

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Effect of indium-modified palladium catalysts on the hydrodechlorination of 4-chlorophenol

Jinbo Zhao, Wanjun Li, Deren Fang*

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

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

ABSTRACT: The influence of In addition on the activity and selectivity of supported Pd catalysts in the hydrodechlorination (HDC) of 4-chlorophenol (CP) was studied. The catalysts were characterized using temperature-programmed reduction, scanning electron microscopy, transmission electron microscopy, and hydrogen pulse chemisorption measurements. Bimetallic Pd–In/Al₂O₃ catalysts containing 1 wt% of Pd and with various In/Pd molar ratios were characterized by a high 4-CP conversion, which reached approximately 100% in a 2-h run. The results demonstrated that adding In to the Pd catalyst improved the dispersion of Pd particles and increased the HDC catalytic activity when the In/Pd molar ratio was less than 1/1.

Keywords: Pd–In bimetallic catalyst; hydrodechlorination; 4-chlorophenol; activity; selectivity

1. Introduction

Chlorophenols (CPs) have been widely used in various products such as disinfectants, pesticides, and personal care formulations and can be detected in some aquatic environments [1]. In recent years, numerous

studies on the catalytic hydrodechlorination (HDC) of CPs in liquid and gas phases have been published. HDC of CPs in aqueous phase has been studied with different metallic supported catalysts. These studies showed that catalysts for the HDC of CPs are primarily supported precious metals, such as Pd [2-10], Pt [11], and Rh [12]. Among these metals, Pd is the most active and selective catalyst [13]. A variety of Pd catalysts deposited on different supports such as active carbon (AC) and Al_2O_3 have been synthesized [14]. It is reported that the catalytic properties of the Pd catalysts can be improved by adjusting the particle size of the Pd metallic phase [14]. The catalysts with smaller Pd particle size hold high surface to volume ratio and are resistant to deactivation from the depositing Cl through the scission of the C-Cl bonds [15]. Some supported Pd-based bimetallic catalysts showed a higher activity and superior selectivity than did pure Pd catalysts, such as Pd-Bi [4] and other bimetallic catalysts studies such as Pd-Fe [16], and Pd-Al [17], in recent literature. Therefore, search for new and full understanding of currently functioning bimetallic catalysts constitute important challenges for researches. The Pd-In bimetallic catalysts supported on Al_2O_3 showed a high activity in liquid-phase denitration [18-19]; however, the HDC of CPs by using this catalyst was not analyzed. We prepared a series of Pd-In bimetallic catalyst supported on Al_2O_3 and found that it has a high activity in the HDC of CPs. In this paper, we present the results of the HDC of 4-CP on

the In–Pd/Al₂O₃ bimetallic catalyst. The results indicated that adding In can improve the catalytic activity of the Pd/Al₂O₃ catalyst for the HDC of CPs, and the action principle of In is discussed.

2. Experimental section

2.1 Catalyst preparation

The Pd–In bimetallic catalysts were prepared using the sequentially incipient wetness impregnation method, and γ -Al₂O₃ with a diameter of 0.045–0.075 mm was used as a carrier. The Pd content was fixed at 1 wt%, and the In content was varied to obtain In/Pd molar ratios of 0.05/1, 0.1/1, 0.3/1, 0.5/1, 1/1, 2/1, and 3/1, and the corresponding catalysts were designated as IP-1, IP-2, IP-3, IP-4, IP-5, IP-6, and IP-7, respectively. A typical catalyst preparation method was used to impregnate the precursors of the catalysts with the designated amount of aqueous PdCl₂ to yield the desired Pd content 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 In(NO₃)₃, then dried at 110 °C for 2 h, and calcined at 350 °C for 2 h. We also prepared a pure supported In catalyst containing 3 wt% of In and a pure supported Pd catalyst containing 1 wt% of Pd by using the same method and designated them as 3% In and 1% Pd, respectively. The catalysts were reduced before HDC was performed using gaseous H₂ at 350 °C for 2 h.

2.2 Catalyst characterization

Powder XRD patterns of the solid products were studied using a Shimadzu XRD-6100 X-ray diffractometer (Cu K radiation) equipped with a computer system to perform automatic operation and data processing.

XPS was performed using a Thermo Fisher Scientific ESCALAB 250 spectrometer equipped with a standard Mg K-alpha source and a high performance Al monochromatic source. XPS spectra were referenced to the C1s peak at 284.6 eV.

Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 FE-SEM equipped with a computer system for performing automatic operations 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 operations and data processing. EDX mapping was performed to visualize elemental and spatial information regarding In and Pd on the Al₂O₃ surface. The particle morphology of Pd and In was determined using transmission electron microscopy (TEM) on 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 reducing gas, and the temperature was increased from 20 to 300 °C at a rate of 5 °C/min. H₂ consumption 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. H₂ (5 vol%) was then 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 Pd surface areas and dispersions of the catalysts are listed in Table 1.

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

Catalysts	Molar ratios of In/Pd	Pd dispersion (%)	Pd surface area (m ² g ⁻¹)
-----------	--------------------------	----------------------	--

1%Pd	—	23.7	52.9
IP-1	0.05/1	30.9	69.0
IP-2	0.1/1	41.6	92.7
IP-3	0.3/1	37.0	82.5
IP-4	0.5/1	29.8	66.5
IP-5	1.0/1	28.3	63.2
IP-6	2.0/1	21.1	47.0
IP-7	3.0/1	12.6	28.2

2.3 Studies on catalytic hydrodechlorination

The HDC of 4-CP (Sigma, purity > 99.6%) was performed at atmospheric pressure in a mixing glass tank reactor with electromagnetic stirring to ensure maximum contact between the catalyst and the reactant [20]. After reduction, 0.2 g of the catalyst was added to 200 ml of an aqueous mixture of 4-CP (1000 ppm) and NaOH (NaOH/4-CP molar ratio = 1.1/1). H₂ was then introduced into the reactor at a rate of 50 ml/min, thus initiating the HDC. After 7.5 min, 1 ml of the solution was extracted and analyzed using gas chromatography with a flame ionization detector and a polyethylene glycol capillary column. We also evaluated the activity of these catalysts in phenol hydrogenation by using the same method.

3. Results and discussion

By using H₂ pulse chemisorption measurements, we calculated the metal

Pd dispersion and surface area [20,21]. The Pd surface areas and dispersions of the catalysts are listed in Table 1. Compared with the 1% Pd monometallic catalyst, bimetallic catalysts with In/Pd molar ratios of 0.05/1, 0.1/1, 0.3/1, 0.5/1, and 1/1 (IP-1, IP-2, IP-3, IP-4, and IP-5, respectively) exhibited incrementally higher Pd dispersions and surface areas. However, bimetallic catalysts with In/Pd molar ratios of 2/1 and 3/1 (IP-6 and IP-7) exhibited lower Pd dispersions and surface areas, indicating that adding In changed the Pd dispersions and surface areas of the bimetallic catalysts. Adding an appropriate amount of In increased the Pd dispersions and surface areas of the Pd-based bimetallic catalysts compared with those of the Pd monometallic catalysts.

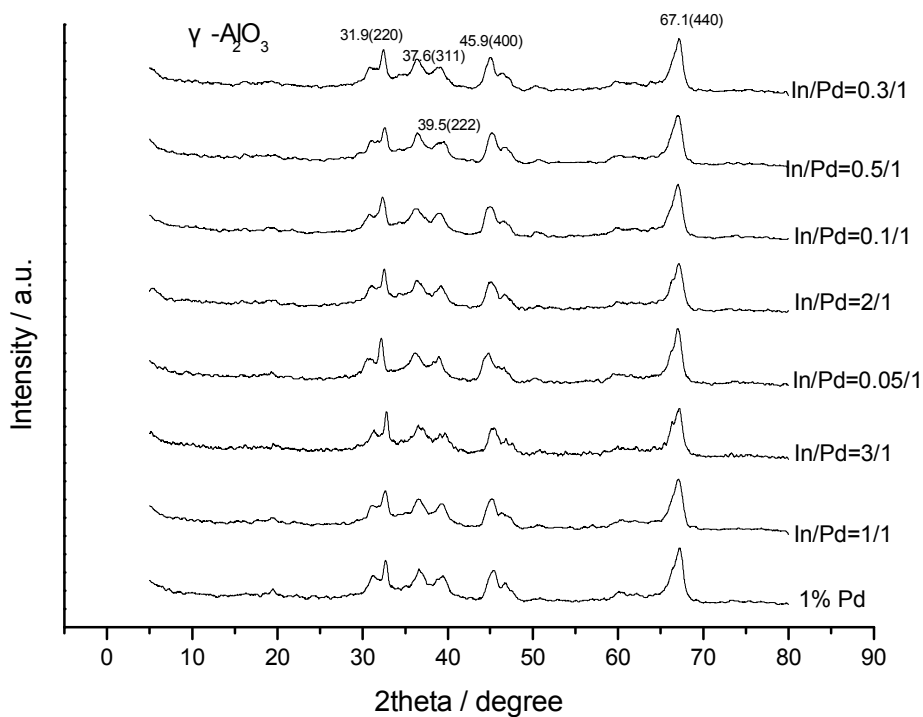
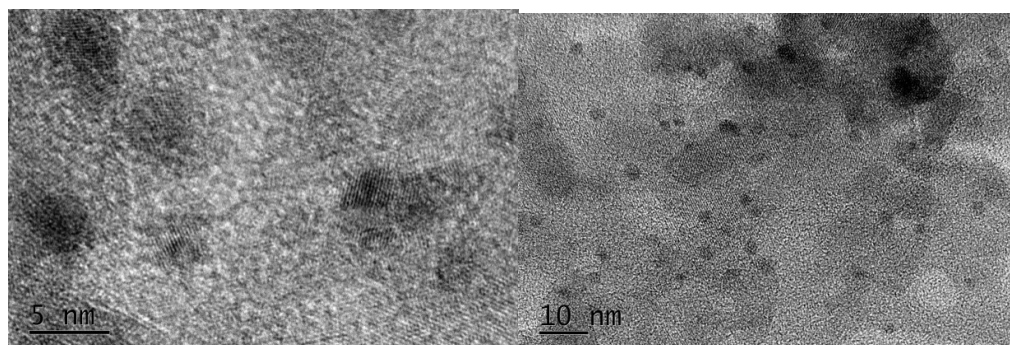


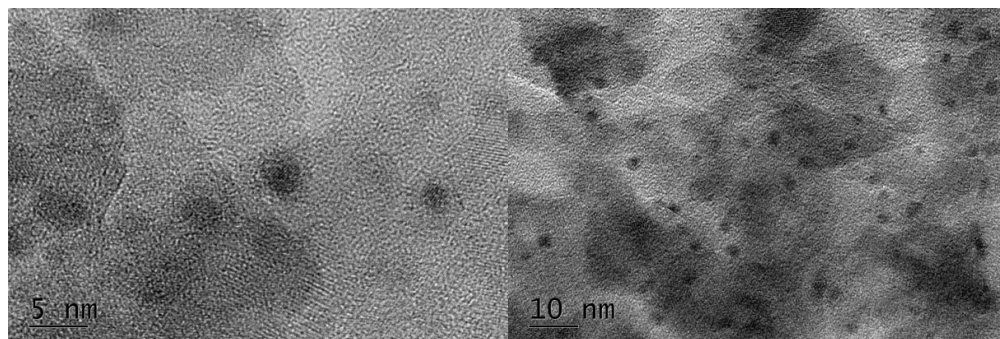
Fig.1 XRD patterns of the reduced catalysts with different molar ratio of In to Pd

Fig. 1 shows the XRD patterns of the catalysts. Diffraction peaks of the γ - Al_2O_3 support at 2θ equals to 31.9, 37.6, 39.5, 45.9 and 67.1 were expected in the XRD patterns of Pd/ γ - Al_2O_3 and Pd-In/ γ - Al_2O_3 (CAS No. 1344-28-1), but Pd and In has not detected. Because of the low content of Pd and In in the catalysts, the reflection peak of which were covered by the background of γ - Al_2O_3 , and was difficult to observe.



(1)

(2)



(3)

(4)

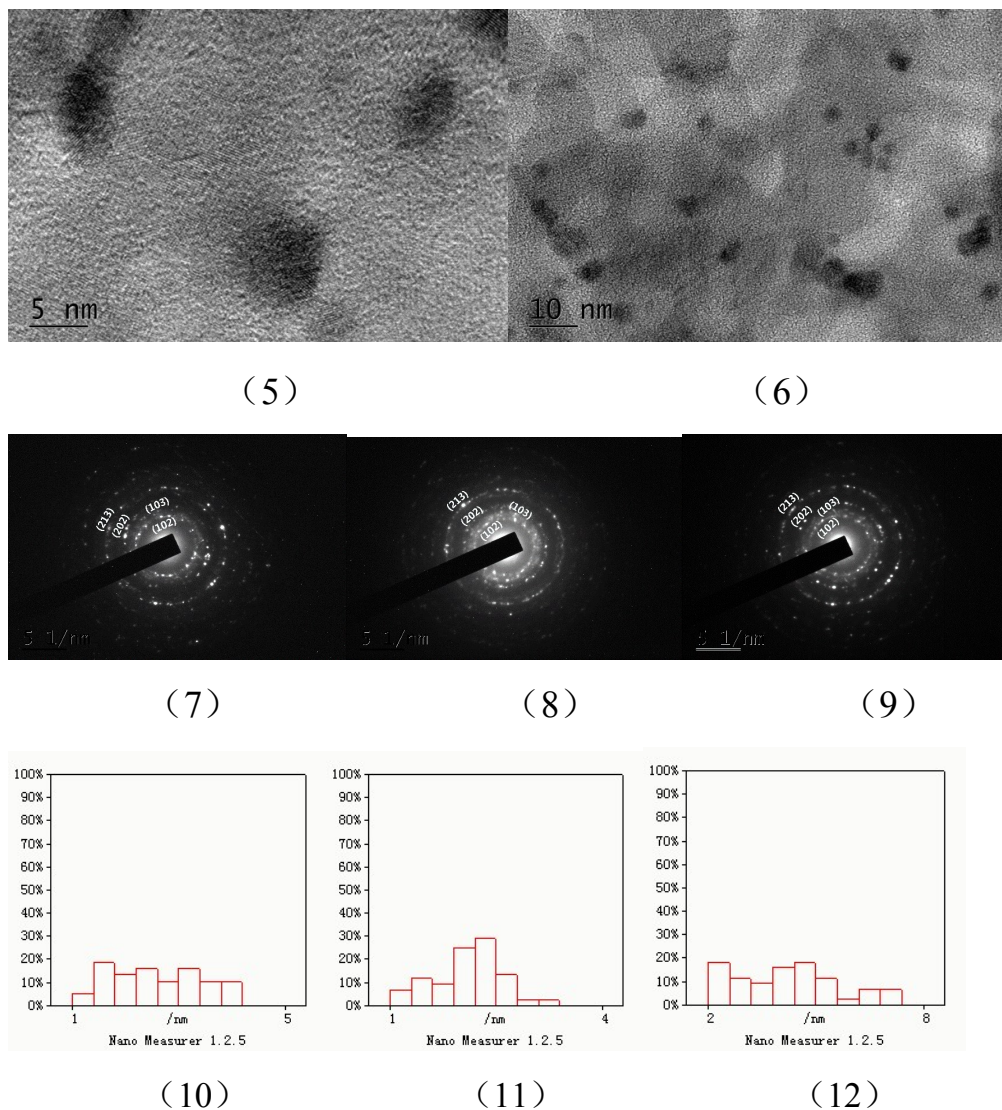


Fig. 2. TEM micrographs of reduced catalyst 1%Pd, IP-2 and IP-7 (1),(2) 1%Pd, (3),(4)IP-2 (In/Pd = 0.1/1), (5)(6) IP-7 (In/Pd = 3/1), (7) 1%Pd diffraction pattern, (8) IP-2 diffraction pattern, (9) IP-7 diffraction pattern, (10) 1%Pd PSD, (11) IP-2 PSD, (12) IP-7 PSD

Fig.2 shows the results of TEM, which demonstrated that the particle sizes of Pd on the catalysts were in the range of 2–5 nm or that specific point was 2.71 nm for 1%Pd, 2.26 nm for IP-2 (In/Pd = 0.1/1) and 4.22 nm for IP-7 (In/Pd = 3/1). The results demonstrated that a small amount of In addition to the Pd/ γ -Al₂O₃ catalyst could improve the dispersion of Pd on the surface of the catalyst. The SEM/EDS images

(Supplementary Info) show that Pd and In coexist in the same microzones of IP-2 and IP-7; this indicates that In and Pd were supported on Al_2O_3 and formed a Pd–In pseudoalloy on the catalysts [20].

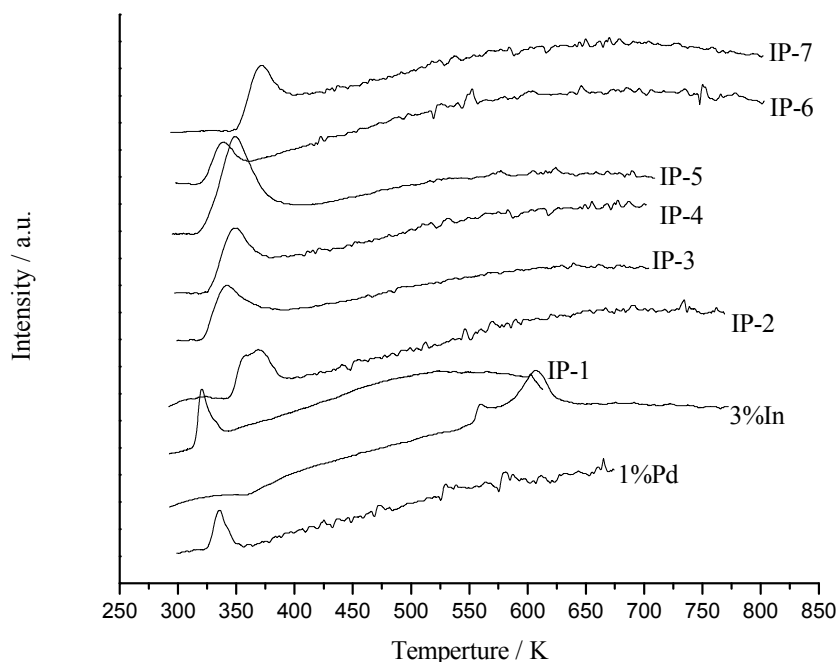


Fig.3 . The TPR profiles of the catalysts

Fig. 3 shows the H_2 -TPR profiles of the catalysts. The TPR profiles of the 1% Pd monometallic catalysts showed only one reduction peak at 345 K, whereas the 3% In monometallic catalysts showed two reduction peaks at 555 K and 600 K, which may correspond to the reduction of In^{3+} to In^{2+} and In^{2+} to In^0 , respectively. The TPR profiles of the Pd–In bimetallic catalysts were similar to those of the 1% Pd monometallic catalyst but differed from those of the 3% In monometallic catalyst. The reduction mechanism of the Pd–In bimetallic catalysts may involve the reduction of PdO initially, followed by the reduction of In_2O_3 by the hydrogen atom

dissociatively adsorbed on the surface of Pd through the overflow effect and formed close contact mixed particle of Pd and In in the case of lower In/Pd molar ratio; a few Pd–In pseudoalloy particles formed after the reduction in the case of higher In/Pd molar ratio, because of the interaction between PdO and In₂O₃ [19]. When the In/Pd molar ratio was bigger than 0.1/1 the reduction peaks was shifted to the higher temperature than pure Pd monometallic catalyst, this may indicate that there are some obstacles to the reduction of PdO particle owing to the existence of In₂O₃ particle in between the PdO particle. Because the reduction of PdO must be precede over In₂O₃ particle. In the case of 1% Pd monometallic catalyst the reduction rate of PdO is fast due to the reduced metal Pd can dissociative adsorb hydrogen molecular and the hydrogen atom on the surface of Pd may migrate to the neighboring PdO through the overflow effect so as to accelerate the reduction of remainder PdO in the particle. In the case of bimetallic Pd–In/Al₂O₃ catalysts, the PdO particle was separated by In₂O₃ particle and reduced in accordance with the order of first PdO then In₂O₃, while the reduction of In₂O₃ is very difficult than PdO, so the reduction peak of them was shifted to the higher temperature.

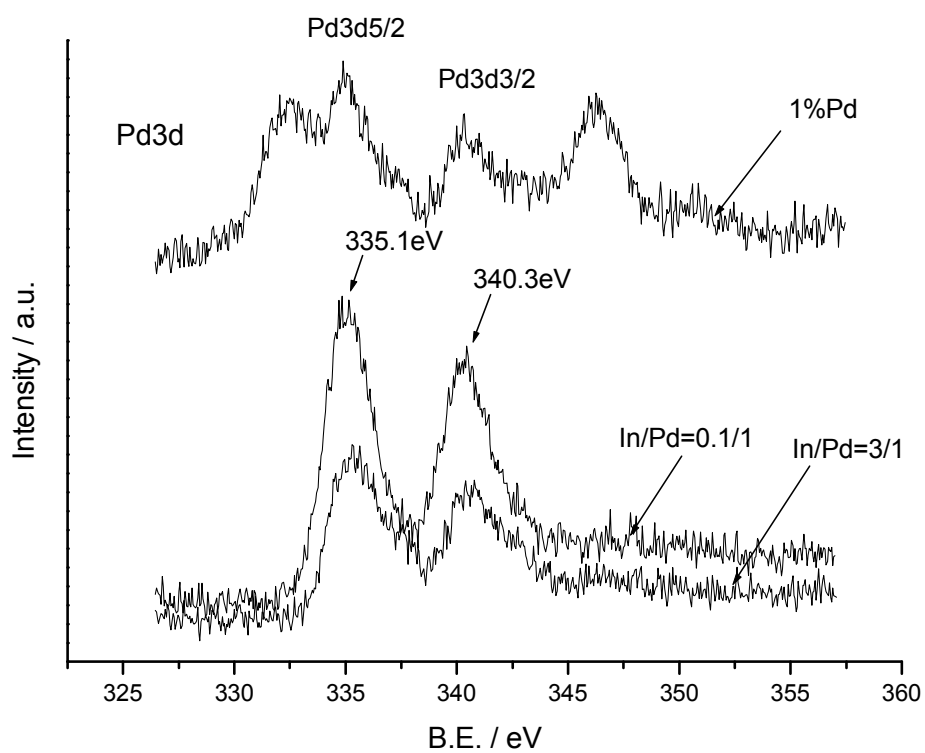


Fig. 4 XPS spectra for Pd3d of catalysts 1%Pd, IP-2 and IP-7

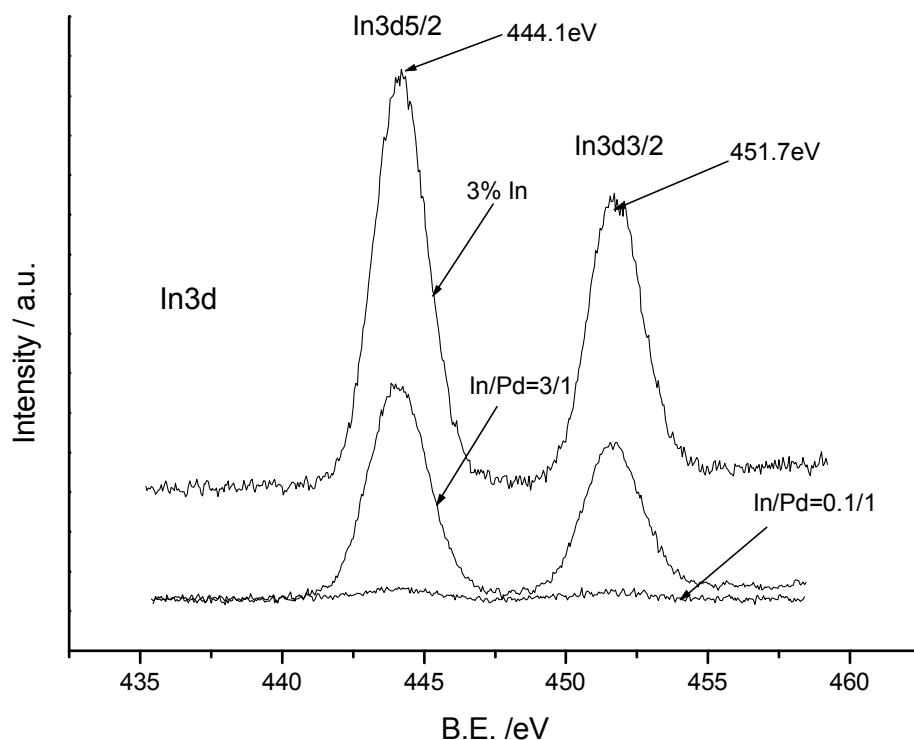


Fig. 5 XPS spectra for In 3d of catalysts 3%In, IP-2 and IP-7

The XPS spectra of Pd 3d (Fig. 4) demonstrated that in all of the three catalysts, Pd 3d had two main peaks at 335.1 eV and 340.3 eV, which correspond to the binding energy of Pd 3d_{5/2} and Pd 3d_{3/2} of Pd⁰, respectively [23]. This demonstrated that the addition of In to Pd monometallic catalyst could not change the state of the metal Pd. The XPS spectra of In 3d (Fig. 5) demonstrated that in all of the three catalysts, In 3d had two main peaks at 444.1 eV and 451.1 eV, which correspond to the binding energy of In 3d_{5/2} and In 3d_{3/2} of In⁰, respectively [24,25]. Combining the results of TEM, XPS and TPR, one may come to the conclusion that in the reduction process the In₂O₃ has

been reduced to the metal atom In and formed close contact mixed particle of Pd and In in the case of lower In/Pd molar ratio; a few Pd–In pseudoalloy particles formed after the reduction in the case of higher In/Pd molar ratio otherwise it cannot interpret why the Pd particle size of sample IP-7 is bigger than the sample 1%Pd. From the H₂-TPR profiles it is demonstrated the indium oxide was really reduced with PdO at the same time. Certainly, perfect alloy or core shell structure was not formed in our catalysts unlike at work of Deepak et al [26-28] in which the sample was made by micelle method which can provide a large number of similar composition of particles as well as they can guarantee the uniform distribution of two kinds of elements in the particle. We will further carry out research in the future in this respect.

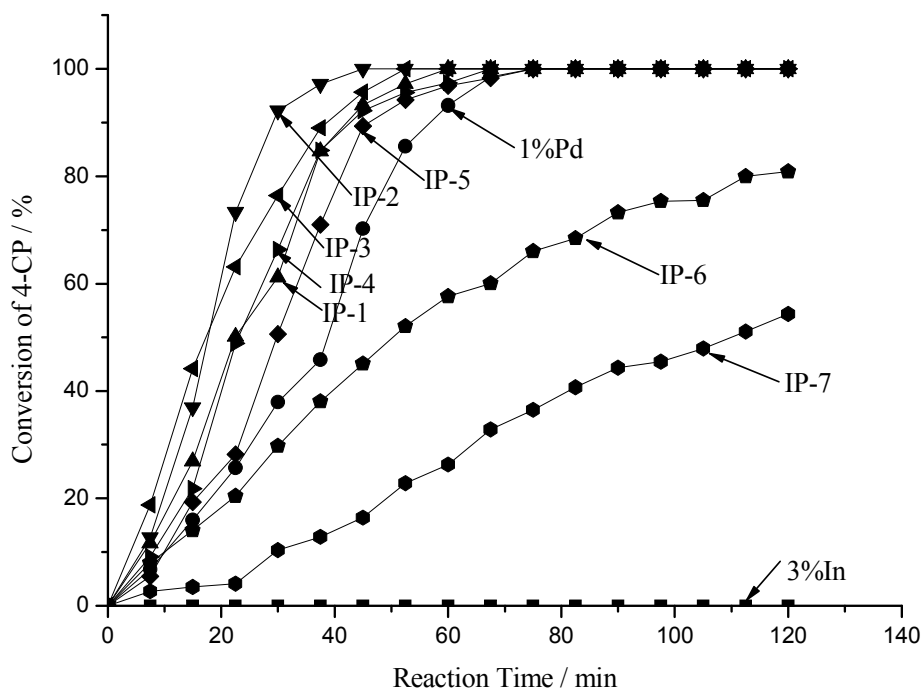


Fig. 6. The influence of different catalysts on the conversion of 4-CP .

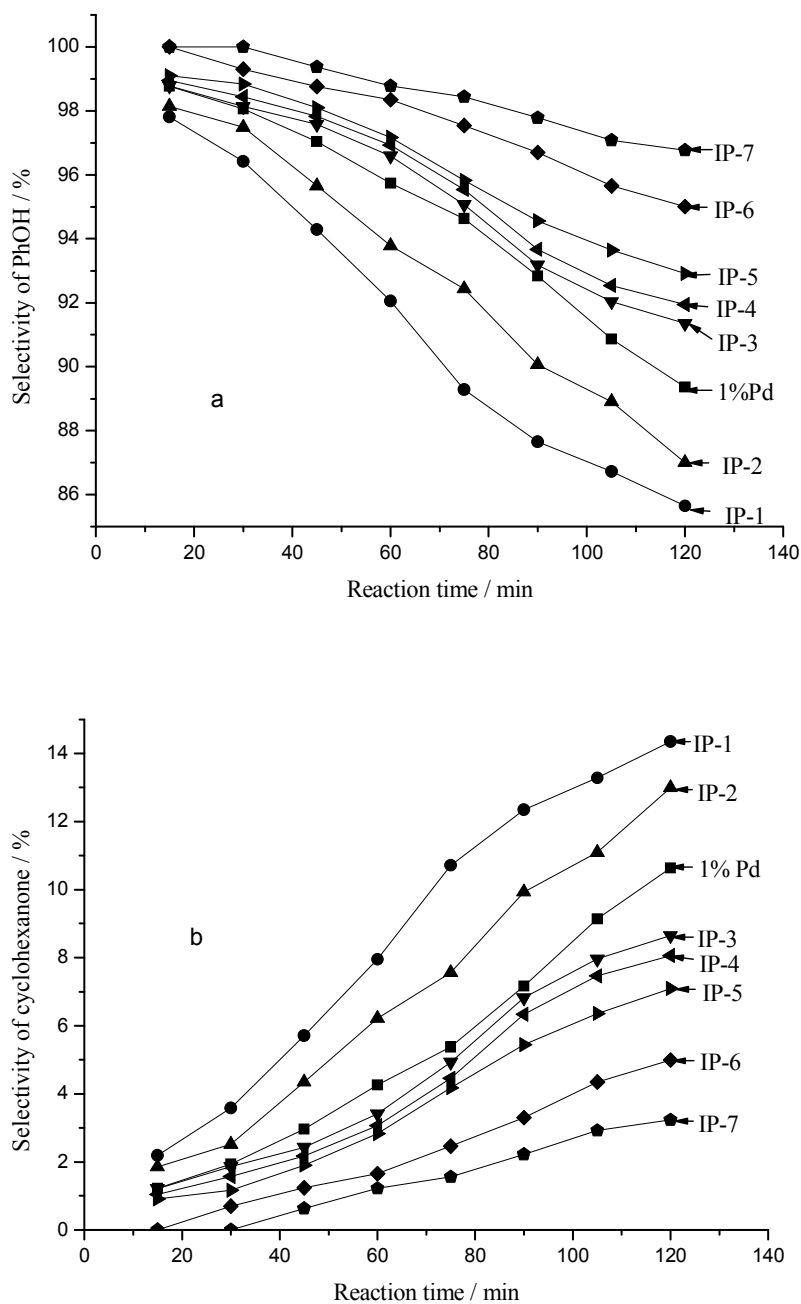


Fig. 7. The influence of the catalysts on the hydrogenation products .

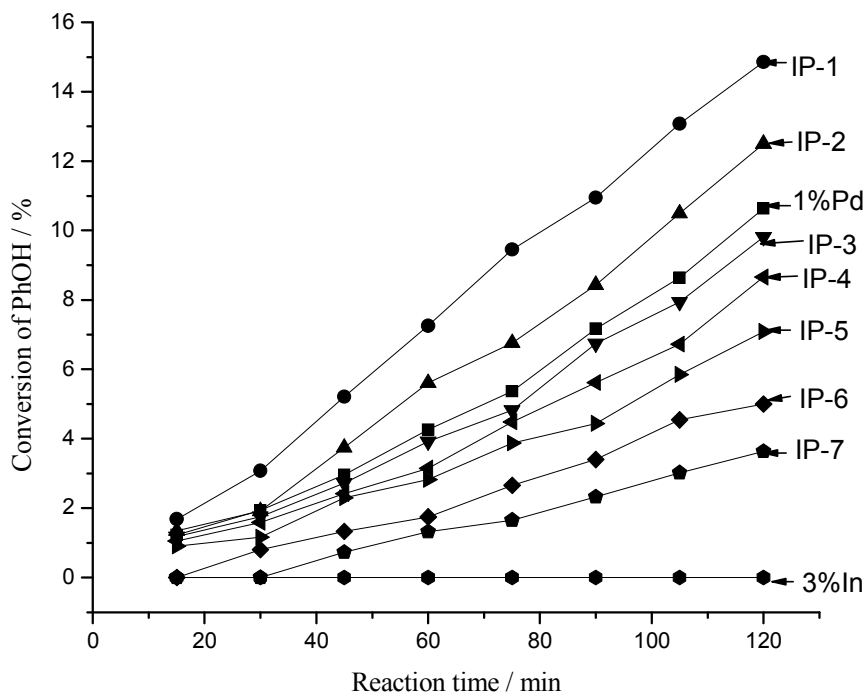
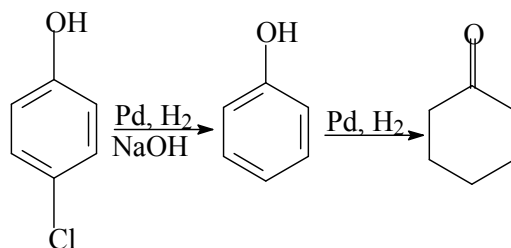


Fig. 8. The influence of different catalysts on the conversion of PhOH .

The HDC catalysis performance of the catalysts is shown in Fig. 6. A great difference obviously existed in the catalytic activity between the various catalysts. The HDC catalytic activity of the catalysts followed the order IP-2 > IP-3 > IP-1 > IP-4 > IP-5 > 1% Pd > IP-6 > IP-7 > 3% In. When the In/Pd molar ratios were 0.05/1, 0.1/1, 0.3/1, 0.5/1, and 1/1, 4-CP was completely hydrodechlorinated within 75 min; however, when the In/Pd molar ratios were 2/1 and 3/1, 4-CP was not completely hydrodechlorinated even within 120 min. This indicated that adding the

appropriate amount of In to modify the Pd monometallic catalyst can improve the catalytic activity. According to the results shown in Table 1, the catalytic activity was correlated with the Pd dispersions and surface areas of the catalysts. The Pd dispersions and surface areas of the catalysts followed the order IP-2 > IP-3 > IP-1 > IP-4 > IP-5 > 1% Pd > IP-6 > IP-7, which is consistent with the catalytic activity order of the catalysts. Among all the catalysts, IP-2 had the highest Pd dispersion and surface area; therefore, IP-2 showed the highest catalytic activity in the HDC of 4-CP. No conversion of 4-CP was observed using the 3% In monometallic catalyst. Therefore, the active center for the HDC of 4-CP was Pd.

According to the gas chromatography–mass spectrometry analysis, cyclohexanone was another product, in addition to phenol, 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 initially subjected to hydrogenolysis over the 1% Pd and Pd–In bimetallic catalysts to form phenol, and the phenol was further hydrogenated to form cyclohexanone; the reaction pathway is shown in Scheme 1 [20,22].



Scheme 1. The equation of the HDC of 4-CP

The selectivity of the products is shown in Fig.8. The selectivity of PhOH followed the order IP-7 > IP-6 > IP-5 > IP-4 > IP-3 > 1% Pd > IP2 > IP-1, whereas the selectivity of cyclohexanone followed the reverse order. Variation tendencies of the selectivity of phenol gradually decreased as the reaction time increased for all catalysts (Fig.7a). However, the selectivity of cyclohexanone gradually increased for all the catalysts (Fig. 7b). According to these results, the catalytic activities of the catalysts followed the order IP-2 > IP-3 > IP-1 > IP-4 > IP-5 > 1% Pd > IP-6 > IP-7 for the hydrogenolysis of the Cl–C bond; whereas the catalytic activities for the hydrogenation of phenol followed the order IP-1 > IP-2 > 1% Pd > IP-5 > IP-6 > IP-7 in an aqueous solution (Fig. 8). This demonstrated that the supported In catalyst has no catalytic activity for the hydrogenation of phenol. Therefore the catalytic active center for both the hydrogenolysis of the Cl–C bond and the hydrogenation of the C=C double bond of phenol was Pd. Fig. 8 and 7b showed that the tendencies of the hydrogenation of phenol and the selectivity of cyclohexanone were similar. This shows that the Pd monometallic catalyst and Pd–In bimetallic catalysts differed in their catalytic activities in the hydrogenolysis of the C–Cl bond of 4-CP and in the hydrogenation of the C=C double bond of phenol. Compared with that of the 1% Pd monometallic catalyst, the cyclohexane selectivity of the Pd–In bimetallic catalysts gradually decreased with an increase in the In content of the

catalyst. These results illustrated that catalysts having a high In content ($\text{In/Pd} > 0.1$) can inhibit cyclohexanone formation during the HDC of 4-CP. The TPR results showed that the Pd–In bimetallic catalysts had only one reduction peak, indicating that Pd–In pseudoalloy formed in the catalysts in the case of higher In/Pd molar ratio. From Figure 4, we can conclude that the Pd–In pseudoalloy formation in the Pd–In bimetallic catalysts did not favor the hydrogenation of phenol to form cyclohexanone. The Pd–In pseudoalloy formation reduced the quantity of Pd active centers, thereby affecting the hydrogenation of the benzene ring of phenol. The hydrogenolysis of the C–Cl bond of 4-CP may require fewer Pd active centers compared with the hydrogenation of the benzene ring of phenol [20]. By combining the results of TPR and H_2 pulse chemisorption (Table 1), we concluded that metal In dispersed around Pd particles adequately, effectively separating the Pd particles and preventing further clustering of the Pd particles when the In/Pd molar ratio was low. When the In/Pd molar ratios were higher, the metal In covered the surface of Pd and formed some amounts of the Pd–In pseudoalloy (Scheme 2); this reduced the surface area of Pd. According to these results, Pd is the sole active center for both reactions, reducing activity.

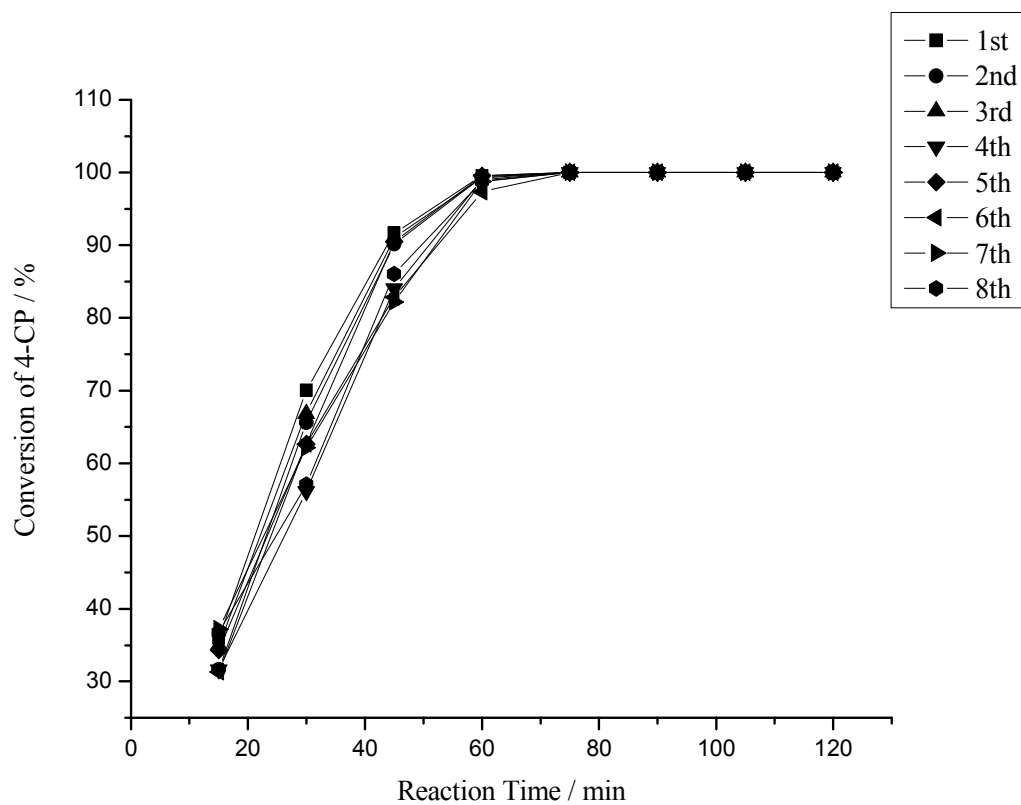


Fig. 9 The influence of reuse times of catalysts on the conversion of 4-CP

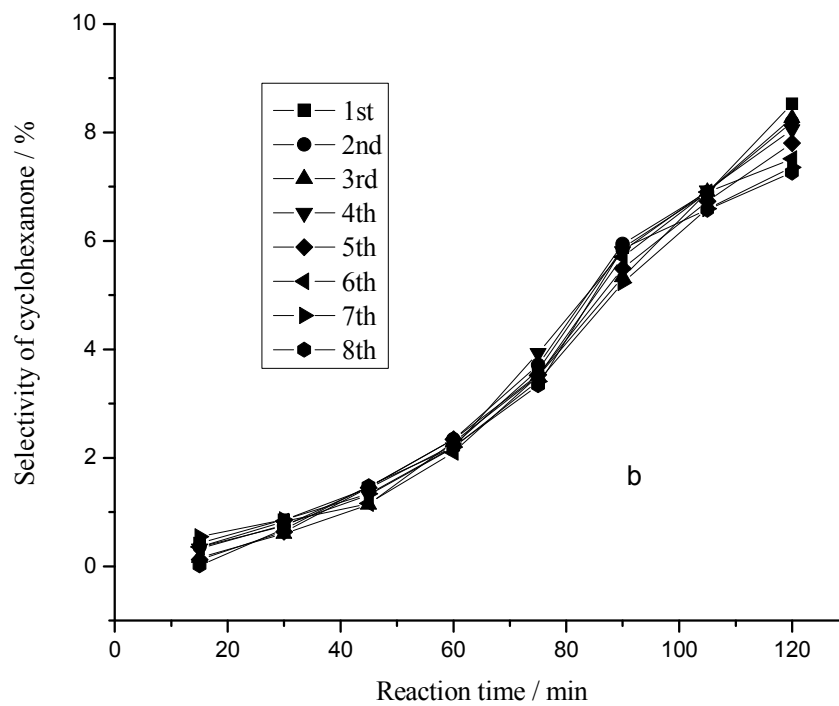
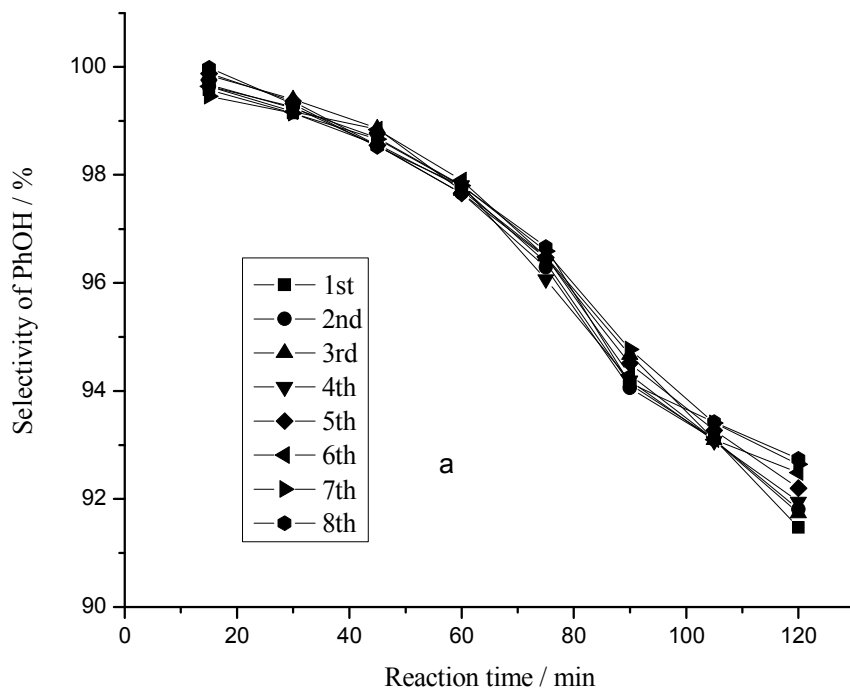
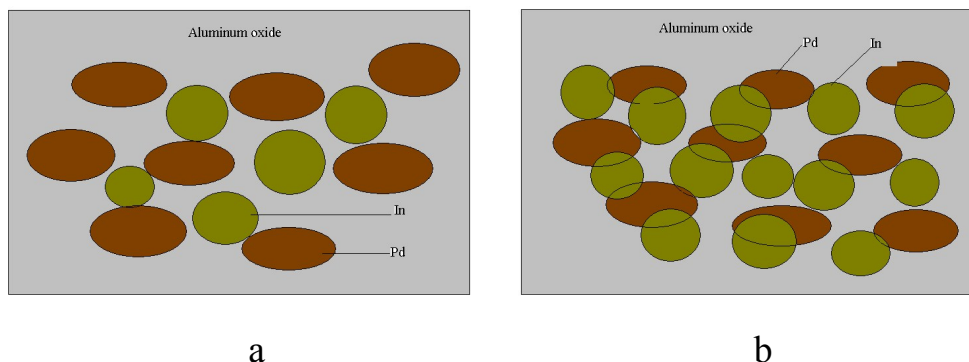


Fig. 10 The influence of reuse times of catalysts on the hydrogenation products



Scheme 2 Schematic diagram of atomic arrangement

The ability to reuse the new catalysts has been made for eight times and the results (Fig.9, 10) showed that the catalyst can be reused for many times.

4. Conclusion

A series of Pd–In/ γ -Al₂O₃ bimetallic catalysts was prepared, and their catalytic performance in the HDC of 4-CP in an aqueous phase was studied. Compared with the Pd monometallic catalyst, Pd catalysts with the appropriate amounts of In added exhibited increased Pd dispersions and surface areas and considerably increased catalytic activity in the HDC of 4-CP. However, adding an excessive amount of In to the Pd–In bimetallic catalysts inhibited the HDC of 4-CP. In addition, with an increase in the In content of the Pd–In bimetallic catalysts, the conversion of phenol through hydrogenation was gradually reduced; that is, the close

contact mixed particle of Pd and In in the Pd–In bimetallic catalysts inhibited the hydrogenation of phenol. The stability of catalytic activity of Pd–In/ γ -Al₂O₃ bimetallic catalysts in the HDC of 4-CP is higher and can be reused many times.

REFERENCES

- (1) S. Ramamoorthy, Chlorinated Organic Compounds in the Environment, CRC Press, Boca Raton. (1997).
- (2) G. Yuan, M.A. Keane, Catal. Commun. 4(2003)195-201.
- (3) E. Diaz, A. F. Mohedano, J. A. Casas, L. Calvo, M. A. Gilarranz, J. J. Rodriguez, Appl. Catal. B: Environ. 106(2011)469-475.
- (4) I. Witon'ska, A. Królak, S. Karski, J. Mol, Catal. A: Chem. 331(2010)21-28.
- (5) C.H.Xia, Y.Liu, J.Xu, J.B.Yu, W.Weil,X.M.Liang, Catal. Commun. 10(2009)456-458.
- (6) Z. M. de Pedro, E. Diaz, A. F. Mohedano, J. A. Casas, J. J. Rodriguez, Appl. Catal. B: Environ. 103(2011)128-135.
- (7) C.B. Molina, A.H. Pizarro, J.A. Casas, J.J. Rodriguez, Appl. Catal. B: Environ. 148-149(2014)330-338.
- (8) H.Y.Deng, G.Y. Fan, C.Y.Wang, L. Zhang, Catal. Commun. 46(2014)219-223.
- (9) N. S. Babu, N. Lingaiah, N. Pasha, J. V. Kumar, P.S.Sai Prasad,

Catal.Today.141(2009)120-124.

(10) A. Pintar, J. Batista, I. Mušević, Appl. Catal. B: Environ. 52(2004)49-60.

(11) T. Yoneda, T. Aoyama, T. Takido, K. Konuma, Appl. Catal. B. 142-143(2013)344-353.

(12) J.A. Baeza, L. Calvo, M.A. Gilarranz, J.J. Rodriguez, Chem. Eng. J. 240(2014)271-280.

(13) J.A. Baeza, L. Calvo, M.A. Gilarranz, A.F. Mohedano, J.A. Casas, J.J. Rodriguez, J. Catal. 293(2012)85-93.

(14) Y.L. Ren, G. Y. Fan*, C.Y. Wang, Journal of Hazardous Materials. 274(2014)32-40.

(15) J. Baeza, L. Calvo, M. Gilarranz, J. Rodriguez, Chem. Eng. J. (2014)271-280.

(16) H. L. Lien, W. X. Zhang, Appl. Catal. B: Environ. 77(2007)110-116.

(17) C.B. Molina, L. Calvo, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, J. Hazard. Mater. 172(2009)214-223.

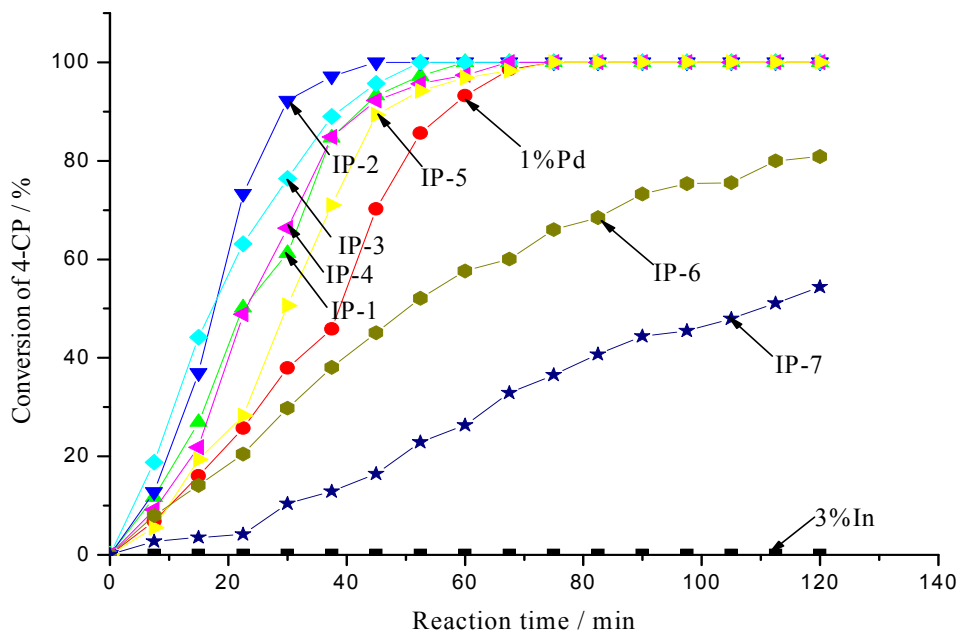
(18) S. Ambonguilat, H. Gallard, A. Garron, F. Epron, J. P. Croue, Water Res. 40(2006)675-682.

(19) F.A. Marchesini, S. Irusta, C. Querini, E. Miro, Appl. Catal. A: Gen. 348(2008)60-70.

(20) D. R. Fang, W.J. Li, J.B. Zhao, S. Liu, X.X. Ma, J.G. Xu, C.H. Xia, RSC Adv. 4(2014)59204-59210.

- (21) A. Pintar, J. Batista, I. Mušević, *Appl. Catal. B: Environ.* 52(2004)49-60.
- (22) C.H. Xia, J. Xu, W. Z. Wu, X.M. Liang, *Catal. Commun.* 5(2004)383-386.
- (23) M.A. Alvarez-Montero*, L.M. Gómez-Sainero, J. Juan-Juan, A. Linares-Solano, J.J. Rodriguez, *Chemical Engineering Journal.* 162(2010)599–608.
- (24) X. Liu, W.Z. Lang, L.L. Long, C.L. Hu, L.F. Chu, Y.J. Guo, *Chemical Engineering Journal.* 247(2014)183-192.
- (25) M. Tahir, N. S. Amin, *Appl. Catal. B: Environ.* 162(2015)98-109.
- (26) F.L.Deepak, G.C.Garcia, R.Esparza, H.Barron, M.J.Yacaman, *Journal of Crystal Growth.* 325(2011)60-67.
- (27) Z.Y.Li, J.Yuan, Y.Chen, R.E.Palmer, J.P.Wilcoxon, *Appl. Phys.Letters.* 87(2005)243103.
- (28) P. Sathishkumar, R.S.Mangalaraja, S. Rozas, H.D.Mansilla, M.A. Gracia-Pinilla, S. Anandan, *Ultrasonics Sonochemistry.* 21(2014)1675-1681.

A table of contents entry.



Adding appropriate amount of In to the Pd catalyst can improve the dispersion of Pd particles and increased the HDC catalytic activity of 4-CP.