

## Research Article

# Catalytic Hydrodechlorination of Trichlorobenzenes with Pd(Phen)Cl<sub>2</sub> as Catalyst Precursor

Guanlin Zhang,<sup>1</sup> Hu Xu,<sup>1</sup> Yuehui Fan,<sup>1</sup> Yuhong Wang,<sup>1</sup> Lirong Zhang,<sup>2</sup> and Guanzhong Lu<sup>1</sup>

<sup>1</sup>Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

<sup>2</sup>School of Perfume and Aroma Technology, Shanghai Institute of Technology, Shanghai 201418, China

Correspondence should be addressed to Hu Xu; xuhu@sit.edu.cn and Yuhong Wang; yuhong\_wang502@sit.edu.cn

Received 11 November 2014; Revised 30 December 2014; Accepted 31 December 2014

Academic Editor: Guoran Li

Copyright © 2015 Guanlin Zhang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We reported the catalytic hydrodechlorination (HDC) of trichlorobenzenes by an organometallic compound Pd(Phen)Cl<sub>2</sub> as a catalyst precursor. The catalyst precursor was prepared by chemical coordination reaction and characterized by FTIR and <sup>1</sup>H NMR techniques. The HDC performance of Pd(Phen)Cl<sub>2</sub> as catalyst precursor was evaluated on 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes (TCBs). All TCBs could be converted to dechlorination products with high conversion. Products distribution was closely related with the substrate structures and C-Cl bond energies. A reasonable reaction mechanism was also proposed.

## 1. Introduction

Aryl chlorides are considered the persistent toxic pollutants because the environment does not possess a comparatively assimilative ability [1]. The dechlorination of aryl chlorides is becoming a global issue [2]. With the ever increasing concerns for environmental protection and human health, the safe disposal of aryl chlorides has attracted much attention [2, 3]. Various methods like incineration and thermal oxidation do degrade aryl chlorides, but incomplete oxidation usually leads to the formation of more toxic species such as dioxins and chlorine [4]. In contrast, catalytic hydrodechlorination (HDC) may become a promising treatment for these chlorinated compounds by means of an environmentally friendly way [5]. Although HDC process does not usually cause the complete destruction of pollutants, it can result in the convenient transformation to less toxic compounds. Other advantages of HDC reflect in high conversion levels, conducting at low temperature and pressure, and so forth [6].

Catalytic HDC can be usually effectively performed in both liquid and vapor phases using the supported noble metal (Pd [2, 4, 6–8], Pt [9], and Ru [10]) or nonnoble metal (Ni [4, 11, 12] and Ni-Mo [11]) as catalysts, among which Pd-based catalysts are considered the most suitable

for liquid phase HDC since it can selectively replace the chlorine element of substrate with hydrogen [7]. On the other hand, organometallic compounds are frequently selected as catalysts for the activation of carbon-halogen bonds [13]. Thus, it is reasonable to infer the utility of metal complexes in the catalytic HDC reactions if only the proper hydrogen sources and reducing agents are provided. In fact, the organometallic complexes containing Rh [14], Fe [15], and Ni [16] have been reported in the HDC of aryl chlorides with the appropriate reagents such as hydrogen [14], hydrides [17], alcohols [18], and Grignard reagents [19] as reducing agents. Recently, our group reported a nickel complexes Ni[Phen]<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> catalyzed HDC of aryl chlorides in the presence of zinc and water and results found that the Ni complexes could be recycled six times without the evident deactivation [20]. However, the reports on palladium complexes used in catalytic HDC of aryl chlorides are still rarely studied. Powell et al. reported PdCl<sub>2</sub>(PhCN)<sub>2</sub> together with bidentate phosphine ligands as catalyst system for the HDC of aryl chlorides in the presence of sodium formate and N,N-dimethyl-acetamide [21].

Herein, we reported the further exploration of HDC of aryl chlorides by organometallic complex Pd(Phen)Cl<sub>2</sub> as catalyst precursor. Under the special conditions, Pd(Phen)Cl<sub>2</sub>

could smoothly promote the HDC reactions of several TCBS to occur and different dechlorination products were detected. Products distribution was closely related with the substrate structures and C-Cl bond energies. The possible reaction pathway was also discussed.

## 2. Experimental

**2.1. General.** PdCl<sub>2</sub>, phenanthroline, and other chemicals were purchased from Sinopharm Chemical Reagent Company. <sup>1</sup>H NMR spectra were acquired on a Bruker Avance III spectrometer (500 MHz). Transmission electron microscopy (TEM) investigations were performed with an FEI Tecnai G2 20 microscope operated at 200 kV. Before the detection, the catalyst was dispersed in ethanol and reduced by NaBH<sub>4</sub> for 10 min until the color of the catalyst became black. To confirm that the catalyst distributed uniformly, the sample should be put into the ultrasonic vibration meter for another 30 min. Catalytic HDC activity of Pd catalysts was evaluated by gas chromatograph (GC-9790, Fuli, MD) equipped with a flame ionization detector (FID), a PEG-20 M capillary column (30 m × 0.25 mm × 0.5 μm), and N<sub>2</sub> as carrier gas. The initial oven temperature was set at 50°C for 3 min and was then raised with a gradient of 10°C/min until 200°C and held for 5 min. The temperature of the FID and injection was settled at 250°C. The FTIR analysis was performed on Nicolet 380 spectrometer with a KBr tablet.

**2.2. The Preparation of Catalyst Precursor Pd(Phen)Cl<sub>2</sub>.** Typically, a solution of PdCl<sub>2</sub> (0.355 g, 2 mmol) in acetonitrile (50 mL) was heated to 70°C under stirring and maintained at this temperature for 2 h. During this process a clear solution appeared, which indicated the formation of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>. Then the solvent was removed at reduced pressure and a pale yellow solid was obtained. The yellow solid was dissolved in 25 mL EtOH, to which a solution of 1,10-phenanthroline (0.396 g, 2 mmol) was dropwise added. With the addition of phenanthroline, the color of solution became gradually violent. Two hours of reaction resulted in the formation of a substantial white precipitate, which was collected by filtration and washed by EtOH (3 × 5 mL). The product was dried in vacuum drying oven at 50°C for 12 h to give the catalyst precursor Pd(Phen)Cl<sub>2</sub> (0.580 g, 81.23%).

**2.3. The Hydrodechlorination of Aryl Chlorides.** Typically, hydrodechlorination reaction was carried out in a 150 mL three-necked, round-bottomed reactor equipped with a balloon for hydrogen supply (1 atm) at a temperature of 333 K. 0.25 mmol catalyst precursor was dispersed in 25 mL of MeOH by means of ultrasonation. To this dispersion the acid-binding agent triethylamine (15 mmol) and NaBH<sub>4</sub> (0.02 g) were added. The reduction process was maintained for 1 h, after which the aryl chlorides substrates (5 mmol) were added and the HDC reaction started counting. The aliquots of reaction solution were taken every 30 min for GC analysis.

## 3. Results and Discussion

**3.1. The Characterization of Catalyst Precursor Pd(Phen)Cl<sub>2</sub>.** Catalyst precursor Pd(Phen)Cl<sub>2</sub> was firstly characterized by FTIR technique (Figure 1(a)). The bands at 1619, 1560, 1510, and 1421 cm<sup>-1</sup> assigned to the skeletal vibration of Phen unit were shifted towards high frequency region (located at 1631, 1581, 1515, and 1425 cm<sup>-1</sup>) after complexation, which was ascribed to the sterohindrance effect. In addition, the signals of C-H bending vibration of aryl rings were shifted from 854, 735 cm<sup>-1</sup> to 840, 707 cm<sup>-1</sup> after complexation, respectively [22]. These data preliminarily implied the formation of Pd catalyst precursor. In order to provide the more definitive information for Pd(Phen)Cl<sub>2</sub> complex, <sup>1</sup>H NMR analysis was performed. Compared with free ligand Phen, the signals of protons on aryl rings of Pd(Phen)Cl<sub>2</sub> were significantly shifted downfield by 0.24~0.48 ppm due to the coordination of N atoms of Phen to Pd<sup>2+</sup> (Figure 1(b)), which definitely indicated the formation of catalyst precursor. Then, TEM was employed to examine the structure and Pd distribution of the materials. The catalyst sample was dispersed in ethanol by ultrasonic vibration, coordinated with phenanthroline ligand. We can see that, after the reduction with NaBH<sub>4</sub>, the particle was uniformly distributed (Figure 1(c)). For estimation of particle size, at least more than 50 individual particles were counted for each catalyst (Figure 1(d)). From the figure of particle size distribution, we can see that most particles (more than 75 percentage points) distributed in the intervals 3 to 4 and the distribution of the eight intervals approached Gaussian distribution; it shows that the particle size was very small and it distributed uniformly.

**3.2. Effect of Temperature and Kinetic Analysis.** In order to investigate the effect of reaction temperature, we performed the HDC reaction at 303, 313, 323, and 333 K, respectively, by the use of the synthesized catalyst precursor. Plots in Figure 2 show the conversion of 1,3,5-TCB as a function of time under the different temperatures condition. Repeated experiments gave the similar results showing considerable reproducibility. For all cases, 1,3,5-TCB conversion always went up with time extension and reached the plateau at different reaction time (longer time for 303, 313 K and shorter time for 323, 333 K). Generally, increasing temperature is always beneficial for chemical reactions. The catalytic HDC of 1,3,5-TCB in the present study was in good accord with this rule. For the reaction temperature we studied, high temperature always provided the higher conversion than those obtained at lower temperature under the same reaction conditions. By plotting ln(c<sub>0</sub>/c) against reaction time (t), we could get a straight line showing a first order feature for the catalytic HDC of 1,3,5-TCB, which was similar to the previous result [23]. From the lines in Figure 2 and ln(c<sub>0</sub>/c) = kt, we had calculated the values of rate constant k that were listed in Table 1. Higher reaction temperature was k that corresponded to a larger value implying the dependence of reaction rate on reaction temperature. According to Arrhenius equation, the overall apparent activation energy in the range 303–333 K was estimated to be 89.0 kJ/mol. The similar temperature effect

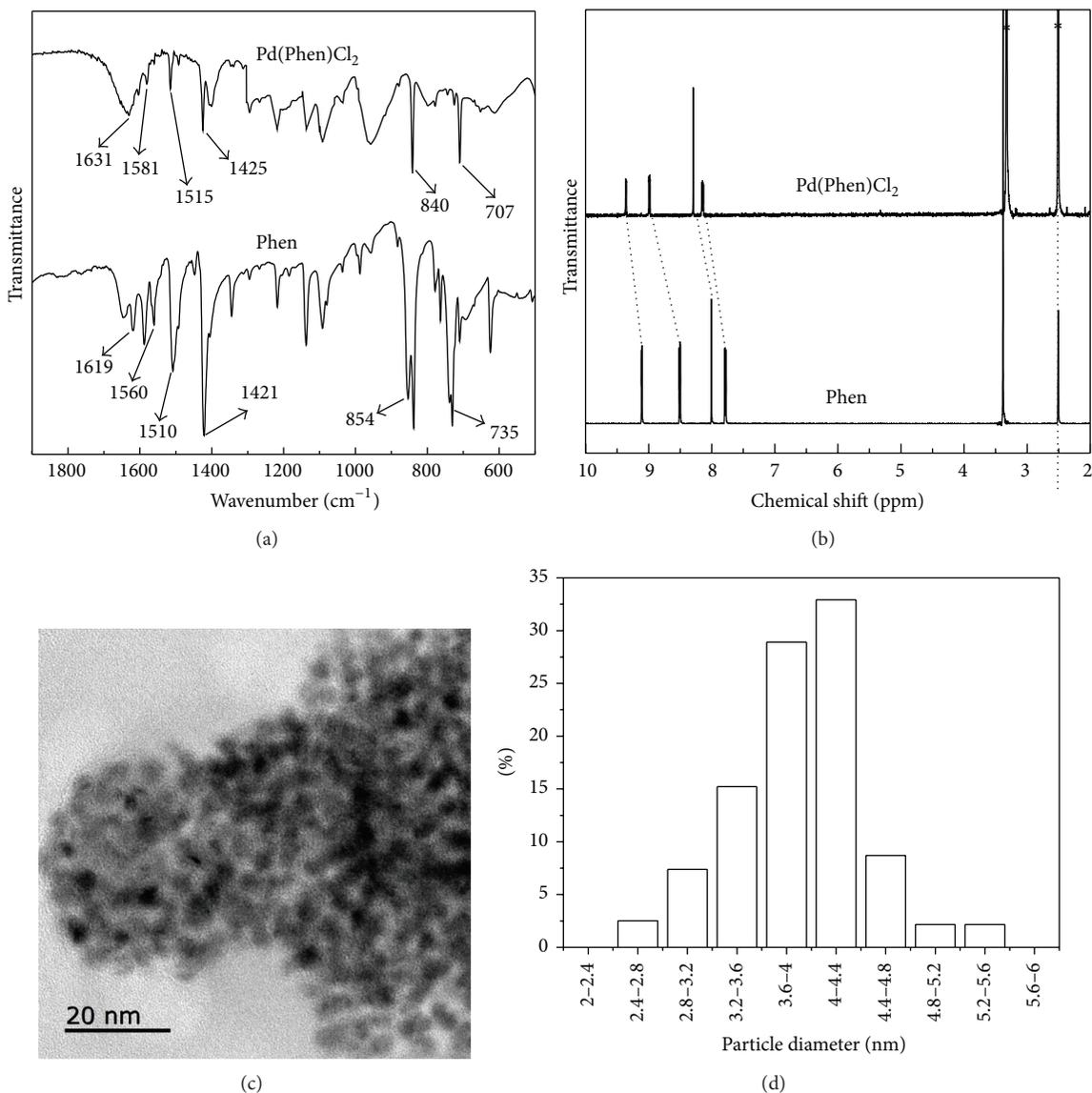


FIGURE 1: Comparison of FTIR spectra (a) and <sup>1</sup>H NMR spectra in [D<sub>6</sub>]DMSO (b) of free Phen ligand and Pd(Phen)Cl<sub>2</sub>. (Asterisks in <sup>1</sup>H NMR spectra denote the residual solvents signals.) The TEM of the redzuate of Pd(phen)Cl<sub>2</sub> (c). Particle size was calculated to analyse the distribution (d).

was also observed in the HDC reactions of 1,2,3-TCB and 1,2,4-TCB and the corresponding activation energy values for these two reactions were estimated to be 49.5 and 39.8 kJ/mol, respectively.

**3.3. Catalytic Activity and Product Distribution.** Figure 3 shows the product distribution of 1,3,5-TCB obtained by catalyst precursor Pd(Phen)Cl<sub>2</sub> at 323 K as a function of reaction time. From this figure, we can see that dichlorobenzene (DCB) as one of the main products appeared at the beginning of the reaction and its yield increased quickly in the first 2 h of reaction time (yield up to 56%). Other products including chlorobenzene (CB) and benzene were always present in the reaction mixture and their yields gradually increased in the first 3 h but their contents were relatively low (<17%). It was

interesting that the content of CB in product mixture at 3 h of reaction time became almost constant (about 15%), while the amounts of 1,3-DCB and benzene went along the reverse directions. Benzene content was drifting higher and 1,3-DCB's continued to decline. This significantly suggested a dynamic equilibrium during HDC reaction of 1,3,5-TCB. After full conversion of 1,3,5-TCB, the sustained decrease of 1,3-DCB content as well as the increase of benzene synergistically contributed to the relative constant CB amount. From the conversion of 1,3,5-TCB (Figure 2), the dechlorination mainly occurred at the first 4 h of reaction (for HDC reactions at 323 and 333 K) and the conversion extent of TCB was fairly large (up to 95%). In the subsequent stage, the reaction rate was sharply decreased and the conversion was almost near to the maximum (98% at 5 h of reaction). Combining the

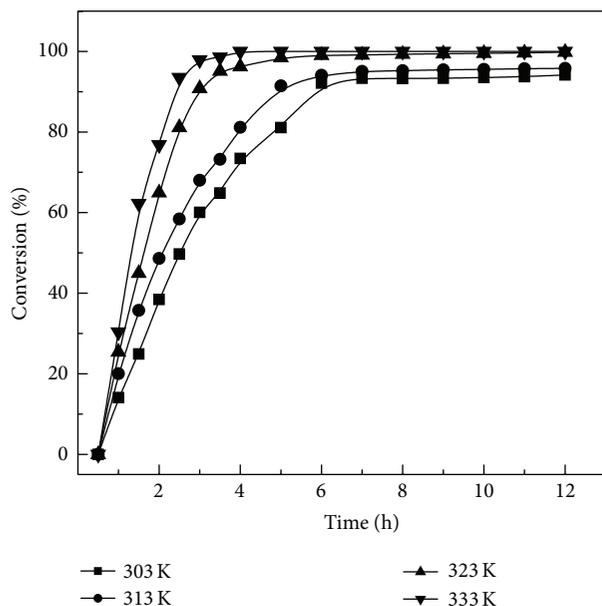


FIGURE 2: Temporal 1,3,5-TCB conversion profiles at 303, 313, 323, and 333 K using Pd(Phen)Cl<sub>2</sub> as catalyst precursor.

TABLE 1: Rate constants ( $k$ ) values for HDC of 1,3,5-TCB at different reaction temperatures.

Temperature (K)	Reaction rate equation	$k$ (h <sup>-1</sup> )	$R^2$
303	$\ln(c_0/c) = 0.4497x - 0.4158$	0.4497	0.9937
313	$\ln(c_0/c) = 0.5382x - 0.4147$	0.5382	0.9928
323	$\ln(c_0/c) = 0.9283x - 0.6100$	0.9283	0.9904
333	$\ln(c_0/c) = 1.6570x - 1.4708$	1.6570	0.9915

above results, the HDC of 1,3,5-TCB by Pd(Phen)Cl<sub>2</sub> catalyst precursor could smoothly proceed in the first 3 h of reaction and the main dechlorination product was 1,3-DCB. The poor HDC performance at later stage (several chloro-containing products rather than the final product benzene) could be attributed to the deactivation of Pd catalyst. The deactivation of Pd catalysts generally originated from HCl formed during HDC reaction, which increased the acidity and caused the poisoning of catalysts.

In order to make sure of the role of Pd(Phen)Cl<sub>2</sub> as a catalyst precursor, we performed the control experiments under the same conditions using 1,3,5-TCB as substrate. The HDC reactions in the presence of free Phen ligand or PdCl<sub>2</sub> salt instead of Pd(Phen)Cl<sub>2</sub> did not undergo the dechlorination and no dechlorination products were detectable. However, when Phen and PdCl<sub>2</sub> (in 1:1 mole ratio) were individually added at the same time, a measurable conversion (32% at 1.5 h of reaction time) was observed (Figure 4). Thus we deduced that Phen and PdCl<sub>2</sub> partly took part in the coordination reaction to form Pd(Phen)Cl<sub>2</sub> during the reduction process, which served as catalyst precursor to participate in the subsequent HDC reaction. Two factors could contribute to the moderate substrate conversion. One was that the amount of Pd(Phen)Cl<sub>2</sub> formed in reduction stage or that really participated in HDC was not as much as the cases by the

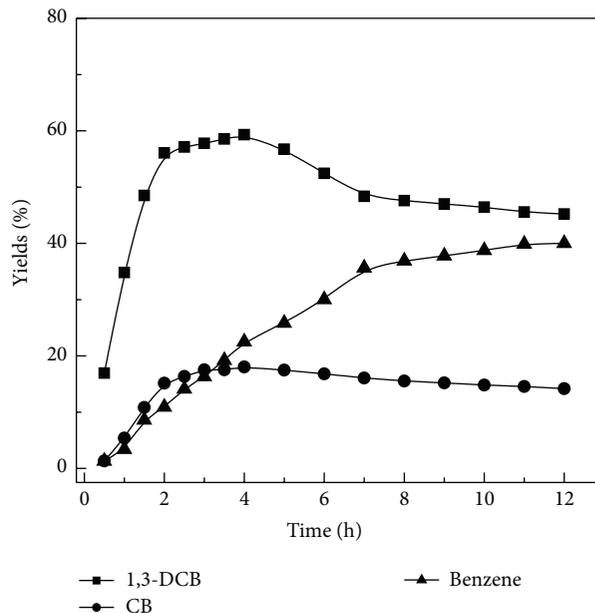


FIGURE 3: Product yields of 1,3,5-TCB as a function of time at 323 K using Pd(Phen)Cl<sub>2</sub> as catalyst precursor.

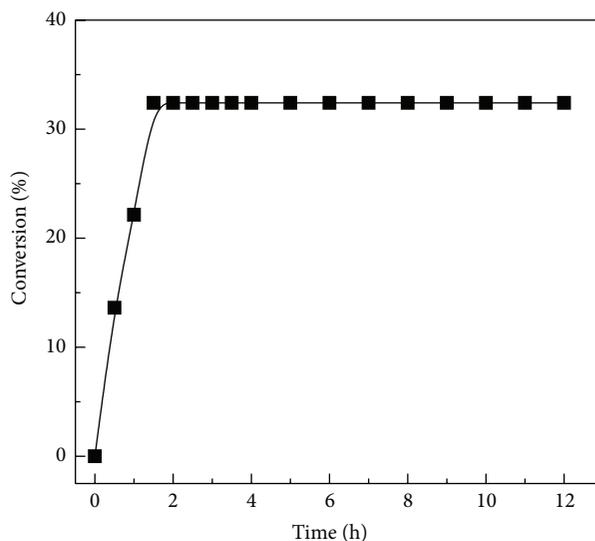


FIGURE 4: Temporal 1,3,5-TCB conversion profiles at 323 K in the coexistence of Phen and PdCl<sub>2</sub> (1:1 mole ratio).

direct use of Pd(Phen)Cl<sub>2</sub> as catalyst precursor. The other reason was the formed HCl in HDC, which poisoned the formed Pd(Phen)Cl<sub>2</sub> and weakened the coordination ability of Phen by acid-base reaction to steadily produce complex Pd(Phen)Cl<sub>2</sub>. Therefore, after the maximum conversion 32% at 1.5 h appeared no further substrate conversion was observable. All these results inferred indirectly the role of Pd(Phen)Cl<sub>2</sub> as catalyst precursor, which really participated in the HDC reaction of aryl chlorides.

Figure 5(a) shows the overall HDC conversion profiles of 1,2,3-, 1,2,4-, and 1,3,5-TCB. No significant difference could

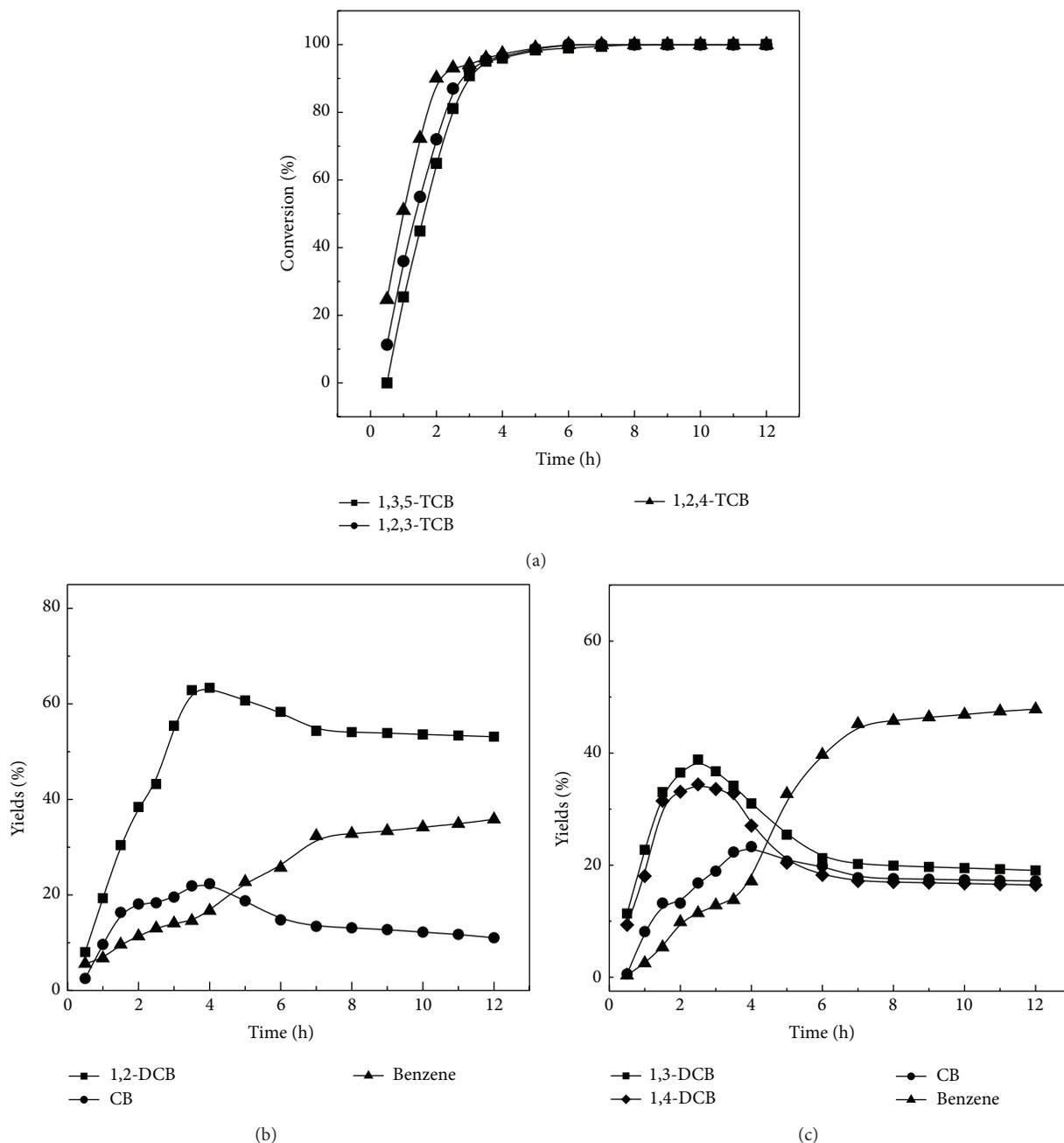


FIGURE 5: Temporal conversion profiles of 1,2,3-, 1,2,4-, and 1,3,5-TCB (a) and product yields of 1,2,3-TCB (b) and 1,2,4-TCB (c) as a function of time at 323 K using Pd(Phen)Cl<sub>2</sub> as catalyst precursor.

be distinguished. As shown by 1,3,5-TCB, HDC of 1,2,3- and 1,2,4-TCB by Pd(Phen)Cl<sub>2</sub> as catalyst precursor also gave the similar products yields tendency except for 1,2,4-TCB case with two DCB products (Figures 5(b) and 5(c)). In the initial reaction stage (2-3 h), DCB converted directly from the corresponding TCBS always served as the main products that existed in corresponding reaction mixtures and their contents were steadily going up with reaction time. After the almost full conversion of the original chlorinated substrates (ca. 2-3 h of reaction time), DCB primarily underwent the further dechlorination to afford CB or benzene due to the lack of

the sustained production of DCB and thus the relative DCB amounts started to decline. In addition, CB appeared at the beginning of the reaction, but the yields passed through a maximum at 4 h of reaction time and then began to drop. As the final dechlorination product, benzene was always present in the reaction mixture but the contents were relatively low. Although the amount of benzene in these two cases always kept rising, the yields were in the range from 35% to 45% even extending to 12 h of reaction time. This phenomenon implied that the deactivation of catalyst was equally encountered in the HDC of 1,2,3- and 1,2,4-TCB.

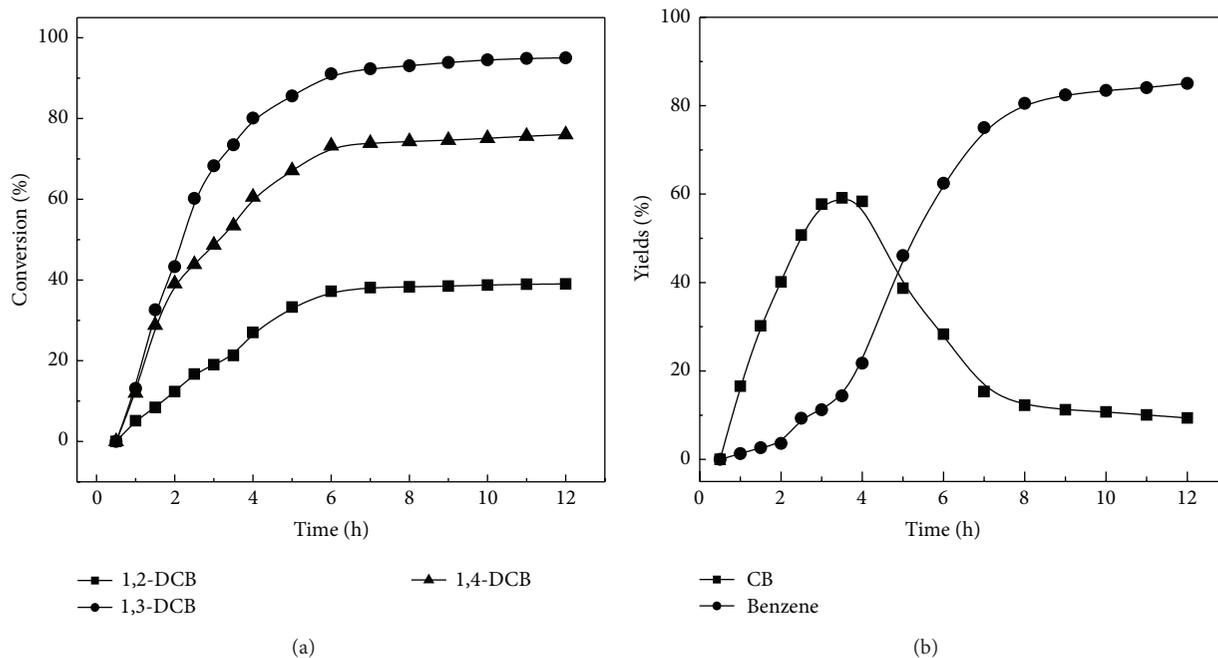


FIGURE 6: Temporal conversion profiles of 1,2-, 1,3-, and 1,4-DCB (a) and product yields of 1,3-DCB (b) as a function of time using  $\text{Pd}(\text{Phen})\text{Cl}_2$  as catalyst precursor at 323 K. Only the product yields of 1,3-DCB were depicted as atypical since the similar results were observed in the cases of 1,2- and 1,4-DCB.

For the DCB products distribution in the HDC reactions of 1,2,3- and 1,2,4-TCB, the C-Cl bond energy as well as the steric hindrance effect of C-Cl bonds could give a reasonable explanation. It is well known that the insertion reaction between C-Cl bond and active catalyst center ( $\text{Pd}(0)$  in our case) forming oxidative adduct complex is the rate determining step for the dechlorination [23]. For polychloride, producing what type of oxidative adduct complex depends not only on the C-Cl bond energy, but also on the steric hindrance of C-Cl position. Generally, the C-Cl bond with the relatively low C-Cl bond energy (having the equivalent steric hindrance compared with other C-Cl bonds) or small steric hindrance (possessing the equivalent C-Cl bond energy compared with other C-Cl bonds) prefers to afford the corresponding oxidative adduct complex. For 1,2,3-TCB in our case, the bigger steric hindrance of C(2)-Cl bond together with the equivalent bond energies of three C-Cl bonds (the bond energies of C(1)-Cl, C(2)-Cl, and C(3)-Cl bonds were 325.6, 325.7, and 325.6 kJ/mol [24], resp.) was responsible for the sole 1,2-DCB production. In contrast, the bond energy of C-Cl bond played a dominant role for producing what type of DCB products in the case of 1,2,4-TCB. Although the steric hindrance on C(1)-Cl and C(2)-Cl bonds was slightly bigger than that on C(4)-Cl bond, much difference in bond energies between C(4)-Cl (336.8 kJ/mol), C(1)-Cl (331.6 kJ/mol), C(2)-Cl (329.4 kJ/mol) bonds caused the insertion reaction to occur in C(1)-Cl or C(2)-Cl bonds, which resulted in the production of 1,3- and 1,4-DCB rather than 1,2-DCB.

In the HDC reactions of 1,2,3-, 1,2,4-, and 1,3,5-TCB, the corresponding DCB as the main products appeared from the beginning of the reaction and their yields passed

through a maximum and then were gradually declined. This phenomenon implied that DCB would be a reaction intermediate. In order to determine whether DCBs were the intermediates, we studied the reactivity of 1,2-, 1,3-, and 1,4-DCB under the same conditions (Figure 6(a)). The results indicated that three DCBs were smoothly dechlorinated and converted into the dechlorination products CB and benzene (Figure 6(b)), which verified the feature of DCBs as an intermediate. The difference in C-Cl bond energy and steric hindrance could account for the reactivity difference of 1,2-, 1,3-, and 1,4-DCB. 1,3-DCB with moderate steric hindrance and lowest C-Cl bond energy (376.1 kJ/mol) [25] demonstrated the best reactivity. The crowded surrounding of two neighbored C-Cl bonds together with the higher C-Cl bond energy (385.8 kJ/mol) [25] made 1,2-DCB exhibit the worst HDC performance. The most preferred spatial situation and the highest C-Cl bond energy (392.0 kJ/mol) [25] allowed 1,4-DCB to have the mediated reactivity.

**3.4. Possible Mechanism of HDC of Aryl Chlorides.** In order to better understand the nature of HDC of aryl chlorides by the Pd catalyst precursor  $\text{Pd}(\text{Phen})\text{Cl}_2$ , we proposed a reasonable mechanism (Figure 7). For palladium-mediated dehalogenation reactions, the palladium (0) is widely considered as the catalytic active specie that promoted the formation of the oxidative adduct complex. In our case, the complex  $\text{Pd}(\text{Phen})\text{Cl}_2$  was reduced by reducing agent  $\text{NaBH}_4$  to form the really active catalyst center  $\text{Pd}(0)$  (**1**). In the presence of hydrogen, active center **1** was further converted into palladium-hybrid complex **2**. The control experiment using nitrogen instead of hydrogen could not

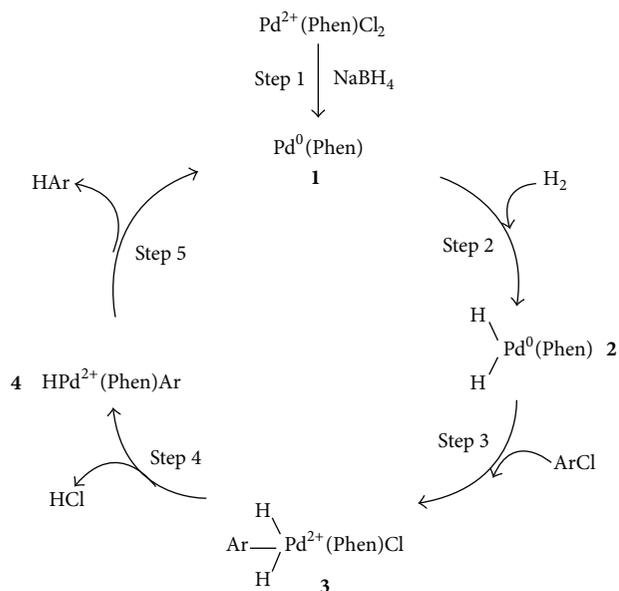


FIGURE 7: Proposed mechanism of HDC of aryl chlorides by  $\text{Pd}(\text{Phen})\text{Cl}_2$  catalyst precursor.

give any dechlorination product, which suggested the real hydrogen source was coming from hydrogen gas rather than the solvent methanol. Then, complex **2** reacted with aryl chloride to afford the oxidative adduct complex **3** as mentioned above. With the aid of acid-binding reagent, complex **3** was further transformed to compound **4** by the release of HCl. Undergoing a beta hydride elimination compound **4** afforded the expected hydrodechlorination product and regenerated the active Pd(0) species. The successive HDC of polychlorinated aryl gave various products. Generally, it is believed that the rate determining step for dechlorination is the oxidative addition of aryl chlorides and the electron-rich ligands are beneficial for this step. The relative high electron donating feature of Phen ligand partly accounted for the relatively fast conversion of chlorinated substrates.

#### 4. Conclusions

In this work, we investigated the HDC performance of  $\text{Pd}(\text{Phen})\text{Cl}_2$  as catalyst precursor using TCBs as substrates. All TCBs could be fully converted under the described conditions, but they could not be degraded completely to produce the final dechlorination product benzene, which was ascribed to the deactivation of catalyst. Products distribution was closely related to the substrate structures and C-Cl bond energies. The possible reaction pathway was also discussed.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

#### Acknowledgments

The authors thank Shanghai Municipal Natural Science Key Research Project of China (no. J51503) and Shanghai Municipal Natural Science Foundation of China (no. 11YZ221) for the financial support.

#### References

- [1] B. L. Kniep, F. Girgsdies, and T. Ressler, "Effect of precipitate aging on the microstructural characteristics of Cu/ZnO catalysts for methanol steam reforming," *Journal of Catalysis*, vol. 236, no. 1, pp. 34–44, 2005.
- [2] F. J. Urbano and J. M. Marinas, "Hydrogenolysis of organohalogen compounds over palladium supported catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 173, no. 1-2, pp. 329–345, 2001.
- [3] M. D. Erickson, S. E. Swanson, J. D. Flora Jr., and G. D. Hinshaw, "Polychlorinated dibenzofurans and other thermal combustion products from dielectric fluids containing polychlorinated biphenyls," *Environmental Science and Technology*, vol. 23, no. 4, pp. 462–470, 1989.
- [4] C. Amorim, X. Wang, and M. A. Keane, "Application of hydrodechlorination in environmental pollution control: comparison of the performance of supported and unsupported Pd and Ni catalysts," *Chinese Journal of Catalysis*, vol. 32, no. 5, pp. 746–755, 2011.
- [5] D. Richard, L. D. Núñez, C. De Bellefon, and D. Schweich, "Depollution of waters contaminated by phenols and chlorophenols using catalytic hydrogenation," *Environmental Chemistry: Green Chemistry and Pollutants in Ecosystems*, vol. 14, pp. 601–613, 2005.
- [6] L. Calvo, M. A. Gilarranz, J. A. Casas, A. F. Mohedano, and J. J. Rodríguez, "Hydrodechlorination of 4-chlorophenol in aqueous phase using Pd/AC catalysts prepared with modified active carbon supports," *Applied Catalysis B: Environmental*, vol. 67, no. 1-2, pp. 68–76, 2006.
- [7] N. S. Babu, N. Lingaiah, R. Gopinath, P. S. S. Reddy, and P. S. S. Prasad, "Characterization and reactivity of alumina-supported Pd catalysts for the room-temperature hydrodechlorination of chlorobenzene," *Journal of Physical Chemistry C*, vol. 111, no. 17, pp. 6447–6453, 2007.
- [8] H.-Y. Wee and J. A. Cunningham, "Palladium-catalyzed hydrodehalogenation of 1,2,4,5-tetrachlorobenzene in water-ethanol mixtures," *Journal of Hazardous Materials*, vol. 155, no. 1-2, pp. 1–9, 2008.
- [9] T. Yoneda, T. Takido, and K. Konuma, "Hydrodechlorination reactivity of *para*-substituted chlorobenzenes over platinum/carbon catalyst," *Journal of Molecular Catalysis A: Chemical*, vol. 265, no. 1-2, pp. 80–89, 2007.
- [10] C. S. Srikanth, V. P. Kumar, B. Viswanadham, and K. V. R. Chary, "Hydrodechlorination of 1,2,4-trichlorobenzene over supported ruthenium catalysts on various supports," *Catalysis Communications*, vol. 13, no. 1, pp. 69–72, 2011.
- [11] M. A. Keane, C. Park, and C. Menini, "Structure sensitivity in the hydrodechlorination of chlorobenzene over supported nickel," *Catalysis Letters*, vol. 88, no. 1-2, pp. 89–94, 2003.
- [12] M. A. Keane and R. Larsson, "On the stepwise change of activation energies in the hydrodechlorination of chlorobenzene over supported nickel," *Catalysis Communications*, vol. 9, no. 3, pp. 333–336, 2008.

- [13] A. M. Zawisza and J. Muzart, "Pd-catalyzed reduction of aryl halides using dimethylformamide as the hydride source," *Tetrahedron Letters*, vol. 48, no. 38, pp. 6738–6742, 2007.
- [14] Y. Zeng, Y. Wang, J. Jiang, and Z. Jin, "Rh nanoparticle catalyzed hydrogenation of olefins in thermoregulated ionic liquid and organic biphasic system," *Catalysis Communications*, vol. 19, pp. 70–73, 2012.
- [15] G. K. Parshetti and R.-A. Doong, "Dechlorination and photodegradation of trichloroethylene by Fe/TiO<sub>2</sub> nanocomposites in the presence of nickel ions under anoxic conditions," *Applied Catalysis B: Environmental*, vol. 100, no. 1–2, pp. 116–123, 2010.
- [16] J. A. Roth, S. R. Dakoji, R. C. Hughes, and R. E. Carmody, "Hydrogenolysis of polychlorinated biphenyls by sodium borohydride with homogeneous and heterogeneous nickel catalysts," *Environmental Science and Technology*, vol. 28, no. 1, pp. 80–87, 1994.
- [17] C. Desmarests, S. Kuhl, R. Schneider, and Y. Fort, "Nickel(0)/imidazolium chloride catalyzed reduction of aryl halides," *Organometallics*, vol. 21, no. 8, pp. 1554–1559, 2002.
- [18] P. Maloney, R. DeVor, S. Novaes-Card et al., "Dechlorination of polychlorinated biphenyls using magnesium and acidified alcohols," *Journal of Hazardous Materials*, vol. 187, no. 1–3, pp. 235–240, 2011.
- [19] J. Terao, A. Ikumi, H. Kuniyasu, and N. Kambe, "Ni- or Cu-catalyzed cross-coupling reaction of alkyl fluorides with grignard reagents," *Journal of the American Chemical Society*, vol. 125, no. 19, pp. 5646–5647, 2003.
- [20] F. Alonso, I. P. Beletskaya, and M. Yus, "Metal-mediated reductive hydrodehalogenation of organic halides," *Chemical Reviews*, vol. 102, no. 11, pp. 4009–4091, 2002.
- [21] K. R. Powell, T. M. McCleskey, W. Tumas, and J. M. DeSimone, "Polymers with multiple ligand sites for metal extractions in dense-phase carbon dioxide," *Industrial and Engineering Chemistry Research*, vol. 40, no. 5, pp. 1301–1305, 2001.
- [22] X. X. Zhang and E. J. Gao, "The study of bending vibration of aryl rings in palladium ligand complex," *Journal of Shenyang Institute of Chemical Technology*, vol. 12, p. 11, 1997.
- [23] P. C. Nam and M. Nguyen, "Oxidative adduct complex formation through the carbon chloride bond cleavage with palladium," *Journal of Chemical Physics*, vol. 109, p. 1034, 2005.
- [24] H.-J. Wang, Y. Fu, C. Wang, and Q.-X. Guo, "Theoretical study of hemolytic C–Cl bond dissociation enthalpies of environmental pollutants," *Acta Chimica Sinica*, vol. 66, no. 3, pp. 362–370, 2008.
- [25] Y. R. Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, Science Press, Beijing, China, 2005, (Chinese).



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

