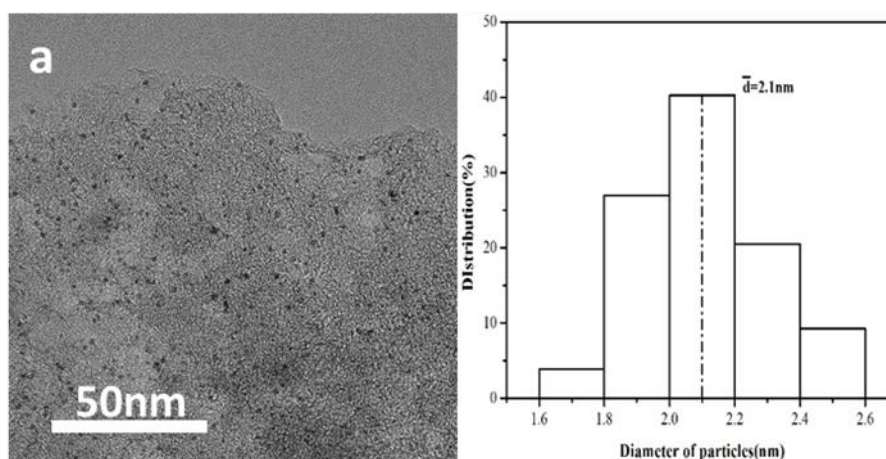
2.2. Synthesis

Bimetallic catalyst with the loading of 1 wt.% was prepared by microwave-assisted polyol process in ethylene glycol (EG) solution. Briefly, 5.658 g actived carbons was dispersed into 14 mL ethylene glycol in 150 mL beaker under ultrasonic treatment to form uniform carbon ink. Then 2.5 mL of 0.0388 g mL^{-1} H_2PtCl_6/EG solution was added into the carbon ink. The mixture was stirred for 30 min and heated for 90 s by a microwave oven (Galanz G8023CSL-K3, 2450 MHz, 800 W). 0.0331 g $PdCl_2$ and 13.5 mL EG was added into the cold mixture. Then the mixture was heated for another 90 s. The solution was allowed to cool down to room temperature with continuous stirring, and then 30 mL H_2O was added into the cold mixture with keeping stirring for 12 h. The black solution was centrifuged for 5 min at 8000 rpm, the product was collected after five consecutive water washing and then dried in a vacuum oven at 40°C for three days. The catalyst denoted as Pt-Pd/C. The catalyst prepared by the addition of $PdCl_2$ at first denoted as Pd-Pt/C. The catalyst prepared by the addition of H_2PtCl_6 and $PdCl_2$ simultaneously denoted as PtPd/C. The preparation method of Pt/C and Pd/C was similar to that mentioned above.
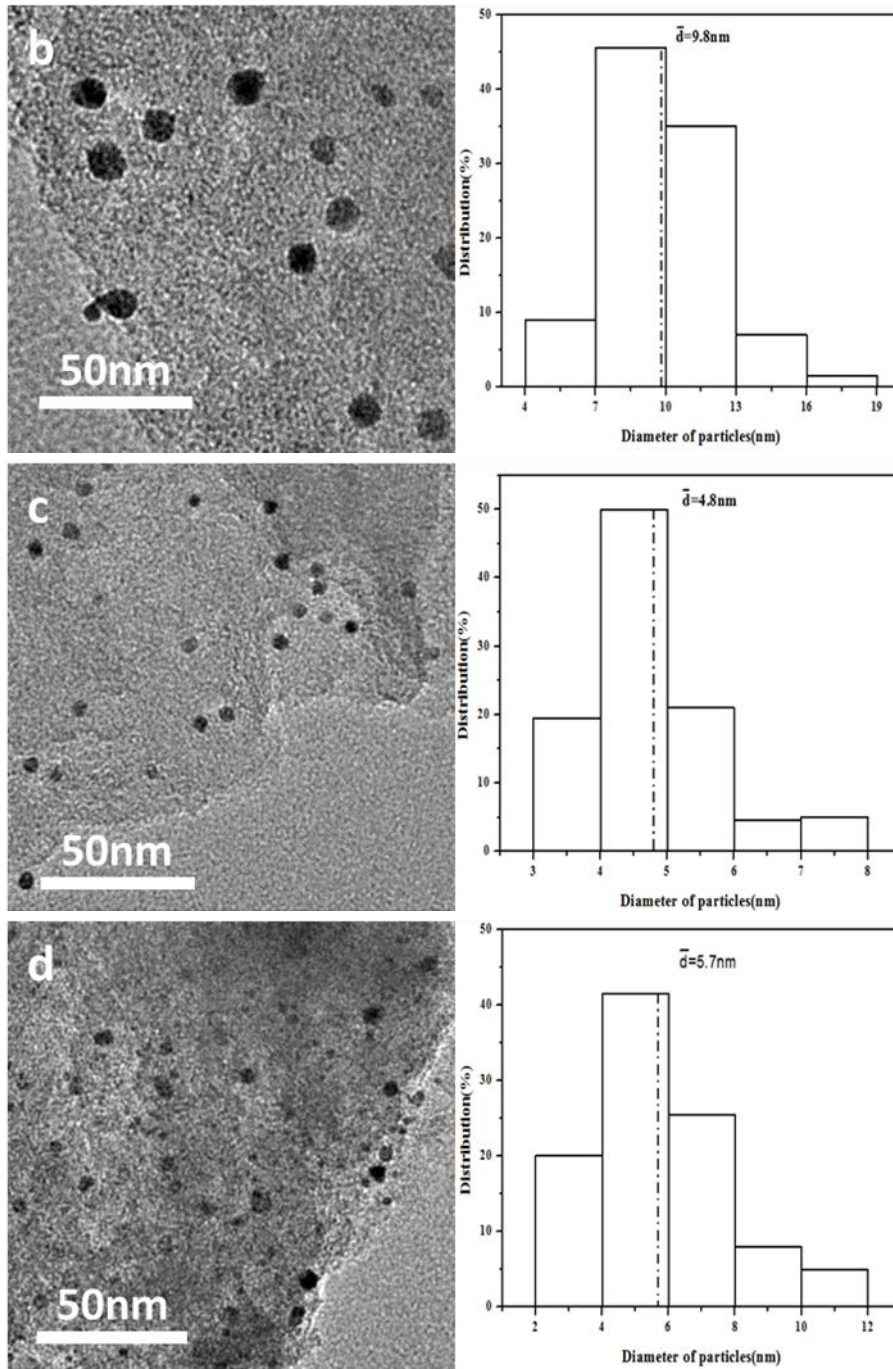
2.3. Hydrogenation Reactions

Hydrogenation of chlorobenzene was carried out at 298 K under 0.1 MPa of hydrogen pressure[12]. The catalyst (containing 5×10^{-5} mol (Pd + Pt)), 2 mL of the reactant solution (1.00×10^{-3} mol reactant in solvents) and extra solvents were added in a 250 mL three-necked flask equipped with a magnetic stirrer and a thermostatic water bath. The total volume of the catalytic system was 30 mL. Air in the system was removed by sweeping the system three times with hydrogen. The mixture was stirred vigorously to start the reaction. Chemical analysis of the products was analyzed by gas chromatography (GC) equipped with a FID detector and an AC-10 column. Reactants and products were identified by comparing with authentic samples.

3. RESULTS AND DISCUSSION

A series of finely dispersed Pt/Pd nanocatalysts were obtained by varying the different order of the precursor addition and characterized by TEM (JEM-2100 electron microscope). The TEM photographs and the corresponding particle size distribution histograms of bimetallic nanocatalysts are shown in Fig 1. The corresponding average particle diameters and standard deviations (σ) obtained on the basis of the measurements of about 200 particles through TEM photographs are shown in Table 1. The nanoparticles are well dispersed on the surface of actived carbons and no aggregation of the metallic particles can be detected. The order of the precursor addition influences the particle size greatly. Average diameters of 9.8, 5.7, 3.4, and 2.1 nm were observed with Pd/C, Pd-Pt/C, Pt-Pd/C, Pt/C, respectively. The average diameters of catalyst prepared by the addition of Pt precursor at first were smaller.
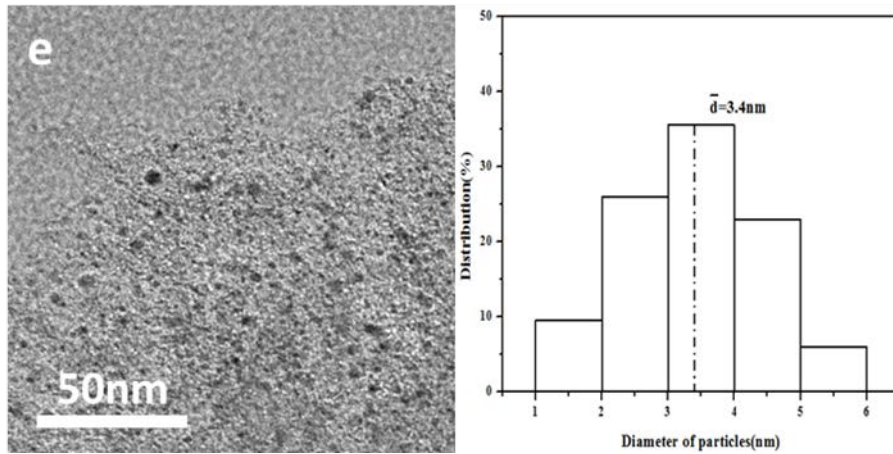
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Fig.1 TEM photographs and corresponding particle size distribution histograms of catalysts(a)Pt/C, (b)Pd/C, (c)PtPd/C, (d)Pd-Pt/C, (e)Pt-Pd/C

Table 1 The average diameters and standard deviations of catalysts

Sample	average diameter (nm)	standard deviation σ (nm)
Pt/C	2.1	0.3
Pd/C	9.8	2.3
PtPd/C	4.8	1.2
Pd-Pt/C	5.7	2.1
Pt-Pd/C	3.4	1.0

XPS was employed to study the surface elemental composition of the Pt-Pd/C as shown in Fig. 2. In Fig. 2a, the $Pt4f_{7/2}$ and $Pt4f_{5/2}$ lines appearing at 71.2 eV and 74.5 eV are attributed to the zero valent state of the Pt. The binding energy at 335.7 eV and 340.9 eV corresponds to metallic $Pd3d_{5/2}$ and $Pd3d_{3/2}$ in Figure 2b. Therefore, it can be concluded that the Pt^{4+} and Pd^{2+} precursors have been successfully reduced by microwave-assisted polyol process. The binding energies of Pt4f7/2 and Pd3d5/2 slightly deviated from the standard binding energy peak values of Pt^0 ($4f_{7/2} = 71.76$ eV, $4f_{5/2} = 75.02$ eV) and Pd^0 ($3d_{5/2} = 334.90$ eV, $3d_{3/2} = 340.15$ eV), which can be contributed to the electronic interaction between the Pd and Pt elements[18].
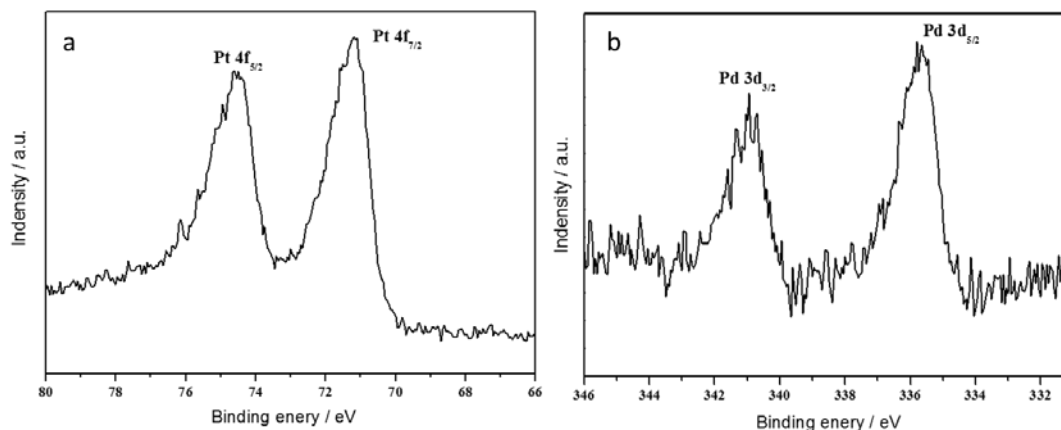
Fig.2 XPS spectra of Pt-Pd/C

The catalytic properties of the as-prepared catalysts were investigated. The hydrodechlorination of dichlorobenzene was carried out over these supported catalysts in methanol and ethanol at 298 K under 0.1 MPa of hydrogen. The hydrodechlorination products determined by GC-MS were benzene, cyclohexane and monochlorobenzene. Results presented in Table 2, 3 shows that the conversion of dichlorobenzene and selectivity of cyclohexane over Pt/C was higher than that of Pd/C. Table 2 shows that the catalytic activity of the bimetallic nanocatalysts was enhanced with decreasing the catalysts particle size, and the catalytic activity (72.14% conversion) of the Pt-Pd/C was the highest among these bimetallic nanocatalysts in methanol. But it was different in ethanol (Table 3), the catalytic activity (72.05% conversion) of the Pt-Pd/C was the highest, the catalytic activity of the Pd-Pt/C was higher than PtPd/C. This is because not only the particle size affected the activity of the catalyst, but also electronic interaction between platinum and palladium atoms would affect the surface atoms to the hydrogenation of chlorobenzene. Liu et al.[13] found that PVP–Pd/Pt bimetallic catalysts had synergetic effect to the hydrogenation of chlorobenzene.

With regard to hydrodechlorination, the reaction medium has been claimed to influence reaction rate and product distribution[19-22]. The conversion of the chlorobenzene was same in different solvents, but the selectivity to cyclohexane was different. The selectivity of cyclohexane in ethanol was higher than that in methanol. Therefore, ethanol solvent is more favorable for the hydrodechlorination of dichlorobenzene to cyclohexane. Ukisu et al.[23] found that when primary alcohols such as 1-propanol and ethanol were used as a solvent, the conversion of

1,2,4-trichlorobenzene and the yield of benzene were very low, on the other hand, secondary alcohols such as 2-butanol and 2-propanol led to a high yield of benzene. It was concluded that 2-propanol functions as a hydrogen-donor as well as a solvent in the catalytic hydrohalogenation of aromatic halides. The effect of organic solvents acting as hydrogen donors on dehalogenation of organohalogen compounds has been reported by different authors[24-28].

Table 2 Catalytic hydrogenation of dichlorobenzene over different catalysts in methanol [a]

catalyst	conversion/%	selectivity/%		
		cyclohexane	benzene	monochlorobenzene
Pt/C	61.76	75.85	19.85	4.3
Pd/C	45.84	0.57	65.35	34.09
PtPd/C	38.16	7.2	82.29	10.5
Pd-Pt/C	24.49	31.74	48.63	19.63
Pt-Pd/C	72.14	51.82	44.51	3.67

[a] Reaction conditions: reaction time = 4 h, P_{H2} = 0.1 MPa, T = 298 K, V = 30 mL, $M_{(Pt+Pd)}$ = 5×10^{-5} mol, dichlorobenzene = 1 mmol.

Table 3 Catalytic hydrogenation of dichlorobenzene over bimetallic catalysts in ethanol [a]

catalyst	conversion/%	selectivity/%		
		cyclohexane	benzene	monochlorobenzene
Pt/C	82.55	97.3	1.2	1.5
Pd/C	32.92	15.29	43.23	41.47
PtPd/C	25.70	63.28	9.15	9.15
Pd-Pt/C	31.78	73.00	16.37	10.63
Pt-Pd/C	72.05	87.53	9.29	2.55

[a] Reaction conditions: reaction time = 4 h, P_{H2} = 0.1 MPa, T = 298 K, V = 30 mL, $M_{(Pt+Pd)}$ = 5×10^{-5} mol, dichlorobenzene = 1 mmol.

Table 4 Catalytic hydrogenation of monochlorobenzene over different catalysts in ethanol [a]

catalyst	time/h	conversion/%	selectivity/%	
			cyclohexane	benzene

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PtPd/C	4	85.88	37.17	62.81
Pd-Pt/C	4	83.36	47.49	52.51
Pt-Pd/C	4	100	71.75	28.25
Pt-Pd/C	3	95.87	61.56	38.44

[a] Reaction conditions: P_{H2} = 0.1 MPa, T = 298 K, V = 30 mL, $M_{(Pt+Pd)}$ = 5×10^{-5} mol, monochlorobenzene = 1 mmol.

Table 5 Catalytic hydrogenation of organics over Pt-Pd/C

reactant	time/min	conversion/%	reaction rate/mol $_{reactant}$/(mol$_{Pt+Pd}$·h)
benzene [a]	180	47.46	3.168
1,2,4-trichlorobenzene [a]	360	45.64	1.512
cyclohexene [a]	60	100	20.061
nitrobenzene [b]	40	96.46	28.944

[a] Reaction conditions: P_{H2} = 0.1 MPa, T = 298 K, V = 30 mL, solvent is ethanol, $M_{(Pt+Pd)}$ = 5×10^{-5} mol, reactant = 1 mmol.

[b] $M_{(Pt+Pd)}$ = 5×10^{-6} mol.

The hydrodechlorination of monochlorobenzene were carried out over these bimetallic catalysts in ethanol. It can be seen from Table 4 that Pt-Pd/C was the most active catalyst compared with the other catalysts and within 3 h the conversion of monochlorobenzene reached 95.87%. After 4 h the monochlorobenzene completely dechlorination. We also investigated the catalytic hydrogenation of other organics over Pt-Pd/C under 298K, 0.1 MPa (Table 5). The more C–Cl bond in chlorinated aromatic compounds, the more resistant to dechlorination. The conversion of benzene and 1,2,4-trichlorobenzene were also relatively high. So HDC of chlorinated aromatic compounds is very effective over Pt-Pd/C, it can reduce environmental pollution. Aniline is an important organic chemical material and fine chemical intermediates, which has been extensively used in synthesizing the accelerator, antioxidant, stabilizer, etc[29]. Many method have been reported for aniline preparation and the hydrogenation of nitrobenzene has been widely used in industrial production. The Pt-Pd/C prepared by microwave method was used as catalyst in the hydrogenation of nitrobenzene, and within 40 min the conversion of nitrobenzene reached 96.46%. Catalytic hydrodechlorination of cyclohexene also can be carried over the Pt-Pd/C, the conversion of cyclohexene reached 100%.

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4. Conclusions

A series of actived carbons supported Pt/Pd catalysts with defined particle sizes and uniform dispersion were prepared by microwave method. In the HDC of chlorobenzene, the catalytic activity of the bimetallic nanocatalysts was enhanced with decreasing the catalysts particle size. The catalytic activity of the Pt-Pd/C was the highest among these bimetallic nanocatalysts. The solvents have important influence on the selectivity to cyclohexane in the catalytic hydrogenation of dichlorobenzene. The Pt-Pd/C has high catalytic activity for the hydrogenation of benzene, 1,2,4-trichlorobenzene, nitrobenzene and other organic compounds. It has an important application prospect in catalysis.

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