

Catalytic hydrodechlorination of 2,4-dichlorophenol on Pd/Rh/C catalysts

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Abstract

Catalytic hydrodechlorination of 2,4-dichlorophenol was studied over 0.97% Pd/C, 0.98% Rh/C and 0.8% Pd–0.19% Rh/C catalysts. The catalysts were prepared by incipient wetness impregnation of support and characterized by BET surface area, temperature programmed reduction (TPR) and X-ray diffraction (XRD). The 0.97% Pd/C catalyst, which had the largest crystallite size, was the most active and selective towards the formation of 2- and 4-chlorophenols among three catalysts in liquid phase. Hydrodechlorination activity of carbon-supported catalysts were in the order of Pd/C > Pd/Rh/C > Rh/C. The kinetic equation explained experimental data well and kinetic parameters of three catalysts were provided and discussed.

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1. Introduction

Soil and water contamination by chlorophenols (CPs) now poses a significant burden due to the widespread industrial usage of cps and their persistency and toxicity enhances the burden [1,2]. Chlorophenols are used in some important industrial processes such as the production of herbicides, i.e. 2,4-dichlorophenoxyacetic, acid dyes, wood protectors and plant regulators but in general they are regarded to be, perhaps more than any other chemical, most widespread pollutants, and therefore, they had to be degraded to less harmful compounds. Most of the degradation methods are oxidative, e.g. wet oxidation, photo catalytic oxidation [3]. A variety of alternative techniques, such as, usage of ultrasound and biocatalyst [4], activated sludge [5], gas phase hydrodechlorination [6], exhaustive dechlorination [7], polymer based and membrane catalysts [8], and hydrodearomatization [9]. Among all these alternatives, catalytic hydrodechlorination is now viewed as an emerging technology since it is suitable for both deep [10,11] and selec-

tive mild hydrodechlorination [12,13] and also it facilitates raw material recycle [9,10]. Hydrodechlorination (HDC) may also prove to be a significant process for the synthesis of fine chemicals as well as for the abatement of chlorinated organic pollutants at mild conditions. Advantages of hydrodechlorination include operations at low temperature and pressure, high conversion of CPs, no more harmful side products, less sensitivity to pollutants concentrations and possibility of selective Cl removal.

Liquid and gas phase hydrodechlorination in general provide a more economical solution than other methods. Gas and liquid phase catalytic HDC has been studied for various chloroorganics over group VIIIA noble metals [13] supported on various supports [14,15]. The high activity of Pd supported on carbonaceous carriers is due, in part, to the hydrogen spillover onto various amorphous and structured carbon [15]. In addition to this, since not only does it promotes C–Cl bond cleavage, but it is also the least affected by the catalyst properties of halide ions.

One important issue in the catalytic dehydrochlorination is the role of second metal [16,17] beside Pd and also the role of the support [18]. Unlike monometallic catalysts, the bimetallic catalysts deactivate less readily with time on stream. The decrease in activity can be attributed to the fact that second metal dilutes Pd, and therefore dilution eliminates deactivation.

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The aim of this work was to study the selective hydrodechlorination of 2,4-dichlorophenol in aqueous phase over Pd/C, Rh/C and Pd/Rh/C catalysts. In view of potential interest of this process, the influence of Rh and kinetic modelling is studied.

2. Experimental

2.1. Materials

2,4-Dichlorophenol (>99%) was purchased from Aldrich Chemical Co., and used as received. Stock solution of 2,4-DCP was prepared using deionized water (18 M Ω). Ultra high purity 10.3% H₂ in N₂ mixture was used in the catalytic experiments. A commercial active carbon (CECA-France) with BET surface area of 950 m²/g and the mean particle diameter of active carbon support was 65 μ m.

2.2. Catalyst preparation

Pd/C, Rh/C and Pd/Rh/C catalysts were prepared by incipient wetness impregnation of active carbon support. Catalysts were prepared by dissolving PdCl₂ and Rh(NO₃)₃ in HNO₃ acid solution. Pd and Rh loading of the catalyst was adjusted by changing Pd and Rh concentration in the impregnation solution. After impregnation, the resulting pastes were dried at 110 °C for 12 h. Then, samples were further treated at 400 °C for 2 h. The actual metal loadings were determined using Thermo Elemental X Series ICP-MS. Actual metal loadings were listed in Table 1.

2.3. Catalyst characterization

Total BET surface areas were measured using Quantachrome Monosorb 17S apparatus using single point BET method. Powder X-ray diffractions of samples were obtained on a Rigaku D/Max-2200 diffractometer by using the Cu K α ($\lambda = 1.5405$) radiation. Samples were scanned from 15 to 50 at a rate of 0.04°/min (in 2 θ). Metal crystallite sizes were calculated from the broadening of the Pd (1 1 1) and Rh(1 1 1) peaks by using the Scherer equation $t = C\lambda/B \cos \theta$, where λ is the X-ray wavelength (\AA), B the full width at half maximum, θ the Bragg angle, C a factor depending on crystallite shape (taken to be 1), and t is the crystallite size (\AA).

2.4. Catalytic activity test

Liquid phase hydrodechlorination of 2,4-dichlorophenol was carried out in a glass reactor at a constant stirring rate of 250 rpm.

The reaction vessel (100 cm³) was placed in a temperature-controlled heating bath. A proportional and integral controller with a precision of ± 1 °C controlled the reaction temperature. The reactor was equipped with a H₂ supply, thermocouple port, reflux condenser and side sampling port. The 10.3% H₂/N₂ mixture at a constant volumetric flow rate (250 cm³ min⁻¹) was sparged via a sintered glass from the bottom of the reactor and this also helped to better stir the content. All the reactions were conducted with initial concentrations (0.08, 0.1, 0.15 and 0.25 M) of the 2,4-dichlorophenol and at 0.1–0.3 atm partial pressures of hydrogen. When 0.1 M 2,4-DCP concentration was used, 0.42 g of catalyst was used. For the other concentrations, same ratio of catalyst to 2,4-DCP was maintained. The reactor was charged with deionized water, the catalyst and appropriate amounts of 2,4-DCP from the stock solutions. The suspension was flushed with N₂ flow (50 cm³ min⁻¹). After the temperature leveled out at reaction temperature and then sparged with hydrogen/nitrogen reaction mixture, reaction time was then registered. As the reaction progressed, an aliquot of sample was withdrawn from sampling port by a syringe. Finally after dilution, aliquots were filtered and the concentration of reaction products was analyzed by HPLC (Spectra system UV6000LP) using a C₁₈ column as stationary phase and a mixture of methanol and water (70:30 vol.) as mobile phase. The entire reaction products were all identified in a HP 5973a GC-MS with the help of NIST library.

3. Results and discussion

3.1. Catalyst characterization

The BET surface area of 950 ± 15 m²/g was obtained for all three catalysts. The surface area of the catalysts did not vary significantly, indicating that the observed changes in activity were due to the metal catalysts. Actual metal loadings and average crystallite sizes determined from X-ray diffractograms by line broadening technique are listed in Table 1. In XRD patterns of 0.97% Pd/C and 0.98% Rh/C, the peaks were weak and broad. Rh₂O₃ and metallic Rh were detected over fresh 0.98% Rh/C catalyst. Over fresh 0.97% Pd/C catalyst, strong Pd and weak PdO phases were identified but over 0.8% Pd/0.19% Rh/C, only Pd metallic phase at $2\theta = 40.03^\circ$ corresponding to cubic symmetry was detected. Palladium oxide, metallic rhodium, rhodium oxide peaks were not detected in 0.8% Pd/0.19% Rh/C catalyst. From XRD patterns, it was noticed that the addition of Rh shifted position of Pd metallic phase and the available phases in 0.8% Pd/0.19% Rh/C catalyst. In X-ray diffractogram of 0.8%

Table 1
Pd and Rh contents, crystallite sizes, initial rates of 2,4-DCP consumption and turnover frequencies at 85 °C

Catalyst metal percentages (w/w)	Metal Crystallite size determined by XRD line broadening (nm)	Initial 2,4-DCP consumption rate ($\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$)	TOF ($\times 10^2 \text{min}^{-1}$)
0.97% Pd/C	Pd (1 1 1)-40.6	173.1	6.6
0.80% Pd/0.19% Rh/C	Pd (1 1 1)-19.3; Rh (1 1 1)- ^a ND	45.3	2.4
0.98% Rh/C	Rh (1 1 1)-35.3	17.6	0.6

^a ND, not detected.

Pd/0.19% Rh/C catalyst, 2θ signal of Pd shifted to higher values from Pd (1 1 1) 39.49 to Pd (1 1 1) 40.03. Similar shifts were reported over the different supports, such as, in Pd/Fe–SiO₂ and Pd/Fe–TiO₂. It was reported that 2θ values of metallic Pd changed from Pd (1 1 1) 40.15 to Pd (1 1 1) 40.56 [7]. Since the TPR patterns of the catalysts did not show any significant consumption of hydrogen, the samples were not reduced with hydrogen before the reaction and they were used after thermal treatment as activation.

3.2. Reaction mechanism and kinetics

Progress of product distributions from 2,4-DCP hydrodechlorination at 85 °C over 0.97% Pd/C catalyst as a representative plot is depicted in Fig. 1. Initial consumption rate and turnover frequencies obtained at the same representative reaction conditions for all three catalysts are also listed in Table 1. 2-CP and 4-CP were found to be the only intermediate products. No ring hydrogenation products were detected, and phenol was detected as final product in most cases over a 5 h of reaction time.

In a similar study at low temperature [19], the product distribution was followed for Pd/C of varying Pd loading (1–10%, w/w) and 2-CP was found to be the only intermediate product at 273 K. They found that as Pd loading increased from 1 to 10% Pd/C, consequently catalyst particle size increased, 2,4-DCP consumption rates were found to be significantly lowered [19]. This is in line with our results, the initial rates were dependent on Pd catalyst loading and consequently on the crystallite sizes of Pd (1 1 1) phase when the Pd metal was decreased from 0.97 to 0.80, and hence crystallite size decreased from 40.6 to 19.3 nm respectively, as result of this sharp decrease, HDC activity decreased by an order of magnitude from 173.1 to 45.3 $\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$ as listed in Table 1. Though the change in Pd concentration was only 20%, the decrease in HDC activity was unproportionally high.

Yu. Shindler et al. [20] studied *p*-chlorophenol hydrodechlorination over activated carbon cloths (AAC) and granule activated carbon as supports for Pd catalyst. Their results indicated that Pd/AAC showed a high activity and 100% selectivity of CP conversion to phenol. In line with our findings, the high-

est conversion and reaction rate is obtained over the 1% Pd/C catalyst.

In this study, experimental results indicated that an increase in temperature from 30 to 85 °C over the 0.97% Pd/C resulted in 20% decrease in yield of phenol after 5 h of reaction time. Maximum 66% yield of mono chlorinated compound and 69% selectivity to chlorinated compounds was achieved. In a study that HDC temperature dependence over 1% Pd/C was revealed, it was found that 2,4-DCP was less susceptible to dechlorination than 2-CP or 4-CP [19].

At 85 °C, decreasing H₂ partial pressures from 0.3 to 0.1 atm resulted in a decrease of phenol selectivity from 66 to 31% over a 2 h of reaction time and similarly selectivity to monochlorinated CPs in total increased from 44 to 69% over the same reaction times. In a similar manner, as the initial concentration of 2,4-DCP increased from 0.08 to 0.25 M, phenol selectivity over 2 h of run increased from 31 to 49%, respectively, whereas selectivity to monochlorinated CPs in total decreased from 69 to 51%, respectively too.

An order of magnitude lower initial HDC rates are obtained over 0.98% Rh/C catalyst at all reaction conditions. When a 0.8% Pd/0.19% Rh/C catalyst used in HDC, it was found that initial catalytic activity was in between two extremes, namely, Pd/C and Rh/C catalysts. This behavior was explained to be a consequence of dilution of Pd by Rh. The 0.97% Pd/C catalyst exhibited higher selectivity toward 2-CP than that to 4-CP. The initial HDC activities were found to be in the following order: 0.97% Pd/C > 0.8% Pd/0.19% Rh/C > 0.98% Rh/C.

LaPierre et al. [21] proposed that dechlorination proceeded by dissociative adsorption of the chloro-organic compound and hydrogen, followed by a rapid recombination between phenyl radical and a proton. According to Kraus and Bazant [22], hydrogen and 2,4-dichlorophenol were adsorbed in accordance to a Langmuir-type dissociative and molecular adsorption, respectively and rate-limiting step was considered to be the reaction between dissociatively adsorbed hydrogen and 2,4-dichlorophenol. In the discussions, attention was directed to the role played by HCl produced in the reaction. From the experiments carried out in this study in relation to the role of HCl, it was found that the rate decreased with increasing concentrations of HCl. In addition to this finding, from experimental runs, it was observed that increase in the concentration of 2-CP and 4-CP had little effect on initial HDC reaction rate. Consequently, it was concluded that 2-CP and 4-CP are weakly adsorbed.

In kinetics modeling, four models utilizing the above mentioned experimental findings and hence four rate expressions selected from literature were tested with our experimental data. Kinetic model by Coq et al. [23] for the hydrogenolysis of chlorobenzene over Pd, Rh, Pd–Rh catalysts fitted better to our experimental data than others. Kinetic model by Coq et al. [23] predicted a first and half order dependence over chlorobenzene and hydrogen, respectively. In the rate-determining step, they proposed that dissociatively adsorbed H₂ reacted with adsorbed 2,4-DCP. This model and corresponding rate equation provided the best representation of our entire experimental data.

In this study, we adopted the same rate expressions developed by Coq et al. [23]. S represented the active site here. Details of

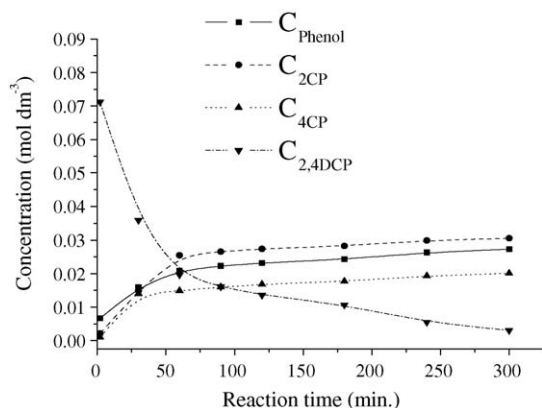


Fig. 1. HDC of 2,4-DCP over 0.97% Pd/C catalyst at 358 K, 0.1 MPa (10.3% H₂/N₂) and C_{2,4-DCP} = 0.08 mol dm⁻³.

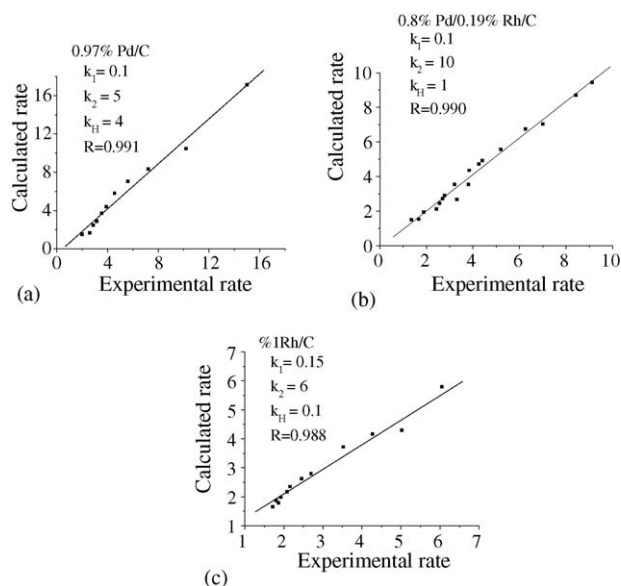


Fig. 2. Comparison of calculated and experimental rates for different catalysts (reaction rates are multiplied by 10^4 for the sake of clarity).

derivation of rate expression can be found in elsewhere [23]:



At the steady state, the rates of reduction and chlorination of the surface must be equal, thus:

$$k_1 \theta_{\text{H}} C_{2,4\text{-DCP}}^\alpha + k_2 \theta_{\text{H}} C_{\text{HCl}}^\beta = k_H \theta_{\text{Cl}} P_{\text{H}_2}^\gamma \quad (4)$$

where θ_{H} and θ_{Cl} represent the fractional coverage of hydrogen and chlorine, respectively. Assuming that $\theta_{\text{H}} + \theta_{\text{Cl}} = 1$, since only these two are considered to have been strongly adsorbed. The rate of the reaction is then given by

$$r = \frac{k_1 k_H C_{2,4\text{-DCP}}^\alpha P_{\text{H}_2}^\gamma}{1 + k_1 C_{2,4\text{-DCP}}^\alpha + k_2 C_{\text{HCl}}^\beta + k_H P_{\text{H}_2}^\gamma} \quad (5)$$

Taking into account the mathematically determined reaction orders and parameters of this study too, the rate equation took the following form for 0.97% Pd/C catalyst and other values are reported in Fig. 2 as comparison:

$$r = \frac{0.1 \times 4 \times C_{2,4\text{-DCP}} P_{\text{H}_2}^{0.5}}{1 + 0.1 C_{2,4\text{-DCP}} + 5 C_{\text{HCl}} + 4 P_{\text{H}_2}^{0.5}} \quad (6)$$

The rate constants k_1 , k_2 and k_H was obtained by fitting Eq. (6) to experimental rate data. The fitting of kinetic models was performed by the minimization of Box-Draper objective function with the numerical derivatives and a FORTRAN subroutine (GREG, version March, 1989) was used for this purpose. Non-linear model (Eq. (5)) was used for the parameter estimation. Fig. 2 shows the quality of fit between the observed and predicted rate data. The correlation was good and sometimes excellent. The relative behaviors of 0.97% Pd/C, 0.8% Pd/0.19% Rh/C,

and 0.98% Rh/C catalysts are also consistent with their relevant respective properties. Higher values of initial rates for 0.97% Pd/C are also obtained from model predictions.

4. Conclusion

Hydrodechlorination of 2,4-DCP in liquid phase over Pd/C catalyst showed a high activity and selectivity to singly chlorinated compounds; no ring hydrogenation products were detected under mild reaction conditions. The 0.97% Pd/C catalyst with the highest crystallite size exhibited higher initial HDC rates. Higher selectivity toward 2-CP than that to 4-CP was obtained over 0.97% Pd/C catalyst. The initial HDC activity decreased in the following order: 0.97% Pd/C > 0.8% Pd/0.19% Rh/C > 0.98% Rh/C. Addition of Rh caused a decrease in activity. The kinetic equation correlated well with experimental data of this study.

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