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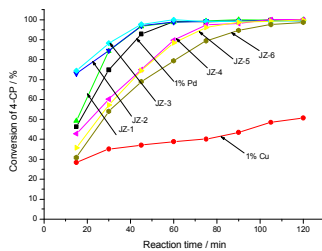
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Colour graphic

A moderate amount of Cu addition to the Pd/ γ -Al₂O₃ catalyst will increase the catalytic activity of hydrodechlorination of chlorophenols.



**Catalytic hydrodechlorination of 4-chlorophenol over a series of
Pd–Cu/ γ -Al₂O₃ bimetallic catalysts**

Deren Fang*, Wanjun Li, Jinbo Zhao, Shang Liu, Xuanxuan Ma,
Jinguang Xu, Chuanhai Xia

Institute of Applied Catalysis, Yantai University, Yantai 264005, China

* Corresponding author E-mail: fdr@ytu.edu.cn

ABSTRACT A series of Pd–Cu/ γ -Al₂O₃ bimetallic catalysts was prepared using the sequentially incipient wetness impregnation method. The catalysts were characterized using X-ray diffraction, temperature programmed reduction, scanning electron microscopy–energy dispersive X-ray, and hydrogen (H₂) pulse chemisorption measurements. The influence of Cu on the Pd–Cu/ γ -Al₂O₃ bimetallic catalyst in the catalytic hydrodechlorination (HDC) of 4-chlorophenol (4-CP) in an aqueous phase in a mixing glass tank reactor was studied using H₂ as the reducing agent. Compared with a Pd/ γ -Al₂O₃ monometallic catalyst, adding Cu to modify the Pd catalyst changed the dispersion of Pd particles and surface area of the metals, thereby significantly influencing the catalytic performance in the HDC of 4-CP in an aqueous phase. The results demonstrated that adding Cu to the Pd catalyst improved the dispersion of Pd particles and increased the HDC catalytic activity when the Cu/Pd

molar ratio was $\leq 0.5/1$. In addition, the formation of a Pd–Cu alloy in the Pd–Cu bimetallic catalyst inhibited further hydrogenation of phenol, the hydrodechlorinated product of 4-CP. The Cu/ γ -Al₂O₃ catalyst had an extremely low catalytic activity in the HDC of 4-CP; however, it did not catalyze the hydrogenation of phenol to form cyclohexanone.

Keywords catalytic hydrodechlorination (HDC); 4-chlorophenol; Pd–Cu/ γ -Al₂O₃ bimetallic catalysts; Pd–Cu alloy

1. Introduction

Chlorophenols (CPs) are widely used in manufacturing pesticides, disinfectants, wood preservatives, and personal care formulations and are the byproducts of several industrial processes [1]. However, a growing concern regarding the toxicity and environmental fate of these compounds has led to strict government regulations. Five CPs are listed by the United States Environmental Protection Agency as priority pollutants [1, 2], and efficient (catalytic) methods must be developed for eliminating poorly biodegradable CPs released from industrial effluents and polluted groundwater.

In past years, catalytic hydrodechlorination (HDC) has received increasing attention for the treatment of wastewater containing

chlorinated organic compounds because HDC is advantageous compared with other potential techniques for treating these hazardous pollutants. HDC proceeds at mild conditions [3, 4]; it does not require high temperature and pressure as incineration or wet oxidation do.

Research regarding the HDC of CPs has typically involved evaluating supported metal catalysts. Bulk or supported forms of precious metals such as Pd [3–16], Pt [17], and Rh [5, 18] are widely used as catalysts in HDC under liquid and gas phase conditions. Among these metals, Pd is the most active and selective catalyst [19]. However, the high cost of Pd hinders its practical application. In recent years, studies have explored the modification of supported Pd monometallic catalysts by combining Pd with a different transitional metal. Several Pd-based bimetallic supported catalysts and nanoparticles, such as Pd–Ni [20], Pd–Fe [21], Pd–Mg [22], and Pd–Al [23], have been widely explored for use in HDC. These catalysts provided more satisfactory catalytic activity in HDC than monometallic catalysts did. In addition, hydroisomerization of the product of the HDC of CCl_4 was observed when Cu was introduced to Pd/C [24].

This study involved preparing Al_2O_3 -supported Pd–Cu bimetallic catalysts by using the incipient wetness impregnation method and examining the catalytic performance of these catalysts in the HDC of

4-chlorophenol (4-CP) in an aqueous phase by using molecular hydrogen as the reducing agent at room temperature and normal pressure. 4-CP was effectively hydrogenated during HDC; moreover, interesting reaction phenomena were observed for the first time.

2. Experimental section

2.1 Catalyst preparation

Beads composed of γ -Al₂O₃ with a diameter of 0.5–1 mm were used as the support, and the Pd–Cu bimetallic catalysts were prepared using the sequentially incipient wetness impregnation method. The content of the noble metal (Pd) was fixed at 1 wt%, and the Cu content was varied to obtain the Cu/Pd molar ratios 0.1/1, 0.25/1, 0.5/1, 1/1, 3/1, and 5/1 for catalysts that were designated JZ-1, JZ-2, JZ-3, JZ-4, JZ-5, JZ-6, respectively. A typical catalyst preparation method was used to impregnate the precursors of the catalysts with the designated amount of aqueous Cu(NO₃)₂ to yield the desired content (wt%) of Cu and then dried at 110 °C for 2 h and calcined at 350 °C for 2 h. After cooling, the catalysts were impregnated with aqueous PdCl₂, and then dried at 110 °C for 2 h and calcined in air at 350 °C for 2 h. The monometallic catalysts with Pd or Cu content of 1% were prepared using the aforementioned procedure and were designated 1% Pd and 1% Cu, respectively. The catalysts were reduced before HDC was performed using aqueous NaBH₄

at room temperature and crashed to the size of 0.045~0.075mm.

2.2 Catalyst characterization

X-ray diffraction (XRD) patterns were obtained using the Rigaku D/MAX-2500 diffractometer with Cu K α radiation (40 kV, 100 mA). Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 FE-SEM equipped with a computer system for performing automatic operation and data processing. The dried sample was carefully transferred to a carbon tape on the SEM template, coated using a gold coater, and analyzed using SEM at 10 kV. Energy dispersive X-ray (EDX) experiments were performed using an EX-350 EDX microanalyzer equipped with a computer system for conducting automatic operation and data processing. EDX mapping was performed to visualize elemental and spatial information regarding Cu and Pd on the Al₂O₃ surface. The particle morphology and size distributions of Pd and Cu were determined by transmission electron microscopy (TEM/EDX), in a JEOL JEM2000EXII microscope.

Temperature-programmed reduction (TPR) was performed using a TP5000 multifunction absorber. The catalyst weight was 50 mg, the particle size was 60–80 mesh, a mixture of 10%H₂/90%N₂ was used as the reduction gas, and the temperature was increased from 20 to 300 °C at a rate of 5 °C/min. Consumption of H₂ was detected using a thermal

conduction detector (TCD).

H₂ pulse chemisorption measurements of the catalysts were performed using a TP5000 multifunction absorber and the TCD. The catalyst weight was 0.10 g. Before the H₂ pulse chemisorption measurements were performed, the catalysts were activated at 623 K for 2 h by using a flow of pure H₂ at atmospheric pressure. The catalysts were then degassed at 623 K for 2 h under flowing Ar and cooled to 308 K. Next, H₂ (5 vol%) was injected into the Ar stream flowing through the sample bed. The injection loop was 0.5 mL. In the subsequent metal dispersion calculations, H₂ was assumed to be chemisorbed only on the Pd ensembles. The surface area and dispersion of Pd of the catalysts are listed in Table 1.

2.3 Studies of catalytic HDC

HDC of 4-CP (Sigma, purity > 99.6%) was performed at atmospheric pressure in a mixing glass tank reactor (demonstrated in Scheme 1) with electromagnetic stirring to ensure full contact between the catalyst and the reactant. After reduction (described in Section 2.1), 0.2 g of the catalyst was added to a 200-mL aqueous mixture of 4-CP (1000 ppm) and NaOH (NaOH/4-CP molar ratio = 1.1/1). Next, H₂ was

introduced into the reactor at a rate of 50 mL/min, thus initiating the HDC. After 15 min, 1 mL of the solution was extracted and analyzed by using gas chromatography, a flame ionization detector, and a polyethylene glycol capillary column.

3. Results and discussion

Figure 1 shows the XRD patterns of the catalysts. Diffraction peaks of the γ -Al₂O₃ support at 2θ equals to 37.2°, 45.9° and 66.6° were expected in the XRD patterns of Pd/ γ -Al₂O₃ and Pd-Cu/ γ -Al₂O₃ (JCPDS 10-0425), but Pd and Cu has not detected. Because of the low content of Pd and Cu in the catalysts, the reflection peak of which were covered by the background of γ -Al₂O₃, and was difficult to observe. The results of TEM demonstrated that the particle size of the Pd and Cu of the catalysts were in the range of 2~3 nm (Fig. 2), so it is difficult to use the XRD determination of phase of Pd and Cu of the catalysts. According to the EDX analysis of JZ-3 (Cu/Pd = 0.5/1), the peaks corresponding to Pd and Cu were observed (Fig. 3), indicating that Pd and Cu were present on the surface of the catalysts.

The dispersion of Pd and surface areas of the bimetallic catalysts were studied using H₂ pulse chemisorption measurements [25], and the results are illustrated in Table 1. Compared with the 1% Pd monometallic catalyst, bimetallic catalysts with Cu/Pd molar ratios of 0.1/1, 0.25/1, and

0.5/1 (JZ-1, JZ-2, and JZ-3, respectively) exhibited incrementally greater dispersions of Pd and surface areas. However, bimetallic catalysts with Cu/Pd molar ratios of 1/1, 3/1, and 5/1 (JZ-4, JZ-5, and JZ-6, respectively) exhibited incrementally lower dispersions of Pd and surface areas, indicating that adding Cu changed the dispersion of Pd and the surface areas of the bimetallic catalysts. Adding an appropriate amount of Cu increased the dispersions of Pd and surface areas of Pd-based bimetallic catalysts compared with those of the Pd monometallic catalyst.

Figure 4 shows H₂-TPR profiles of the catalysts. The TPR profiles of 1% Pd and 1% Cu monometallic catalysts showed only one reduction peak, and their reduction temperatures were 358 K and 472 K, respectively. The negative peak of 1% Pd at 431 K corresponded to the decomposition of Pd β-hydride [26].

The TPR profiles of the Pd–Cu bimetallic catalysts were different from those of the 1% Pd and 1% Cu monometallic catalysts. The TPR profile of JZ-1 (Cu/Pd molar ratio = 0.1/1) was similar to that of the 1% Pd monometallic catalyst, indicating that adding a small amount of Cu to the Pd monometallic catalyst did not alter the microstructure of the Pd particle. As the Cu content was increased (JZ-2, JZ-3, JZ-4, JZ-5, and JZ-6), the TPR profiles gradually became more complex. Three reduction peaks appeared in the TPR profiles of these catalysts; the reduction peak

centered at 358 K was attributed to PdO, the reduction peak in the range 433–463K was attributed to CuO, and the reduction peak in the range 393–413 K (middle peak) was attributed to the interaction between PdO and CuO, which transformed into Pd–Cu alloy particles after the reduction [27, 28]. The TPR profiles of JZ-2 (Cu/Pd = 0.25/1), JZ-3 (Cu/Pd = 0.5/1), JZ-4 (Cu/Pd = 1/1), JZ-5 (Cu/Pd = 3/1), and JZ-6 (Cu/Pd = 5/1) clearly showed that the intensity of the middle peak (PdO–CuO interaction species) as well as the reaction temperatures increased with the Cu content. Moreover, the intensity of the reduction peak of PdO decreased. This indicates that, as the Cu content in the Pd–Cu bimetallic catalysts was increased, the amount of the Pd–Cu alloy increased. The TEM/EDX images (Fig. 5) demonstrated that in the same micro zone of JZ-3 and JZ-6 there coexist Pd and Cu, this means that the formation of Cu-Pd alloy on the catalysts.

The catalytic HDC performance of the catalysts is shown in Fig. 6. A marked difference in the catalytic activity of the catalysts was observed. When the Cu/Pd molar ratios were 0.1/1, 0.25/1, and 0.5/1, 4-CP was completely hydrodechlorinated within 60 min; however, when the Cu/Pd molar ratios were 1/1, 3/1, and 5/1, 4-CP was not completely hydrodechlorinated within 60 min. The HDC catalytic activity of the catalysts followed the order JZ-3 > JZ-2 > JZ-1 > 1% Pd > JZ-4 > JZ-5 >

JZ-6 > 1% Cu. This result indicated that a moderate amount of Cu added to modify the Pd monometallic catalyst improved the catalytic activity. According to the results shown in Table 1, the catalytic activity of the catalysts was correlated to the dispersion of Pd and surface area of the catalysts. The dispersion of Pd and surface area of the catalysts followed the order JZ-3 > JZ-2 > JZ-1 > 1% Pd > JZ-4 > JZ-5 > JZ-6, which is consistent with the order of the catalytic activity of the catalysts. Among all catalysts, JZ-3 had the highest dispersion of Pd and surface area; therefore, JZ-3 showed the highest catalytic activity in the HDC of 4-CP.

According to the gas chromatography–mass spectrometry analysis, in addition to phenol, cyclohexanone was a product in the HDC of 4-CP in an aqueous phase. This indicated that the HDC of 4-CP was a tandem reaction in which 4-CP was first hydrogenated to form phenol over 1% Pd and Pd–Cu bimetallic catalysts, and phenol was further hydrogenated to form cyclohexanone [4, 6, 15, 29]. The change in the selectivity of the catalysts is shown in Fig. 5a and 5b, and the reaction pathway is shown in Scheme 2. Figs. 6 and 7 show that the competitive hydrogenation of phenol occurred in the HDC of 4-CP over 1% Pd and all Pd–Cu bimetallic catalysts. For example, when 1% Pd was used in the HDC of 4-CP, approximately 75% of 4-CP was hydrogenated (Fig. 6) after 30 min; furthermore, the selectivity of phenol and cyclohexanone were

approximately 98.36% (Fig. 7a) and 1.64% (Fig. 7b), respectively, indicating that the HDC of 4-CP and the hydrogenation of phenol occurred simultaneously over the 1% Pd monometallic catalyst. For Pd–Cu bimetallic catalysts, competitive hydrogenation between 4-CP and phenol occurred during the HDC of 4-CP (Fig. 7). Furthermore, the variation tendencies in the selectivity of phenol gradually decreased as the reaction time increased over 1% Pd and Pd–Cu bimetallic catalysts (Fig. 7a). However, the selectivity of cyclohexanone gradually increased for all 1% Pd and Pd–Cu bimetallic catalysts (Fig. 7b). According to these results, the catalytic activity of the catalysts was concluded to follow the order JZ-1 > JZ-2 > JZ-3 > 1% Pd > JZ-4 > JZ-5 > JZ-6 for the HDC of 4-CP; however the catalytic activity for the hydrogenation of phenol followed the order 1% Pd > JZ-1 > JZ-2 > JZ-3 > JZ-4 > JZ-5 > JZ-6 in an aqueous solution. Therefore, the Pd monometallic catalyst and the Pd–Cu bimetallic catalysts showed different catalytic activities in the hydrogenolysis of the C–Cl bond of 4-CP and C=C double bond of phenol. Compared with the 1% Pd monometallic catalyst, adding Cu inhibited the formation of cyclohexanone in the HDC of 4-CP over Pd–Cu bimetallic catalysts throughout the reaction process. The higher the Cu content in the Pd–Cu bimetallic catalysts was, the lower the cyclohexanone selectivity in the HDC of 4-CP. The TPR results (Fig. 4) showed that, as the Cu content in the Pd–Cu bimetallic catalysts was

increased, the intensity of the reduction peak of PdO decreased, and the reduction peak of the PdO–CuO interaction species increased; in other words, as the Cu content was increased, the amount of Pd particles in the Pd–Cu bimetallic catalysts gradually decreased and the amount of the Pd–Cu alloy increased. This means that the formation of the Pd–Cu alloy in the Pd–Cu bimetallic catalysts did not favor the hydrogenation of phenol to form cyclohexanone, which may require multiple adsorption or plurality of an active center (demonstrated in Scheme 3). The Pd monometallic catalyst not only catalyzed the hydrogenolysis of the C–Cl bond of 4-CP but also catalyzed the hydrogenation of phenol. By contrast, the Pd–Cu bimetallic catalysts mainly catalyzed the hydrogenolysis of the C–Cl bond of 4-CP, which was possibly related to the formation of the Pd–Cu alloy. The Cu/ γ -Al₂O₃ catalyst had an extremely low catalytic activity in the HDC of CP and did not catalyze the hydrogenolysis of phenol to form cyclohexanone (Fig. 7b). The active center was mainly Pd in both reactions. The formation of the Pd–Cu alloy reduced the quantity of active Pd centers, thereby affecting the hydrogenation of the benzene ring of phenol, and the hydrogenolysis of the C–Cl bond of 4-CP required few active centers of Pd clusters. The reason for the inhibition of the hydrogenation of the C=C double bond of phenol by the Pd–Cu alloy in the Pd–Cu bimetallic catalysts is unclear and requires further investigation.

4. Conclusion

A series of Pd–Cu/ γ -Al₂O₃ bimetallic catalysts was prepared, and their catalytic performance was studied in the HDC of 4-CP in an aqueous phase. Compared with the Pd/ γ -Al₂O₃ monometallic catalyst, adding a moderate amount of Cu to modify Pd catalysts increased the dispersion of Pd and surface area of the catalysts and considerably increased catalytic activity in the HDC of 4-CP. However, adding an excessive amount of Cu to the Pd–Cu/ γ -Al₂O₃ catalyst inhibited the HDC of 4-CP. In addition, the Pd monometallic catalyst was more advantageous than the Pd–Cu bimetallic catalysts because it catalyzed the hydrogenation of phenol to form cyclohexanone, whereas the Pd–Cu alloy in the Pd–Cu bimetallic catalysts was disadvantageous because it inhibited the hydrogenation of phenol, the HDC product of 4-CP.

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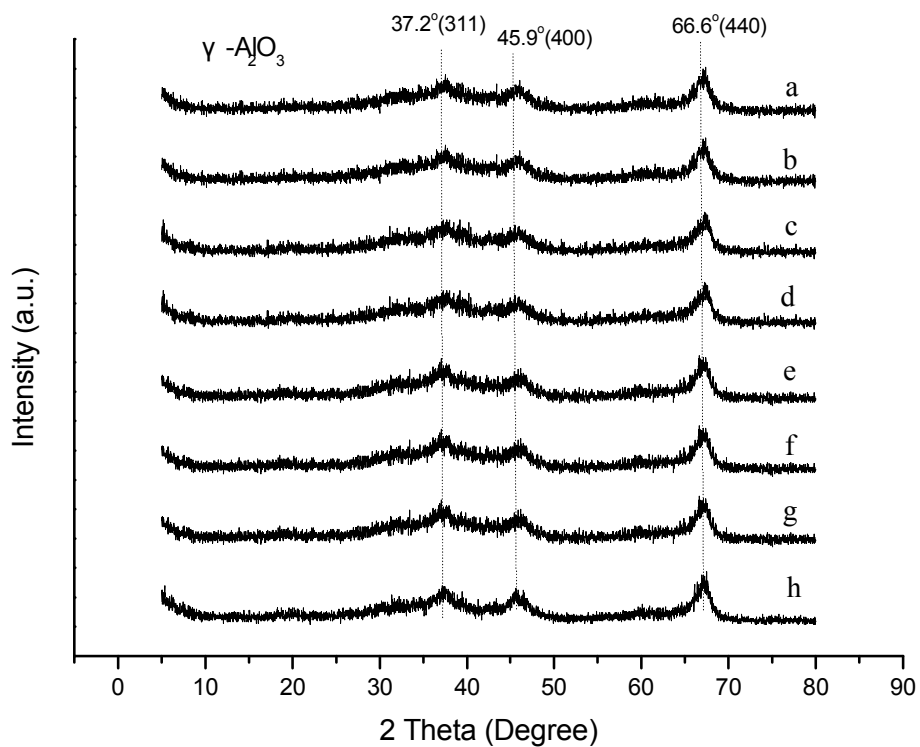
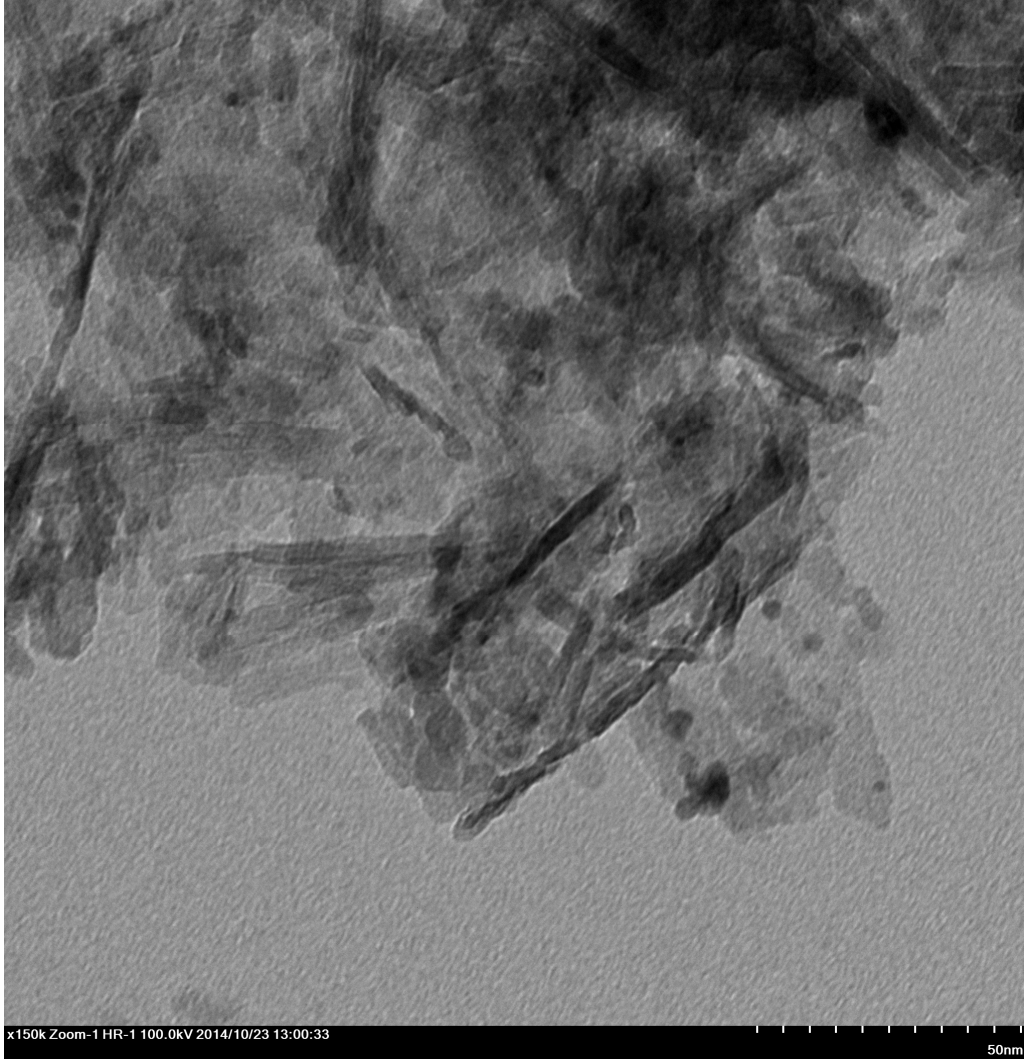
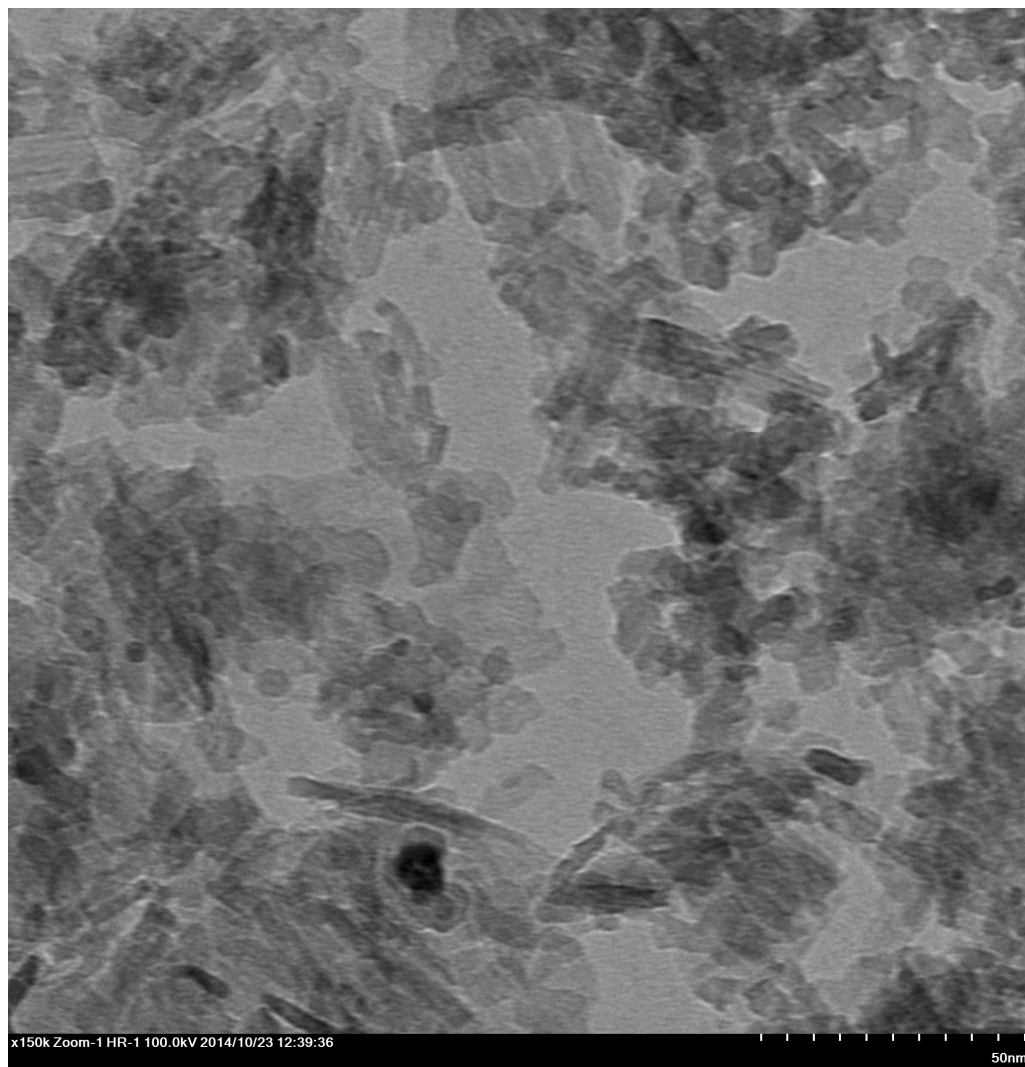


Fig. 1. XRD patterns of the reduced catalysts with different molar ratio of Cu to Pd

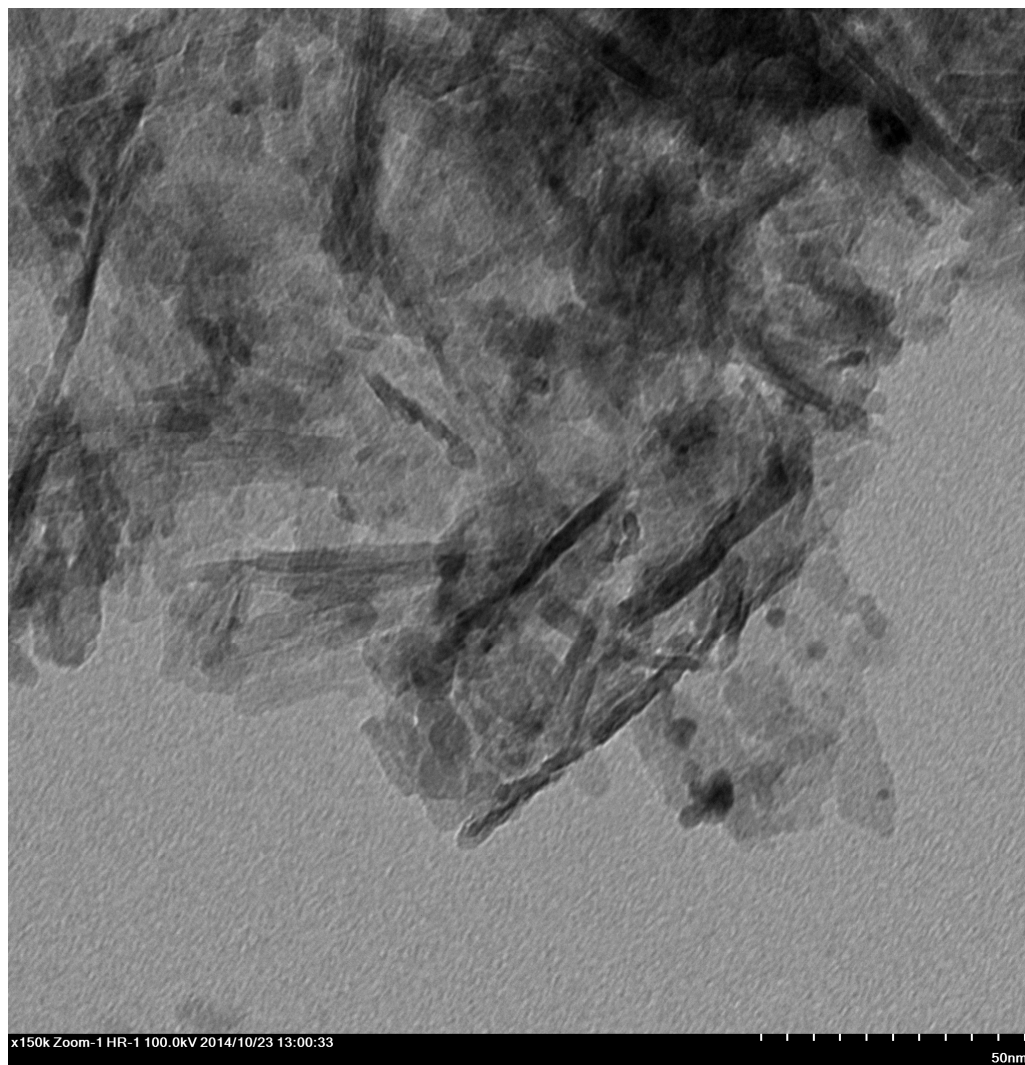
a: 1%Pd, b: JZ-1 (Cu/Pd=0.1/1), c: JZ-2 (Cu/Pd=0.25/1), d: JZ-3 (Cu/Pd=0.5/1), e: JZ-4 (Cu/Pd=1/1), f: JZ-5 (Cu/Pd=3/1), g: JZ-6 (Cu/Pd=5/1), h: γ -Al₂O₃



a



b



c

Fig.2. TEM micrographs of reduced Pd-Cu/ γ -Al₂O₃ catalysts (a) JZ-3 (Cu/Pd=0.5/1), (b) JZ-4 (Cu/Pd=1/1), (c) JZ-6 (Cu/Pd=5/1)

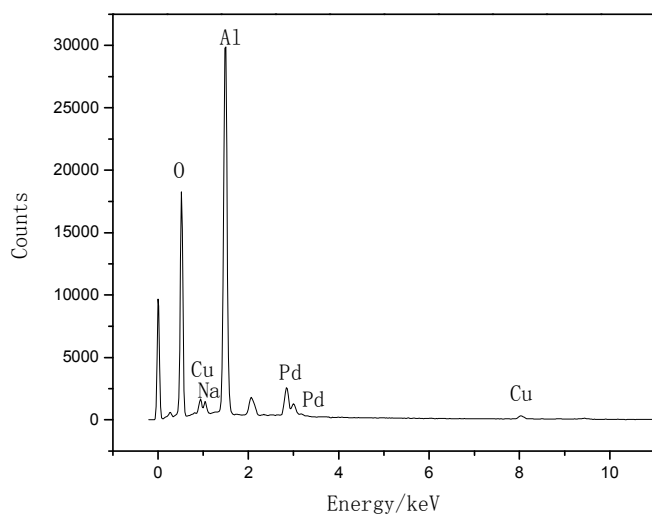
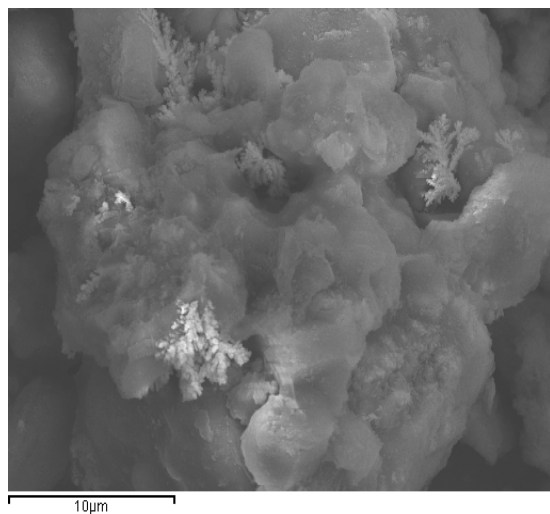


Fig.3. EDX image of reduced Pd-Cu/ γ -Al₂O₃ (Cu/Pd=0.5/1) catalyst

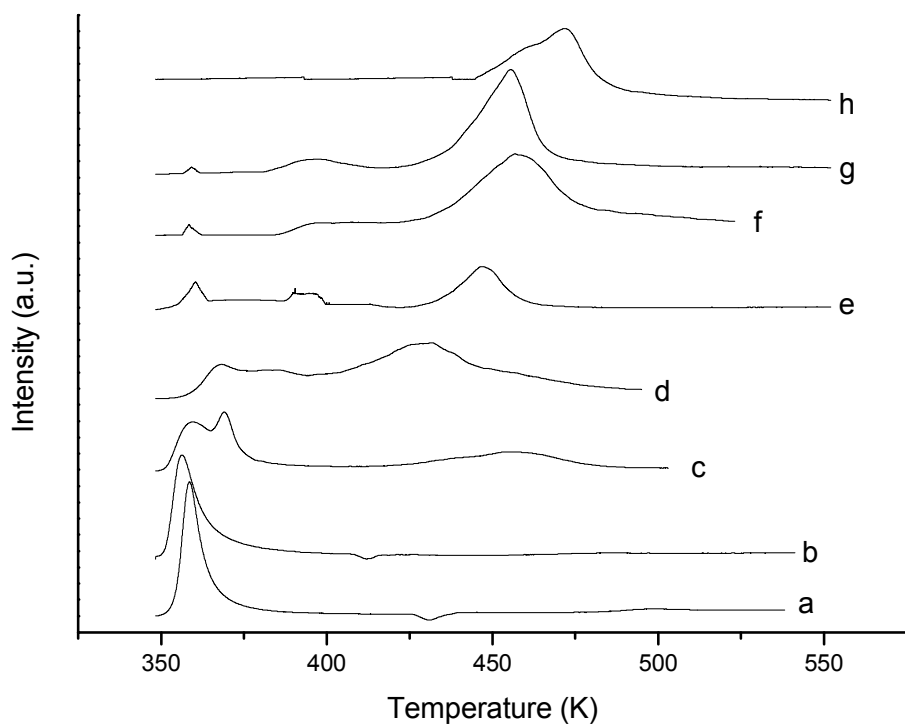


Fig. 4. The TPR profiles of the catalysts

a: 1%Pd, b: JZ-1 (Cu/Pd=0.1/1), c: JZ-2 (Cu/Pd=0.25/1), d: JZ-3 (Cu/Pd=0.5/1), e: JZ-4 (Cu/Pd=1/1), f: JZ-5 (Cu/Pd=3/1), g: JZ-6 (Cu/Pd=5/1), h: 1%Cu

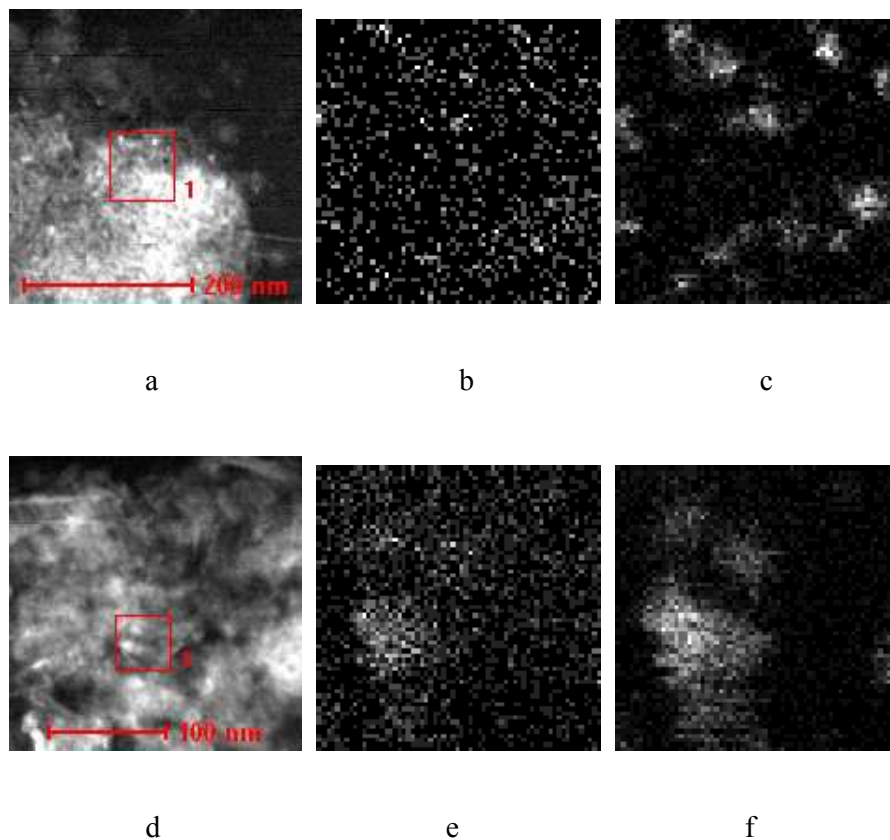


Fig. 5. TEM/EDX images of reduced catalyst JZ-3 and JZ-6

(a) JZ-3 (Cu/Pd=0.5/1), (b) Cu K α 1 in JZ-3, (c) Pd L α 1 in JZ-3, (d) JZ-6(Cu/Pd=5/1), (e) Cu K α 1 in JZ-6, and (f) Pd L α 1 in JZ-6.

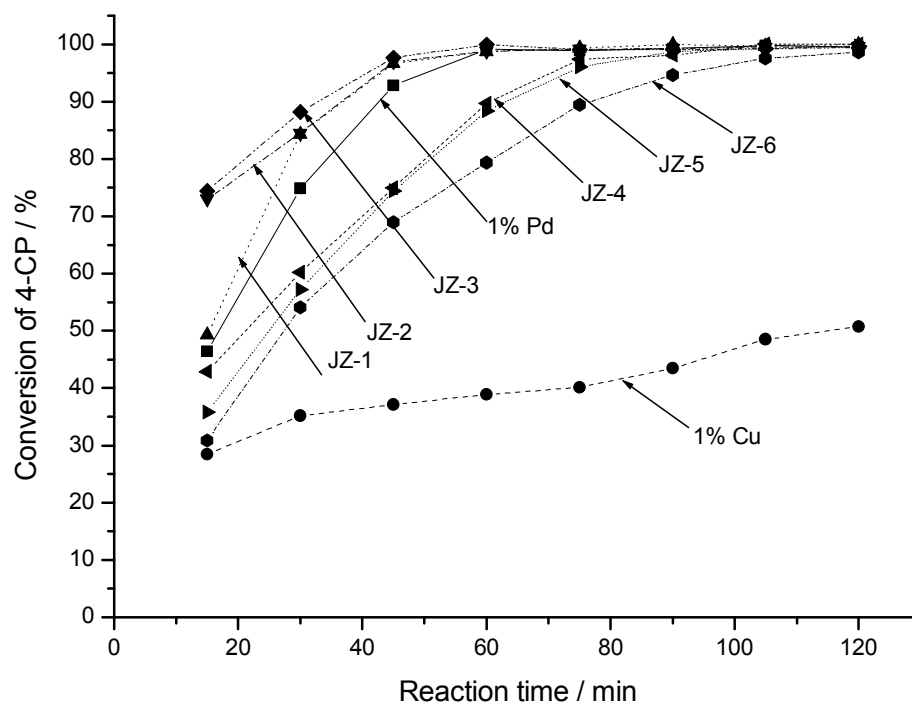


Fig. 6. The influence of different catalysts on the conversion of 4-CP

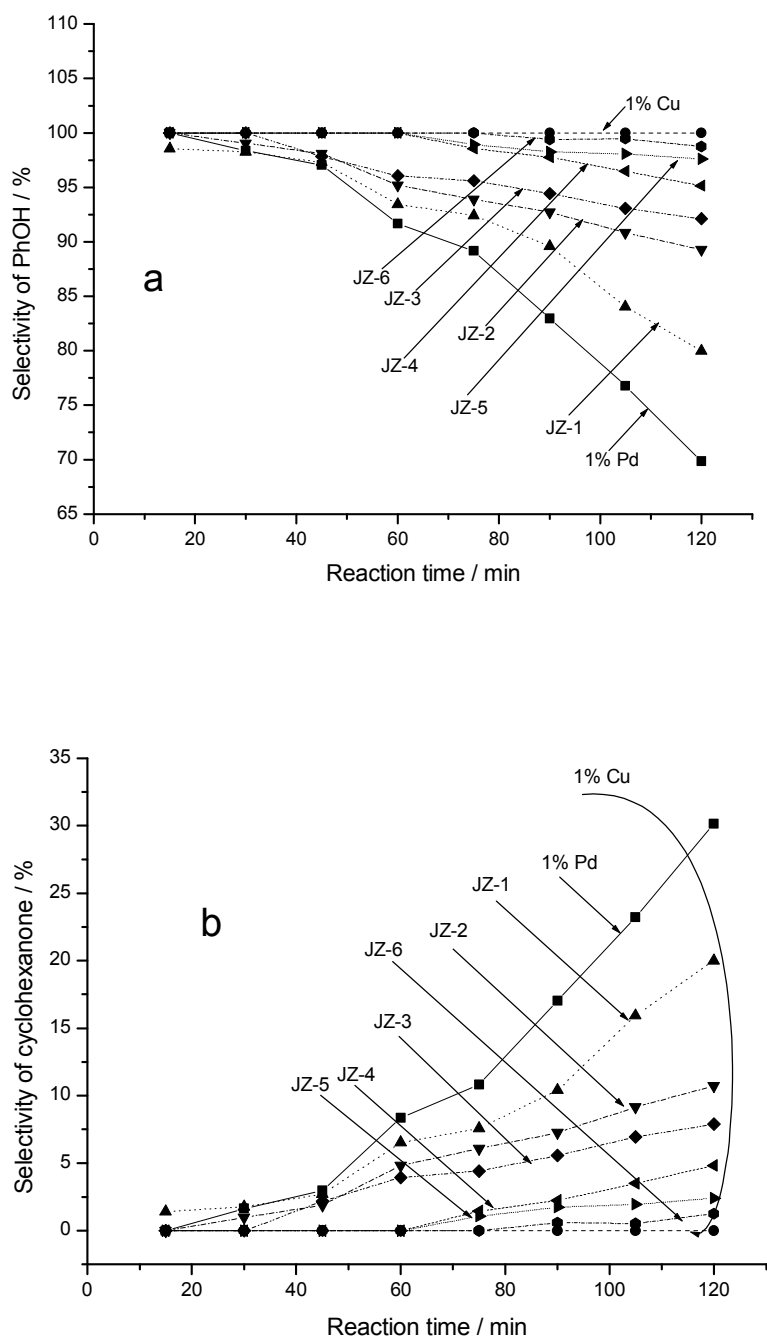
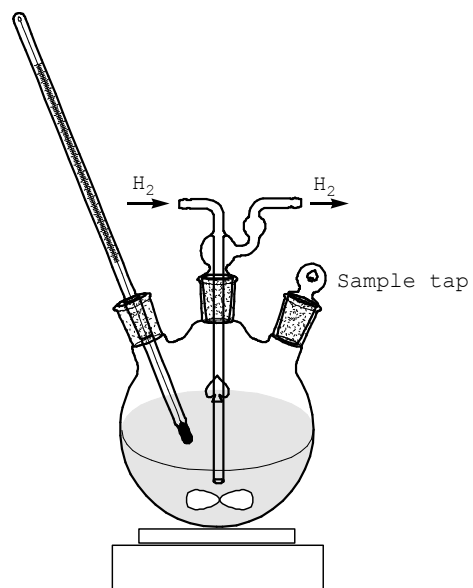
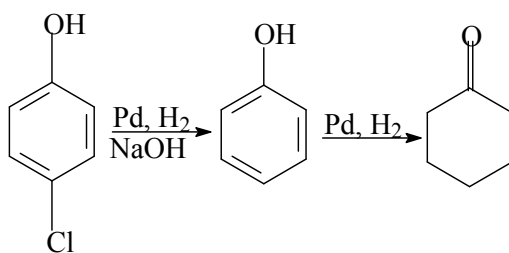


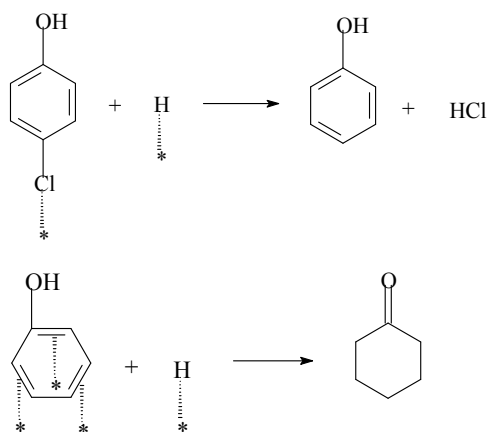
Fig.7. The influence of the catalysts on the hydrogenation products



Scheme 1 Schematic diagram of reaction device



Scheme 2. The equation of the HDC of 4-chlorophenol.



Scheme 3 Model of path-way of single point or multi-point adsorption

Table 1 The dispersion and surface area of Pd of the catalysts

Catalysts	Molar ratios of Cu / Pd	Pd dispersion (%)	Pd surface area (m ² /g)
1% Pd	--	24.9	55.6
JZ-1	0.1/1	31.2	69.6
JZ-2	0.25/1	34.1	75.9
JZ-3	0.5/1	38.2	85.2
JZ-4	1/1	22.6	50.5
JZ-5	3/1	16.0	35.7
JZ-6	5/1	15.8	35.1