

Chitosan-Supported Palladium Catalyst. II. Chlorophenol Dehalogenation

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Preliminary treatment with glutaraldehyde increased the stability of chitosan in acidic solution and the sorption of palladium from HCl solutions at high loading. A reduction procedure was used to partially reduce the palladium. The resulting chitosan-supported palladium catalyst was efficiently used for the hydrodehalogenation and partial dehydrodearomatization of 2-chlorophenol (2-CP). The reaction proceeds via hydrogen transfer using sodium formate. The optimum pH for the degradation of 2-CP was close to pH 3. The effects of catalyst dosage, formate concentration, 2-CP concentration, and temperature were studied to define the optimum conditions for the conversion of 2-chlorophenol into phenol and cyclohexanone. A limit on the formate/2-CP molar ratio was found to be required to achieve the complete dehalogenation of 2-CP: The formate excess needed to be higher than 50 times the 2-CP concentration. Increasing the temperature from 20 to 60 °C continuously increased the degradation rate, and the activation energy ranged between 20 and 25 kJ mol⁻¹ under nonlimiting experimental conditions (formate excess at the required level and pH 2.7).

Introduction

Chlorinated organic compounds have been found to be toxic to humans, generally causing cancer. As a result, laws strictly control the discharge of wastewaters containing such organic compounds, and there are stringent regulations concerning limits on their concentrations in food and water. For example, in the European Community, the permissible level in drinking water must not exceed 30 µg L⁻¹ for organic chlorinated compounds. Although several processes exist for the treatment of such wastewaters, including adsorption and thermal treatments, there is still a need for alternative treatments because the usual processes result in the production of toxic byproducts (HCl and dioxin for incineration processes) or huge amounts of waste materials (for adsorption processes). Among the alternative processes that have recently been developed are chemical dehalogenation processes: the conversion of halogenated compounds into less toxic compounds (dehalogenated) is a promising route for the treatment of these harmful solutions. Two chemical processes are commonly proposed for the decontamination of these solutions: (a) reduction techniques and (b) oxidative processes. The reductive route frequently uses hydrogen as a clean reagent for the reductive chloroderivative decomposition and platinum or palladium on various supports (alumina, titania, carbon),¹⁻⁶ although using a hydrogen donor has also been suggested as a promising route.⁷⁻⁹ Indeed, the sorption properties of the hydrogen donor on the support might add to the selectivity of the reaction.⁹ Supporting catalytic metals on specially tailored supports can add new functionalities such as reaction enantioselectivity.¹⁰⁻¹⁵ Biopolymers have been extensively studied during the past decade for chiral separation.¹⁶⁻¹⁸ For this reason, inter-

est is now focusing on the use of biopolymers as supports for catalysis.

Recently, research into supported catalysis has been carried out on chitosan.¹⁹⁻²⁶ Chitosan is obtained by deacetylation of chitin (the most abundant biopolymer in nature after cellulose). Chitosan is characterized as a heteropolymer consisting of D-glucosamine and N-acetyl D-glucosamine units. The main characteristics of the biopolymer are, therefore, its high amine function content and its cationic behavior in acidic solutions.^{27,28} The presence of amine functions leads to interesting chelating properties for metal cations,²⁹⁻³³ but the protonation of these amine functions (-NH₃⁺) gives the polymer the behavior of a weakly basic anion exchanger.^{30,34} Many studies have also focused on the sorption of platinum group metals (PGMs) on chitosan.^{30,35,36} Because chitosan is soluble in most mineral acids, it is necessary to increase its stability by means of a cross-linking treatment. Glutaraldehyde has frequently been used to stabilize chitosan in acidic solutions.^{32,35,36} The strong ability of chitosan to sorb PGMs explains why many studies have focused on the use of chitosan for supporting catalysts, as pointed out above.

A preliminary work focused on the use of palladium supported on chitosan for chromate reduction.²⁶ This preliminary study served to optimize the catalyst synthesis procedure and to evaluate the influence of conventional experimental parameters. The present work concerns the dehalogenation of chlorophenols using palladium immobilized on glutaraldehyde cross-linked chitosan, palladium being reduced after sorption onto the support using a combination of reductive procedures. This treatment consists of contacting the loaded sorbent with a sodium borohydride solution, and then treating it with hydrogen (generated in situ by contacting sulfuric acid solution with zinc powder). The hydrogen donor used in this study was sodium formate instead of hydrogen. Indeed, hydrogen-transfer hydrogenolysis was preferred to direct hydrogen use because

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the sorption properties of the hydrogen-transfer agent can add to the selectivity of the catalytic reaction.^{7,9} The effects of experimental parameters, including pH, catalyst mass, formate concentration, chlorophenol concentration, and temperature, were tested.

Materials and Methods

Materials. The chitosan was supplied by Aber Technologies (Plouvien, France). It had previously been characterized,³⁵ giving a degree of deacetylation of 87% and a molecular weight of 125 000 g mol⁻¹. The chitosan was ground and sieved, and the fraction with particle size lower than 125 μm was used.

Analytical-grade NaBH₄ was purchased from Fluka (Buchs, Switzerland). PdCl₂ was purchased from Acros (Morris Plains, NJ). Other reagents (acids, zinc, HCOONa) were supplied by Carlo Erba (Milan, Italy). 2-Chlorophenol (2-CP) was supplied by Riedel-De-Haën (Seelze, Germany).

Sorbent Preparation. Because chitosan is soluble in hydrochloric acid, it cannot be used as supplied, and a cross-linking treatment is required. The chitosan was cross-linked with glutaraldehyde by contacting it with glutaraldehyde solution (10%, w/w). The volume of glutaraldehyde solution and the mass of chitosan were set to obtain a 1:1 molar ratio between the amine groups of the polymer and the aldehyde functions of the cross-linking agent. Finally, the particles were abundantly rinsed to remove traces of unreacted glutaraldehyde and dried at 70 °C.

The cross-linking ratio is an important issue in the characterization of the sorbent. However, contrary to sorption processes involving a chelation mechanism (in which case, the cross-linking dramatically reduces the sorption capacity), in the case of ion-exchange processes such as those involved in platinum or palladium uptake, the cross-linking ratio has a limited effect on sorption capacities.³⁶ With a 4-fold excess of glutaraldehyde (compared to amine groups of chitosan), the maximum sorption capacity of palladium was reduced by only 20%. The actual fraction of amine groups bonded to glutaraldehyde was not determined. Because the polymer is stable in hydrochloric acid solutions, it was assumed that a majority of amine groups were involved in cross-links.

Palladium Sorption. The sorbent (1 g) was mixed for 24 h with a palladium solution (2 L) with a concentration of 200 mg of Pd L⁻¹ at pH 2. The solution was then filtered, and the residual concentration of palladium in the solution was measured using inductively coupled plasma atomic emission spectrometry (ICP-AES, Jobin-Yvon JY 2000, Longjumeau, France). The sorption capacity (amount of palladium adsorbed on the sorbent, q , in milligrams of Pd per gram) was obtained by the mass balance equation. The sorption capacity was close to 80 mg of Pd g⁻¹ of cross-linked chitosan.

Procedures for Palladium Reduction. The palladium loaded on the sorbent was reduced using a sequence of different treatments: with sodium borohydride and with in situ generated hydrogen. For the reduction treatment with borohydride, the loaded sorbent was mixed with 500 mL of the reducing agent solution (1 g L⁻¹) for 4 h; the pH was not adjusted. The second treatment, which was considered as a complementary reducing treatment, consisted of bringing the loaded sorbent (200 mg) into contact with 100 mL of

sulfuric acid solution (1% w/w) containing 300 mg of zinc (provided as a fine powder). Because these drastic treatments can partially dissolve chitosan, it was necessary to measure the actual weight of the solid at the different stages in the synthesis process.

By taking into account the change in the weight of the solid during the sorption and reduction steps, it was possible to calculate the amount of palladium contained in the final catalyst. The palladium content was approximately 105 mg of Pd g⁻¹ of catalyst. A digestion/mineralization procedure was used to disrupt the polymer and dissolve the metal. ICP analysis confirmed the actual palladium content: 102 mg of Pd g⁻¹ of catalyst.

The variation in the palladium content during the synthesis procedure can be explained by a partial loss of polymer (due to polymer dissolving) and to the disappearance of chloride ions, which are involved in the chloro-metal complex bound to chitosan, during the reduction step. The exact structure of the final palladium nodule was not determined; a fraction of the metal ion remained under its oxidized state, and a fraction was reduced to metal state, Pd(0). This latter fraction is suspected to be occluded or entrapped within the chitosan chains, as palladium crystals appear in the form of nodules by scanning electron microscopy analysis.

Characterization of the Catalysts. Transmission electron microscopy (TEM) was used to measure the size of the Pd nodules or crystals. The catalyst particles were included in a liquid resin. After cross-linking of the resin, thin slices of resin (60 μm) were cut using a microtome. TEM observations showed that the size of the metal crystals was close to 4–5 nm. The particles were highly dispersed in the material, although a slight gradient was observed between the center and the periphery of the particles. Some aggregates were also observed: the agglomeration of small nodules led to the formation of large palladium particles (around 30 nm).

X-ray photoelectron spectroscopy (XPS) analysis was also performed to determine the oxidation state of palladium on the catalyst. It was shown that only 50–60% of the palladium was reduced from Pd(II) to Pd(0).

Procedure for Chlorophenol Dehalogenation. Chlorophenol dehalogenation was performed, unless specified, by contacting 25 mL of chlorophenol solution, containing the organic compound at a concentration of 25 mg L⁻¹ (0.2 mM) and sodium formate at a concentration of 25 mM, with 10 mg of catalyst. The pH was initially controlled at pH 3 (unless specified) using a molar sulfuric acid solution. Samples were collected at selected contact times and filtered. The filtrates were analyzed using HPLC. A Supelcosil LC-8, 5 μm (15 cm \times 4.6 cm) column purchased from Supelco (France) was used, the eluant being acetonitrile/water (60:40). The flow rate was 1.0 mL min⁻¹. The measurements were performed at 280 nm on a Millipore Waters (600 Controller) HPLC equipped with a UV-visible detector (Varian 2550); the volume injected was 10 μL .

Trial experiments were performed to check the actual influence of the catalyst and hydrogen donor and to verify that this parameter was not sufficient to accelerate the reaction reactions at high relative temperature.

Determination of Kinetic Parameters. The half-time of reaction ($t_{1/2}$) was systematically determined to compare the time required to halve the initial concentration of chlorophenol. Additionally, two other parameters were determined: (a) the catalytic activity (in-

trinsic or specific rate, micromoles of chlorophenol per minute per gram of Pd), which was obtained by determining the amount of chlorophenol that was dechlorinated within the first 5 min of contact, taking into account the concentration of palladium in the catalyst; (b) the initial kinetic coefficient (k_0 , min^{-1}); and (c) the overall kinetic coefficient (k , min^{-1}). The catalytic activity coefficient, which can also be called the intrinsic or specific rate, was obtained by determining the amount of chlorophenol transformed in a given contact time (5 or 2 min) divided by the time and the actual mass of Pd contained in the catalyst. The initial and overall kinetic coefficients were calculated assuming the reaction to be an apparent first-order reaction for chlorophenol: $\ln[C(t)/C_0]$ was used to fit experimental data during the initial stage (within the first 5–10 min) for the initial kinetic parameter and within the time required to decrease the initial concentration by a factor of 10, and the slope of the curve was used to calculate the kinetic parameters.

Results and Discussion

Products of Chlorophenol Degradation. Mass spectrometry analysis was performed using the purge-and-trap procedure. Although phenol was the main reaction product during the first hour of contact, after 90 min, its concentration began to decrease. After 16–24 h of contact, the final product was identified as cyclohexanone.

The degradation of chlorophenol can be described as a two-step hydrogenation procedure: dehalogenation of chlorophenol to form phenol, followed by dearomatization of phenol to produce cyclohexanone. Similar mechanisms have been identified in the degradation of chlorophenol using Ru-based and Pd-based catalysts.^{1,2} Morales et al. recently showed that the hydrogenation of chlorophenol and phenol on Pd bimetallic catalysts leads to the formation of cyclohexanol and/or cyclohexanone.^{3,37} Recently, Yuan and Keane also identified cyclohexanone as one of the degradation products in the dehalogenation of various chlorophenols.³⁸

Influence of pH. The initial pH was varied from 2.3 to 6. At low pH, the final pH was close to the initial pH and varied by less than 0.1 units. When the initial pH was 3, it increased to only 3.1 after 60 min, but it then went up to 6.3 after 4 days' reaction time. Increasing the initial pH to 4 resulted in a dramatic increase in the pH of the solution, which reached up to pH 6 after 60 min of contact and pH 7.9 after 4 days. At pH 5 and 6, the pH was increased to 7.9–8.2 after only 60 min of contact and did not vary significantly at higher contact time. This increase in the pH contrasts with the results obtained by Aramendia et al., who observed the production of HCl in the hydrodechlorination of chlorobenzene using a palladium-supported catalyst, where the sorption of HCl on activated carbon led to a progressive poisoning of the catalyst, which can be avoided by the addition of sodium salts.⁴ However, in their experiments, they used molecular hydrogen as the electron donor. In the present case, formate decomposition induced the formation of CO_2 . Gallezot et al. also observed an increase of the pH (from 2 to 5.5) when oxidizing formic acid with carbon-supported platinum catalyst.³⁹

Figure 1 shows kinetics for 2-CP dehalogenation (top panel) and for the appearance of phenol (bottom panel). In most cases, the equilibrium or complete conversion

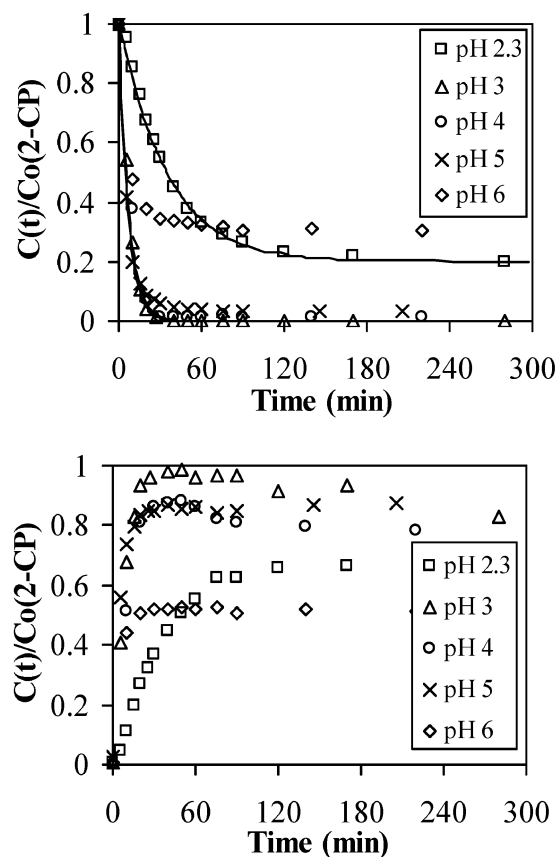


Figure 1. Influence of pH on 2-CP dehalogenation kinetics (CD = 400 mg L^{-1} , 2-CP concentration = 25 mg L^{-1} , formate concentration = 25 mM, $T = 20^\circ\text{C}$, PS = 0–125 μm).

of 2-CP was achieved within the first 30 min of contact. Considering the degradation of 2-CP, the kinetic curves can be classified into three groups. Between pH 3 and 5, the pH did not significantly influence 2-CP dehalogenation: the curves overlapped, and under selected experimental conditions, 2-CP was completely dehalogenated for contact times lower than 30 min. At pH 6, the low acidity of the solution resulted in a decrease in both the sorption rate (larger contact time required to reach the equilibrium, although the initial dehalogenation rate was comparable to those obtained at higher initial pH) and the yield (which did not exceed 70%). At pH 2.3, a strong decrease in the degradation rate and the dehalogenation yield was observed: the initial conversion rate was strongly reduced compared to those observed at other intermediary pH's, and the final yield did not exceed 80%. The second part of the figure shows the appearance of phenol, the same differences can be observed for the pH 2.3, 3–5, and 6 series. At medium acidic pH, a strong increase in phenol concentration was observed during the initial period (up to a contact time of 45–50 min), followed by a decrease in phenol concentration. At the optimum contact time, the amount of phenol produced ranged between 85 and 97% of the initial concentration of 2-CP. However, increasing the contact time resulted in a further decrease in phenol concentration, which indicates a complementary degradation of this organic compound. Felis et al. investigated the hydrodechlorination of chlorophenols using ruthenium supported on activated carbon and observed that, under selected experimental conditions, chlorophenols can be converted into cyclohexanol.² Schüth and Reinhard observed that palladium im-

Table 1. Influence of pH on 2-CP Dehalogenation Rates

pH	$t_{1/2}$ (min)	CAC ^a	$k \times 10^2$ ^b
2.3	35	43	2.08 [40] ^c (0.996) ^d
3	5–6	436	15.2 [40] (0.995)
4	8	280	15.4 [30] (0.980)
5	4	508	13.9 [15] (0.983)
6	10	261	4.86 [20] (0.913)

^a CAC = catalytic activity measured during the first 5 min of contact ($\mu\text{mol min}^{-1} \text{g}^{-1} \text{Pd}$). ^b k = kinetic coefficient (min^{-1}). ^c $[N]$ time range for kinetic modeling, 0– N min. ^d (R^2) correlation coefficient.

mobilized on alumina was able to simultaneously dehalogenate and hydrogenate aromatic compounds: the reactions were not limited to the elimination of halogen substituents.¹ Actually, at these intermediary acidic pH values, the total concentration of phenol and derivatives tended to about 80% of the initial concentration of 2-CP. This result might be related to the transformation of phenol into other compounds such as those found by mass spectroscopy analysis, cyclohexanone, or other intermediate products. At pH 2.3, the production of phenol was significantly slower than for the other pHs. In this case, the phenol concentration was continuously increasing, although it tended to a constant value at large contact time. The total concentration of phenol and derivatives was again close to 85–90%. At pH 6, phenol rapidly appeared during the first several minutes of contact, after which the phenol concentration stabilized. With long contact time (over 4 days), however, the total concentration of phenol compounds was only about 60% of the initial 2-CP concentration. The nonstoichiometric transformation of 2-CP into phenol can be explained by several mechanisms: (a) the degradation of phenol (into cyclohexanol, for example) or (b) the sorption of either 2-CP, phenol, or other derivatives. The kinetic correlation between chlorophenol degradation and phenol appearance and the decrease in the phenol concentration at high contact time suggested that phenol degradation (if that is the explanation for the decrease in residual phenol concentration) has a significantly lower kinetic rate.

Table 1 shows the reaction half-time ($t_{1/2}$) and initial catalytic activity (calculated from the change in 2-CP concentration within the first 5 min of contact, taking into account the amount of palladium in the catalyst). Except in the case of pH 2.3, the orders of magnitude are comparable for the reaction half-time and for the initial catalytic activity between pH 3 and 6, although the reaction is slower in the case of pH 6. In the latter case, the greatest difference in the catalytic behavior (compared to more acidic pH's) was the dehalogenation yield: even after 3 h of contact, 2-CP was not completely transformed, and the yield did not exceed 70%. The increase in pH resulting from the catalytic reaction brought the solution to a pH at which the reaction was no longer efficient. The influence of the pH might be related to the acidic properties of the hydrogen donor and substrate (formate and 2-CP, respectively), which have $\text{p}K_a$'s of 3.7 and 8.55, respectively. Table 1 also shows that the kinetic parameter was not significantly influenced between pH 3 and 5: it varied only between 14 and 15.4 min^{-1} . The key parameter seems to be the adsorption of formate sodium close to its $\text{p}K_a$ value, whereas 2-CP adsorption should be less affected by the pH in the acidic range (2-CP being in its molecular form).

Influence of Solution Aging. Figure 2 compares the dehalogenation of 2-CP (top panel) and the formation

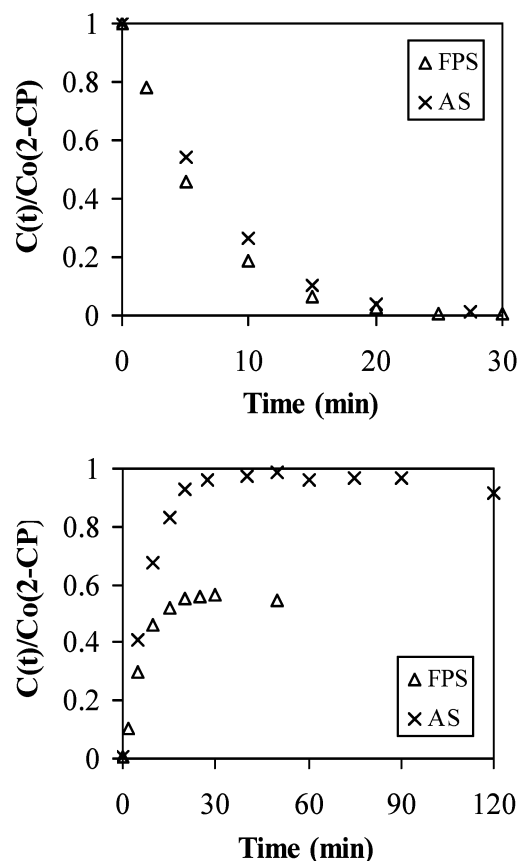


Figure 2. Influence of solution aging on 2-CP dehalogenation kinetics (CD = 400 mg L^{-1} , 2-CP concentration = 25 mg L^{-1} , formate concentration = 25 mM, $T = 20$ °C, PS = 0–125 μm , FPS = freshly prepared solution, AS = aged solution).

of phenol (bottom panel) from two solutions that had been prepared under similar experimental conditions (concentrations, temperature, catalyst dosage, etc.). The only difference was the aging of the solution: one solution was freshly prepared (FPS), while the other had been stored for 5 days before being used (AS). Although dehalogenation kinetics was only slightly lower for the aged solution, the rate and especially the yield for phenol formation were significantly lower in the case of the aged solution. A similar conclusion was reached for the reduction of chromate in the presence of sodium formate using a similar catalyst. The prereaction of the catalyst with the formate solution strongly reduced, and in some cases completely inhibited, chromate reduction when the metal was introduced into the solution, whereas a further addition of sodium formate reinitiated the reaction. In the simultaneous presence of oxygen and palladium/platinum catalysts, formic acid can be oxidized to CO_2 , and the formate concentration can be markedly decreased, leading to a lack of hydrogen donor. This phenomenon might explain the strong influence of solution aging on the dehalogenation kinetics and yield.

Influence of Catalyst Dosage. Increasing the amount of catalyst (catalyst dosage, CD, or solid/liquid ratio) resulted, as expected, in a reduction of the time required to achieve the complete hydrodechlorination of 2-CP (Figure 3). The time required to transform 90% of the 2-CP initially present in the solution progressively decreased at increasing catalyst dosage: 6 min was sufficient at a catalyst dosage (CD) of 800 mg L^{-1} (Table 2). This contact time increased to 15 min for a CD of

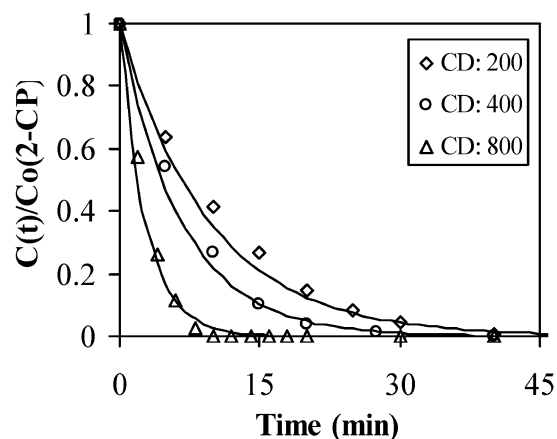


Figure 3. Influence of catalyst dosage (CD) on 2-CP dehalogenation kinetics (pH 3, 2-CP concentration = 25 mg L⁻¹, formate concentration = 25 mM, *T* = 20 °C, PS = 0–125 μm).

Table 2. Influence of Catalyst Dosage (CD, mg L⁻¹) on 2-CP Dehalogenation Rates

CD	<i>t</i> _{1/2} (min)	CAC	<i>k</i> ₀ × 10 ² ^a	<i>k</i> × 10 ²
200	8	626	8.75	10.4 [30] (0.993)
400	5–6	436	13.2	15.2 [40] (0.995)
800	2–3	371	33.8	36.3 [6] (0.993)

^a *k*₀ = kinetic coefficient calculated from the initial section of the curve (0–5 min) (min⁻¹). For other abbreviations see Table 1.

400 mg L⁻¹ and to 24 min for a CD of 200 mg L⁻¹. Considering the initial conversion rate and taking into account the amount of palladium, the catalytic activity (measured between 0 and 5 min) increased from 0.37 mmol of Pd min⁻¹ g⁻¹ for CD = 800 mg L⁻¹ to 0.44 and 0.63 mmol of Pd min⁻¹ g⁻¹ for CD = 400 and CD: 200 mg L⁻¹, respectively. Increasing the catalyst dosage decreased the time required to reach a given degradation level, although the efficiency of the catalyst decreased with increasing dosage. Considering the concentration of 2-CP (25 mg L⁻¹, ca. 0.2 mM) used in these experiments and the amount of palladium for the lower catalyst dosage (200 mg L⁻¹, or 16 mg of Pd L⁻¹, ca. 0.15 mM), an excess of catalyst appears to be necessary to accelerate the process. Gallezot et al. observed that oxalic acid oxidation on a Pt/C catalyst was considerably accelerated by increasing the amount of catalyst.³⁹ Pintar et al. investigated the influence of several parameters on nitrate reduction using a bimetallic catalyst (Pd/Cu) supported on activated carbon.⁴⁰ They observed a linear increase in the “intrinsic (or specific) rate” and the catalyst dosage with increasing catalyst dosage. Whereas in a slurry system the overall reaction rate is typically proportional to the 0.5 power of the catalyst concentration, when the reaction occurs only on the catalyst surface, the observed rate per unit weight of catalyst is independent of the catalyst dosage. In the present case, the kinetics parameters were found to increase nonlinearly with catalyst dosage: it seems that the increase in the kinetic parameters was greater at high catalyst dosage. Felis et al. correlated the initial hydrogen consumption with the catalyst dosage for the hydrodechlorination and dearomatization of phenolic compounds on a Ru/C catalyst.²

The optimization of the process requires the definition of the main objective: namely, the maximum catalytic activity, degradation yield, or processing time. Increasing the catalyst dosage resulted in a decrease in the final concentration of phenolic compounds after long contact

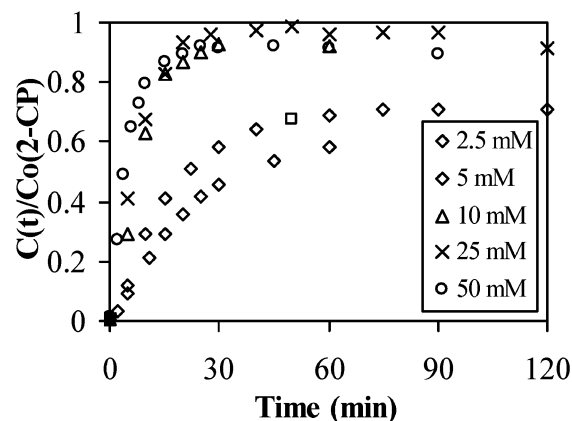
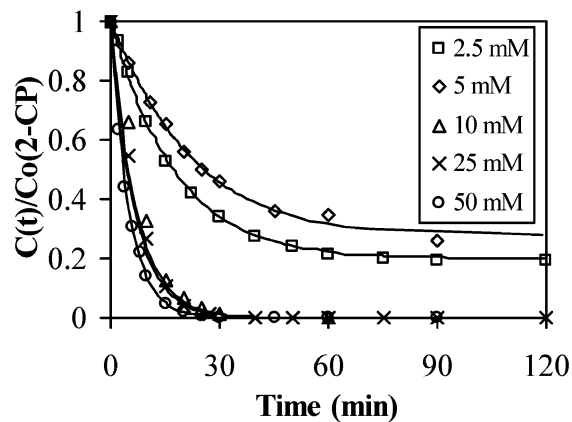


Figure 4. Influence of hydrogen donor (sodium formate) concentration on 2-CP dehalogenation kinetics (CD = 400 mg L⁻¹, pH 3, 2-CP concentration = 25 mg L⁻¹, *T* = 20 °C, PS = 0–125 μm).

Table 3. Influence of Hydrogen Donor Concentration (FC, mM) on 2-CP Dehalogenation Rates^a

FC	<i>t</i> _{1/2} (min)	CAC	<i>k</i> ₀ × 10 ²	<i>k</i> × 10 ²
2.5	17	178	3.83	3.69 [30] (0.990)
5	25	154	2.87	2.65 [30] (0.993)
10	7–8	346	11.3	14.5 [30] (0.994)
25	5–6	436	13.2	15.3 [40] (0.996)
50	3–4	655	20.6	20.0 [30] (0.998)

^a See Tables 1 and 2 for symbol explanations.

times, but the difference was not very marked and was not proportional to the catalyst dosage. Complete phenol degradation might be controlled by the lack of a hydrogen donor (sodium formate) rather than being correlated with the catalyst dosage.

Influence of the Hydrogen Donor Concentration. To verify the influence of the hydrogen donor concentration on the 2-CP degradation kinetics and the appearance of phenol, the concentration of sodium formate was progressively varied between 2.5 and 50 mM. Figure 4 shows the 2-CP transformation kinetics (top panel) and phenol appearance kinetics (bottom panel). The differences between the kinetic curves are not very marked for formate concentrations above 10 mM, whereas the catalytic activity decreases dramatically for concentrations below 10 mM (Table 3). On the other hand, the initial kinetic rate was found to triple when the formate concentration was increased above 10 mM compared to the rate observed at low hydrogen donor concentrations. The differences were less significant (with respect to experimental and analytical inaccuracies) for formate concentrations of 2.5 and 5 mM. Considering the 2-CP molar concentration used in these experiments (ca. 200 μM), it appears that a large excess

of hydrogen donor (at least 10 mM) was necessary to achieve the rapid and complete hydrodechlorination of 2-CP: a 50:1 excess of hydrogen donor appeared to be a good compromise between efficiency and kinetics. Indeed, at lower excesses of formate, both the dehalogenation kinetics and degradation yield were significantly reduced: 2-CP conversion did not exceed 80%. The catalytic activity coefficient (CAC, micromoles of Pd per minute per gram) varied as a logarithmic function of the formate concentration ([FC], mM)

$$\text{CAC} = 162.7 \ln([\text{FC}]) - 35.3 \quad (R^2 = 0.910)$$

The plots of kinetic parameters versus formate concentrations (not shown) indicated that they varied almost linearly at formate concentration greater than 10 mM. However, below this limit, the curves broke off suddenly. In this case, the amount of formate was not sufficient to achieve the complete dehalogenation of 2-CP.

Regarding the appearance of phenol, at high formate concentration, the phenol formation was around 90%, with a dramatic increase in the concentration of the dehalogenated product followed by a slight decrease at long contact time. With low formate concentrations, the kinetics for phenol formation was significantly slower and correlated with the disappearance of 2-CP, and the total phenol species concentration was lower than 90%.

Influence of the 2-CP Concentration. The concentration of 2-CP was varied between 10 and 50 mg L⁻¹ (ca. 80–400 μM). The concentration of chlorophenol did not influence the degradation efficiency and kinetics (Figure 5). The perfect overlapping of both the degradation curves (top panel) and the phenol formation (bottom panel) curves demonstrates that, in this concentration range, the amount of hydrogen donor and the catalyst activity were sufficient to maintain fast kinetics. The preceding section concluded that a 50-fold excess is necessary to maintain the kinetics at the optimum rate. At selected 2-CP concentrations, this ratio holds true even with the highest chlorophenol concentration.

As a consequence, increasing the 2-CP concentration resulted in a proportional increase in the initial catalytic activity from almost 270 to 1140 μmol of Pd min⁻¹ g⁻¹. The initial catalytic activity varied linearly with the initial concentration of 2-CP ([2-CP], mM), under the selected experimental conditions

$$\text{CAC} = 22.48[2\text{-CP}] - 21.3 \quad (R^2 = 0.961)$$

In the present work, the concentration range was quite low compared to the ranges used in other published works, so comparisons with other systems (most of which use hydrogen gas as the hydrogen donor) are difficult. Yuan and Keane obtained very high degradation rates close to 0.5 mol of Pd min⁻¹ g⁻¹ for 2-CP degradation on Pd/C with H₂. This is significantly higher than the levels reached with the present catalyst. However, several factors might explain the low catalytic activity of this catalyst: (a) a different hydrogen donor; (b) a significantly lower substrate concentration (0.4 versus 100 mM); and (c) a larger particle size, which was found to be a limiting parameter. Moreover, experiments on nitrophenol degradation using the same catalyst have shown that most of the reaction is limited to the external surface of the catalyst.⁴¹ Diffusion limitations restrict catalytic degradation to the surface of the catalyst, so that the metal, which is almost

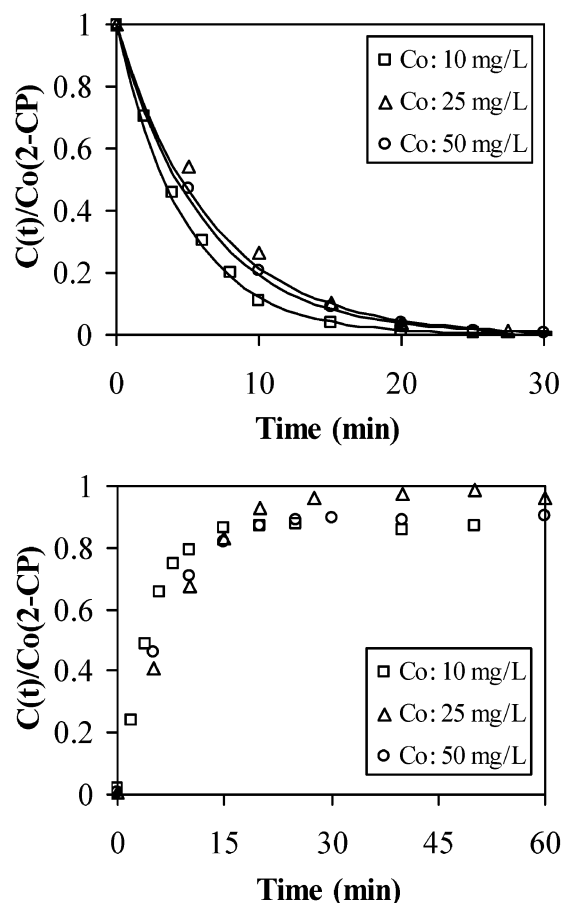


Figure 5. Influence of 2-CP concentration on its dehalogenation kinetics (CD = 400 mg L⁻¹, pH 3, formate concentration = 25 mM, T = 20 °C, PS = 0–125 μm).

Table 4. Influence of 2-CP Concentration (CPC, mg L⁻¹) on 2-CP Dehalogenation Rates^a

CPC	<i>t</i> _{1/2} (min)	CAC	<i>k</i> ₀ × 10 ²	<i>k</i> × 10 ²
10	3–4	269	19.5	21.0 [25] (0.996)
25	5–6	436	13.2	15.3 [40] (0.996)
50	4–5	1142	15.9	16.5 [40] (0.997)

^a See Tables 1 and 2 for symbol explanations.

homogeneously distributed in the whole mass of the sorbent particle, is not accessible to the substrate. A better use of the metal and an enhanced catalytic activity can be obtained using either chitosan as a coating agent for the immobilization of catalytic metals on inert surfaces or thin layers of chitosan, such as obtained when preparing chitosan-based hollow fiber systems. Chitosan hollow fibers have been prepared with the objective of optimizing the mass-transfer performance. Such systems are based on the separation of the reagent medium (sodium formate solution or hydrogen gas at the outside shell of the fiber) and the wastewater compartment (the substrate-containing solution flowing in the lumen of the fiber).⁴²

Table 4 shows that the reaction half-time did not vary significantly with increasing 2-CP concentration between 10 and 50 mg L⁻¹ (ca. 0.08–0.2 mM). The excess of formate compared to 2-CP might explain the weak effect of the substrate concentration on the relative dehalogenation rate. The kinetic coefficients were not significantly affected by changing the 2-CP concentration (in the experimental range): the initial and overall kinetic coefficients varied between 13 and 19.5 min⁻¹ and between 15 and 21 min⁻¹, respectively.

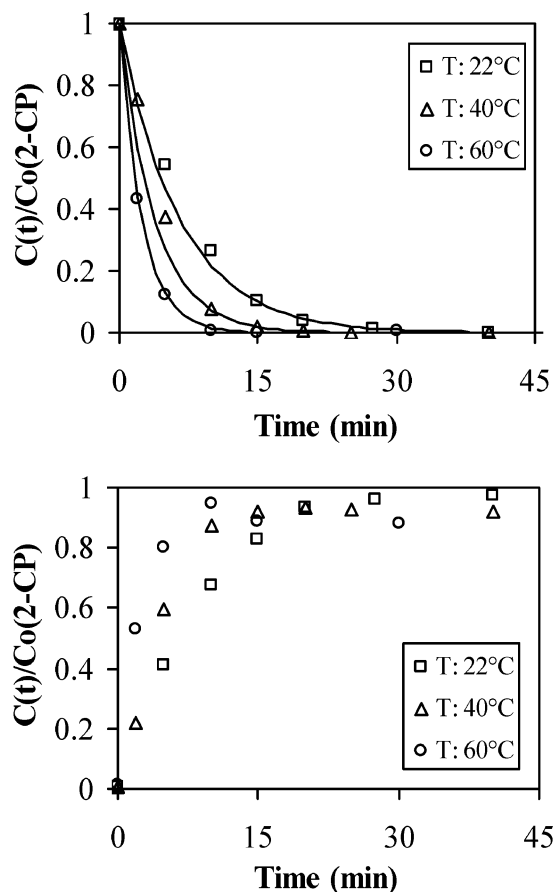


Figure 6. Influence of temperature on 2-CP dehalogenation kinetics (CD = 400 mg L⁻¹, pH 3, 2-CP concentration = 25 mg L⁻¹, formate concentration = 25 mM, PS = 0–125 μm).

Increasing the 2-CP concentration did not significantly change the rate of phenol formation: small differences appeared only at large contact times (last section of the curves and final yield), and they were not very marked. The total concentration of phenolic compounds decreased slightly, and the final percentage (compared to the initial concentration of 2-CP) was independent of the chlorophenol concentration and close to 88%.

Influence of Temperature. Temperature has been found to be a critical parameter for reductive catalytic dehalogenation of chlorocarbons by platinum and palladium metals supported on porous glass material.⁵ This parameter influences not only the conversion yield but also the selectivity. In the present study, increasing the temperature at which the conversion was operated significantly influenced the reaction kinetics of 2-CP dehalogenation (top panel) and phenol formation (bottom panel) (Figure 6). Table 5 shows that, under the selected experimental conditions, the reaction half-time decreased by 2 min for every 20 °C increase in the reaction temperature. A reaction period of 2 min was sufficient to halve the initial concentration of 2-CP at 60 °C.

The Arrhenius law was used to calculate the activation energy, E_a

$$k = Ae^{-E_a/RT}$$

where A is the preexponential factor, T is the absolute temperature, and k is the kinetic rate.

Table 5. Influence of Temperature on 2-CP Dehalogenation Rates

temperature	$t_{1/2}$ (min)	CAC ^a	$k_0 \times 10^2$	$k \times 10^2$
20	5–6	436 [432]	13.2	15.3 [40] (0.996)
40	4	658 [640]	20.1	26.0 [25] (0.992)
60	2	810 [1310]	41.7	41.4 [15] (0.981)

^a Catalytic activity measured during the first 5 min of contact (within brackets, measured within the first 2 min of contact). For other symbols, see Tables 1 and 2.

The logarithm of k was plotted versus the reciprocal of temperature, and the slope of the curve was used to determine the activation energy. Under the selected experimental conditions, E_a was found to be 21.4 kJ mol⁻¹ using the overall kinetic parameter and 24.7 kJ mol⁻¹ with the initial kinetic parameter. Using the initial rate (obtained from Table 5), the activation energy was 25.1 kJ mol⁻¹. This activation energy has to be considered as an apparent activated energy because the contribution of diffusion mechanism in the control of conversion kinetics cannot be determined at this stage. The low value of the activation energy confirms the very high efficiency and suitability of chitosan-supported palladium as a catalyst for chlorophenol dehalogenation.

Gallezot et al. also found that increasing the temperature accelerated the oxidation of formic acid on a Pt/C catalyst.³⁹ Perrone et al. reached similar conclusions for trichloroethylene dehalogenation on carbon-supported palladium catalysts.⁶

Conclusion

Chitosan-based palladium catalyst was obtained by (a) the sorption of palladium on glutaraldehyde cross-linked chitosan and (b) the chemical reduction of loaded sorbent (using a two-step reduction procedure consisting of a first reaction with sodium borohydride and a second reaction with hydrogen produced in situ upon contact of sulfuric acid with zinc powder). The catalyst was used for the dehalogenation of 2-chlorophenol using sodium formate as the hydrogen-transfer agent. An analysis of the products of the reaction showed that 2-CP was fully degraded into phenol and partially degraded into cyclohexanone. Actually, the degradation of 2-CP consisted of the dehalogenation of the organochloride compound and the dearomatization of the intermediate products.

Several experimental parameters were tested, leading to the following conclusions:

- The optimum pH was close to pH 2.7.
- Increasing the catalyst dosage increased the degradation rate but decreased the effectiveness of the metal catalyst.
- Sodium formate should be used in a 50-fold excess compared to the 2-CP concentration to achieve complete degradation of the halogenated compound.
- Higher temperature increased the degradation rate.
- The activation energy was found to be close to 20–25 kJ mol⁻¹.

Future investigations will focus on testing the dehalogenation of more toxic chlorophenol derivatives (polychlorophenols, PCB), in single-component and multi-component solutions, to verify whether this support can cause the dehalogenation reaction to be selective.

This preliminary study confirms the interest in using chitosan as a support material for catalysis. Although,

at this stage of the development of these new materials, the catalytic activity appears lower than that of common palladium catalysts supported on activated carbon or mineral materials, an optimization of the process is required, especially in the design of an appropriate chitosan support that minimizes diffusion restrictions. Research will specifically focus on a new method of conditioning the support (immobilization of catalytic metal at the surface of inert materials using chitosan as a coating agent or chitosan-based supports with optimized diffusion characteristics, such as hollow fiber systems). Preliminary experiments on nitrophenol degradation using catalytic hollow fibers made of chitosan showed promising results: the process separates the hydrogen donor medium from the reaction compartment and optimizes the reaction on both sides. The catalytic activity increases significantly compared to that observed for the use of the catalyst in the form of flakes.

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