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Effect of HCl acid on the hydrodechlorination of chlorobenzene over palladium supported catalysts

G. Del Angel [a,*], J.L. Benitez [b]

[a] Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, P.O. Box 55-534, México, D.F. 09340, Mexico
[b] Instituto Mexicano del Petróleo, Eje Central Norte Lázaro Cárdenas 152,
Departamento de Desarrollo de productos Químicos, A.P. 14-805, México, D.F. 07730, Mexico

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Abstract

Ammonia and hydrochloric acid effects have been studied in the chlorobenzene hydrodechlorination in liquid phase on Pd/C catalysts. The addition of NH_4OH to the reactant medium does not modify the reaction rate while in hydrochloric acid medium the activity was increased. The role of HCl acid in the activity is explained by a partial oxidation of the Pd particles.

Keywords: Chlorobenzene; Hydrodechlorination; NH_4OH effect; HCl effect; Pd catalysts; Carbon

Recent studies have been focused on the hydrodechlorination of halogenated hydrocarbon compounds in organic liquids [1–3] and water [4–6]. Chlorobenzene is often chosen as a test molecule for the study of catalytic hydrodechlorination, since it is present as part of toxic compounds. In chlorobenzene hydrodechlorination, HCl acid is a stoichiometric product and as it has been reported, it plays an important inhibiting effect on the hydrodechlorination rate. Chlorine effects on Rh/SiO_2 and Rh/Al_2O_3 are attributed to a strong chlorine adsorption on Rh particles, if the reaction occurs in gas phase. It has been observed that the hydrodechlorination of chlorobenzene rate decreases when metallic size decreases. This behavior is related to the electrodeficient character of small particles [7]. Comparing Pd/Al_2O_3 and Rh/Al_2O_3 the inhibiting effect of HCl has been found to be stronger on Rh than on Pd. The Rh has more affinity to chorine than Pd. In gas phase reaction, the chlorine adsorbed on the metallic atoms is released from the surface since H_2 removes the adsorbed chlorine [8].

On the other hand, when the hydrodechlorination was carried out in liquid phase, the HCl acid produced during the reaction cannot be eliminated from the reactant system. Its concentration in the liquid phase increases as the reaction progresses. The chlorine inhibiting effect, then, must be more important in liquid phase than in gas phase. Such effect is observed during chlorophenol hydrodechlorination, in ammonium medium, on Pd/C liquid phase catalysis [9]. Overall, the initial rate of hydrodechlorination decreased with increasing chlorine substitution on the phenol ring. In general, a constant decreasing rate is observed during the reaction. Moreover, the authors repeat that without ammonia the reaction did not occur. The ammonia role is not totally known [10]. It has been proposed that it plays a role as a proton scavenger for HCl liberated during the reaction course.

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* Corresponding author. Fax: +52-5-804-46-66.
E-mail address: gdam@xanum.uam.mx (G.D. Angel).

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In the present work, with the aim to study the effect of chlorine (Cl^-) released during the chlorobenzene hydrodechlorination on the Pd/C catalyst, we carried out the reaction adding HCl acid or ammonia to the reaction medium. The results are surprising since it was found that HCl acid increased the activity whereas ammonia, at high concentration, had an inhibiting effect opposite to previously reported results.

The Pd/C catalyst was prepared by impregnation of the carbon support (carbon GAC 1240, ELF Attochem, of surface area, 1200 m^2/g). Before impregnation, the support was treated with nitric acid (1.5 M) stirred for 2 h, dried at 110°C overnight and then calcined at 300°C, for 6 h. For impregnation, an aqueous ammonium hydroxide (pH 11) solution of the metallic precursor, Pd $(NH_3)_4(NO_3)_2$ (ICN), was used. Afterwards, the catalyst was dried at 110°C overnight and reduced at 450°C under hydrogen flow.

The metal content, 0.72 wt.%, was determined by atomic absorption spectroscopy. The metallic dispersion was determined by CO chemisorption at 70°C using a conventional gravimetric system. Samples (300 mg) were reacted under hydrogen stream for 1 h at 400 K and then outgassed at the same temperature. The chemisorption was determined by introducing CO in the gravimetric system at 70°C and 100 Torr. The irreversibly adsorbed CO amount was obtained after evacuating the samples for 1 h at the same temperature. To calculate the number of active sites, a stoichiometry ratio CO/Pd equal to one was assumed.

The mean particle size was also determined by the independent transmission electron microscopy (TEM) technique using a JEOL 100CX instrument. Around 1000 particles per sample were counted. The histograms showed a particle size monodistribution whose maximum was found at around 48 Å. The catalytic activity was determined in a glass reactor of 150 cc with magnetic stirring; the reactant was chlorobenzene from Aldrich (99.9%). An aliquot of 70 cc of methanol (MeOH) and water (H_2O), MeOH/H_2O 50:50, at a chlorobenzene concentration of 200 ppm was put in the reactor together with 0.08 g of catalyst previously reduced. This mixture was stirred for 20 min before introducing hydrogen. Equilibrium between the adsorbed chlorobenzene on the surface of the catalyst and chlorobenzene into the solution was already reached [11]. The reactor was heated at 30°C and then purged four times with hydrogen before reaction. The reactor pressure was maintained at 2 bar throughout the experiments.

A plot of the reciprocal initial rate against the reciprocal catalyst mass was found to be linear for masses ranging from 40–160 mg and for a stirring speed of 900 rpm implying that the hydrogenolysis rates are free of external transport phenomena [12]. The absence of internal transfer limitations was demonstrated with the Koros–Nowak criterion [13]. The initial activity of two samples, 0.72 and 2.7 wt.% Pd content, with very close dispersions (30 and 35%), was (turnover frequency (TOF) for $t=0$) 15 and 17.3×10^{-2} molecules per site per second. A constant value of the TOF is taken as a proof of the absence of internal diffusion limitations [14].

Samples were analyzed at various reaction times to follow the progress of the reaction. The product analysis was made by gas chromatography. The activities are reported as TOFs or activities per surface metal atom. The TOF is determined at $t=0$ from the activity slope. The only product found after the hydrodechlorination reaction was benzene. Benzene hydrogenation was not observed.

The NH_4OH addition effect to the reactant medium is illustrated in Fig. 1. At low (200 ppm) and high chlorobenzene (10 000 ppm) concentration and at NH_4OH/chlorobenzene stoichiometric ratios of 1:1 and 1:2, respectively, no clear effect of the NH_4OH on the activity (TOF) was observed. A similar behavior was observed without NH_4OH in the reactant medium as shown in Table 1. However, an excess of NH_4OH (1:50) produces an important decrease of the activity.

In the hydrodechlorination in aqueous media, the addition of a base has been performed to neutralize the HCl acid formed during the reaction; with NH_4OH the best results were obtained [9]. It has been reported that in absence of a base, the reaction does not occur. However, this is not observed in the present study. In Fig. 1, it was found that the total transformation of 200 ppm of chlorobenzene was reached in 40 min, in presence of a stoichiometric amount of NH_4OH to neutralize the HCl. The same activity was obtained in absence of base. An excess of NH_4OH decreases the activity reaching a conversion of 95% in 160 min. The same behavior is observed at higher concentrations of chlorobenzene (10 000 ppm). Therefore, the reaction can be carried out without the presence of a base (Fig. 1). The excess of NH_4^+ inhibits the reaction.

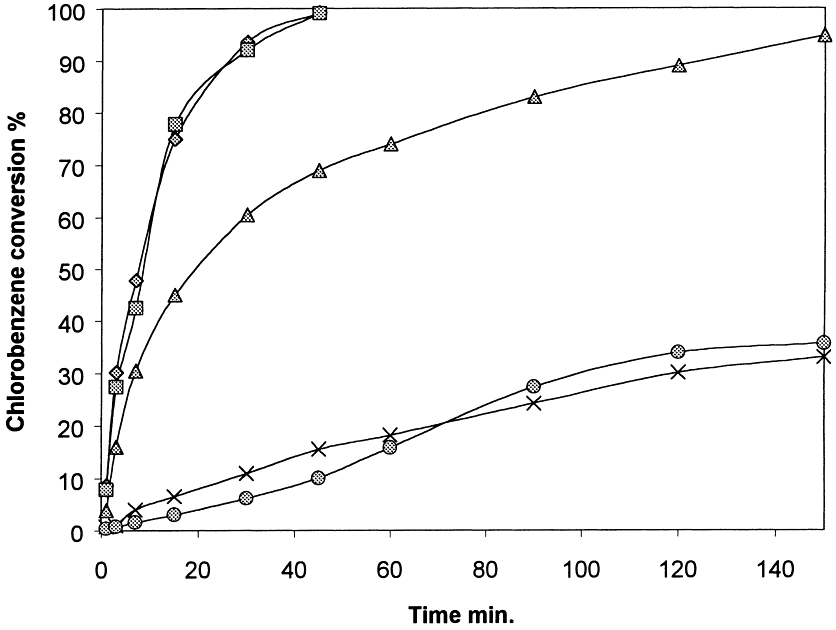

Fig. 1. Effect of the NH_4OH addition in the chlorobenzene hydrodechlorination on the Pd/C catalyst: (◇) 200 ppm chlorobenzene without NH_4OH; (□) 200 ppm chlorobenzene 0.01 ml NH_4OH; (△) 200 ppm chlorobenzene 0.5 ml NH_4OH; (×) 10000 ppm chlorobenzene 1.7 ml NH_4OH; (○) 10 000 ppm chlorobenzene without NH_4OH.

The effect of HCl acid addition to the reactant medium (0.15 ml) under hydrogen pressure produces an important increase in the reaction rate. A transformation of 90% is reached in only 3 min. In this case, the HCl acid favors the reaction and a TOF of 42×10^{-2} molecules per site per second is observed. Unexpected results were obtained with HCl acid since the reaction can be carried out without hydrogen pressure. Twenty-five percent of the reactant was transformed in 25 min, and this conversion was maintained for the following 24 h, a TOF of 7.4×10^{-2} molecules per site per second was observed as shown in Table 2. Carbon support and carbon support in presence of HCl acid did not present any activity. Thus, it is clear that the metal plays an important role in the HCl acid effect. In our experimental conditions, almost 5×10^{19} molecules of chlorobenzene (25%) are transformed from the solution when only 1.3×10^{18} atoms of Pd are accessible, then a positive effect of HCl acid is present.

Table 1

Activities for the hydrodechlorination of chlorobenzene on the Pd/C catalyst: effect of NH_4OH addition

Chlorobenzene concentration (ppm)	NH_4OH (ml)	Conversion of chlorobenzene (%)	Reaction time (min)	$V\times10^6$ (mol/s g)	$TOF\times10^2$ (molecules per site per second)
200	–	100	45	2.5	12
200	0.01[a]	100	45	2.2	11
200	0.5[b]	95	160	1.1	5
10000	–	36	160	1.0	51
10000	1.7[c]	34	160	5.0	24

[a] 1:1.

[b] 1:50.

[c] 1:2 Chlorobenzene/NH_4OH ratio.

Table 2
Activities for the hydrodechlorination of chlorobenzene on Pd/C catalyst: effect of the addition of HCl acid

Catalyst	Pressure of H_2 (bar)	HCl (37%) (ml)	Conversion of chlorobenzene (%)	Reaction time (min)	$V\times10^6$ (mol/s g)	TOF$\times10^2$ (mol/site s)
Carbon	2	–	–	–	–	–
Carbon	2	0.15	–	–	–	–
Pd/C	2	–	100	45	–	5.0
Pd/C	2	0.15	90	3	8.6	42.0
Pd/C	–	0.2	25	25	1.5	7.4

Since the reaction can occur in absence of hydrogen, one may assume that the hydrogen arising from the HCl acid is playing an active role in the reaction. In the reaction media (MEOH/H_2O 50/50), the HCl acid can be dissociated and an oxidation–reduction reaction could explain the results

$$\mathrm{Pd\,(s)} \rightarrow \mathrm{Pd}^{2+} + 2\mathrm{e}^- \qquad \text{(a)}$$

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2 \qquad \text{(b)}$$

In fact, taking into account the redox potentials, such direct oxidation of Pd by H^+ is unlikely, although the oxidability of small metallic particles is largely increased if compared to the bulk metal.

The conversion of chlorobenzene implies the dissociative adsorption of chlorobenzene on the surface of palladium followed by the hydrogenation of the benzyl species giving benzene as product.

$$2\mathrm{Pd} + \mathrm{C_6H_5Cl} \rightarrow \mathrm{Pd\text{-}Cl} + \mathrm{PdC_6H_5} \qquad (1)$$

$$\mathrm{Pd\text{-}H} + \mathrm{PdC_6H_5} \rightarrow \mathrm{C_6H_6} + 2\mathrm{Pd} \qquad (2)$$

or

$$\mathrm{Pd\text{-}H} + \mathrm{C_6H_5Cl} \rightarrow \mathrm{Pd\text{-}Cl} + \mathrm{C_6H_6} \qquad (3)$$

The oxidation of Pd by HCl acid is known to be a very slow reaction. The reaction rate is improved in presence of chlorine [15]. Thus, the surprising activity in chlorobenzene hydrodechlorination in absence of hydrogen could be the result of a dissociative adsorption of chlorobenzene which could induce the oxidation of the small Pd particles by HCl acid. The hydrogen in this way yields benzene and oxidizes palladium as $PdCl_4$, which was observed by UV–VIS in the reactant solution [16]. Such partial oxidation of Pd can also occur in presence of hydrogen. However, in this case, Pd^{4+} is again reduced by hydrogen. Thus, the metallic phase is continuously regenerated. This assumption could explain the higher activity in presence of HCl acid. Ionic strength effects as well as possible role of methanol as hydrogen donor certainly cannot be excluded. They will be matters of complementary studies in which such variables will be taken into account.

The role of NH_4OH to neutralize the HCl acid formed in the reaction does not operate in our system, since the reaction could be completed without ammonia in the reaction media. An inhibition of the reaction is observed at high concentrations of NH_4OH.

The important increase in the reaction rate by HCl acid is explained by a partial oxidation of Pd promoted by the chlorine coming from the dissociative adsorption of chlorobenzene.

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