Hydrodechlorination of 4-chlorophenol in water with formic acid using a Pd/activated carbon catalyst

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A B S T R A C T

This work reports on the feasibility of hydrodechlorination as a treatment technique for chlorophenols-bearing wastewaters using formic acid as a hydrogen source. 4-Chlorophenol (4-CPhOH) has been used as target compound and the experiments were carried out in batch and continuous mode with a commercial activated carbon-supported Pd (0.5 wt.%) catalyst. The variables studied in the batch runs were HCOOH/4-CPhOH molar ratio (10–1000), temperature (25–75 °C) and catalyst concentration (250–1000 mg/L). The continuous experiments were performed in a fixed bed reactor where aqueous solutions of formic acid and 4-CPhOH with molar ratios between 50 and 100 were continuously fed to the reactor, at different space–time values in the range of 10.7–42.8 kg$_{cat}$ h/mol. Reaction temperatures from 35 to 100 °C were tested and the pressure was fixed at 2.5 bar. Conversion values above 99% for 4-CPhOH were obtained in batch experiments, but using a HCOOH/4-CPhOH molar ratio as high as 500. Moreover, most of the phenol produced was adsorbed on the catalyst. Continuous runs were performed to evaluate the efficiency of the catalyst under lower HCOOH/4-CPhOH ratios and to explore the possibility of converting phenol to more hydrogenated products. The results indicated that the HCOOH/4-CPhOH molar ratios needed were an order of magnitude lower than those required in batch runs to achieve conversions of 4-CPhOH close to 95%. Besides, phenol was not the only reaction product formed, since a more hydrogenated product such as cyclohexanone was detected in the effluent, which indicates additional hydrogenation of phenol in contrast to the behaviour observed in batch experiments. A loss of activity was observed in the continuous runs after 20–30 h on stream.

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1. Introduction

Nowadays, increasing attention is being paid to the preservation of water resources and their quality. As a consequence, the removal of toxic organic pollutants from wastewaters has attracted significant research efforts. Chlorinated organics are among the most widespread pollutants encountered in industrial wastewaters and receiving water systems. Special attention has been paid to chlorophenols because they are used in a number of important industrial processes such as the production of germicides, algaecides, fungicides, herbicides, dyes, wood protectors and plant growth regulators. Chlorophenols also are formed during wood pulp bleaching and as by-products of water chlorination. Due to their high toxicity, strong odour emission and persistence in the environment and suspected carcinogenity and mutagenity to living organisms, chlorophenols are now recognized as hazardous substances according to their toxicity values [1]. These pollutants may

be transformed into more toxic compounds under the action of natural factors and are quite persistent and resistant to chemical, photochemical and biological degradation [2].

From both economic and environmental points of view, the development of efficient methods for the elimination of chlorophenols is much needed. Several methods have been proposed for the elimination of waste chlorinated organics stocks and for the treatment of wastewaters containing these compounds. Although incineration is a well-established method for the elimination of chlorinated organic wastes, the application to wastewaters leads to a large consumption of energy and formation of toxic by-products such as chlorinated aromatics and polycyclic aromatic hydrocarbons [3,4]. Both aerobic and anaerobic biodegradation of chlorophenols have been studied in depth [5–7]. Although biodegradation may prove to be efficient, requirements for specific environmental conditions (methanogenic or sulphate reducing) particularly in case of anaerobic degradation, and long acclimation and hydraulic retention times in general, can strongly restrict its field of application. The use of advanced oxidation processes such as wet air oxidation, Fenton, or photochemical processes has been studied extensively in the last years, showing good results but

also some drawbacks or limitations such as the need of relatively high temperatures and/or pressures, large amounts of reagents and/or complex equipment [8–10]. The catalytic hydrogenation of the carbon–chlorine bond – hydrodechlorination – is an emerging technique for the degradation of halogenated organics in wastewaters. The advantages of hydrodechlorination include operation at low temperature and pressure, the absence of by-products which are more harmful than chlorophenols and low sensitiveness to pollutants concentration.

Much of the success of hydrodechlorination lies on the type of catalyst used. The catalytic hydrodechlorination of chlorinated organics has been reported in liquid phase over a variety of catalysts, although palladium supported on activated carbon can be considered among the most active [11,12]. Activated carbon is of interest as catalyst support because it can satisfy most of the desirable properties required for a suitable support, i.e. high surface area, high porosity and low reactivity [13]. Moreover, the porous structure and the surface chemistry of activated carbon can be tailored to the required for a given application. Thus, metal dispersion and metal–support interactions can be controlled in some extent as needed.

The hydrodechlorination of chlorinated organics has been generally performed with molecular hydrogen, although the low solubility of hydrogen in water can be a drawback for its application in water treatment, specially when dealing with high concentrations of pollutants. Other sources of hydrogen proposed for hydrodechlorination reactions include metal hydrides, formic acid and its salts, isopropanol, hydrazine or alkoxides possessing a β-hydrogen [14–16]. Tabaei et al. [14] reported the dehalogenation of organic compounds such as 4-chlorobiphenyl and chloro-*p*-xylene with alkoxyborohydrides; although the dechlorination was successfully achieved, the reaction medium was tetrahydrofuran and the results could not be applied to water treatment. Hydrazine hydrochloride was also studied as a hydrogen donor in the hydrodehalogenation of aryl halides in different organic media with palladium catalysts in basic conditions [15]. Both, the base and the solvent were found to play an important role on the conversion of the aryl halide, being the more efficient combination sodium *t*-butylate (base) and tetrahydrofuran (solvent).

Kopinke et al. [16] have reported the use of formic acid as a source of hydrogen in the hydrodechlorination of chlorobenzene in water using palladium catalysts, showing that formic acid can be as reactive as molecular hydrogen under acidic and neutral conditions. Formic acid is in liquid state at room temperature, which from an engineering point of view provides some advantages. Likewise, the miscibility in water of formic acid makes possible the treatment of wastewaters with a large concentration of pollutants. However, there is a lack of information in the literature about the application of formic acid in hydrodechlorination reactions. The aim of this work is to evaluate the feasibility of the hydrodechlorination of chlorinated organics in water using formic acid as a source of hydrogen. The target chlorinated organic selected was 4-chlorophenol (4-CPhOH) due to the availability of data on its hydrodechlorination with molecular hydrogen. Thus, previous works have reported a high efficiency in the removal of chlorine from chlorophenols with molecular hydrogen at mild conditions using palladium catalysts supported on activated carbon [1,11].

2. Experimental

The hydrodechlorination of 4-CPhOH in aqueous phase (100 mg/L) was carried out both in batch experiments and in a continuously fed fixed bed reactor using a 0.5 wt.% Pd/C commercial catalyst (Engelhard). The textural properties of the catalyst were

the following: BET area 899 m^2/g, external area 9 m^2/g, total volume 0.549 cm^3/g, micropore volume 0.450 cm^3/g and mesopore volume 0.019 cm^3/g. To check the activity of the catalyst at different conditions batch experiments were carried out in 100 mL stoppered glass bottles shaken in a thermostatic bath at an equivalent stirring velocity of around 200 rpm. A volume of 50 mL of a 4-CPhOH aqueous solution was used in all the experiments. The ranges studied for HCOOH/4-CPhOH molar ratio, temperature and catalyst concentration were 10–1000, 25–75 °C and 250–1000 mg/L, respectively. The reaction runs lasted 4 h.

The continuous experiments were performed in a fixed bed reactor under controlled temperature, pressure and liquid flow. The reactor consisted of a stainless steel tube (9 mm i.d.) where 0.5 g of catalyst was placed. Aqueous solutions of formic acid and 4-CPhOH at molar ratios between 50 and 100 were continuously fed to the reactor at different flow rates (0.25–1.0 mL/min) allowing for different space–time values in the range of 10.7–42.8 kg$_{cat}$ h/mol (basis on catalyst weight). Reaction temperatures of 35–100 °C were used and the pressure was fixed at 2.5 bar. Before each experiment the catalyst was saturated in 4-CPhOH solution to reduce the time required to reach the steady state and to improve catalyst wetting.

Both in batch and continuous runs the activity of the catalysts under the reaction conditions studied was evaluated by means of the conversion of 4-CPhOH, considered as the percentage of the initial mass of 4-CPhOH that was converted.

To evaluate the evolution and extension of the reaction in batch experiments, the amount of reaction products dissolved and adsorbed on the catalyst was determined throughout the 4 h reaction time. The reaction products in all the experiments (batch and continuous) were determined by HPLC/DAD (Prostar, Varian) using a C$_{18}$ as stationary phase and a mixture of acetonitrile and water (1:1, v/v) as mobile phase. The organic compounds adsorbed on the catalyst were desorbed with acetonitrile and then analyzed by GC/MS (Saturn 2100 T, Varian) using a 30 m long × 0.25 mm i.d. capillary column (Meta X5 Tracsil 5). Previous to GC/MS analysis the aqueous samples were extracted with solid-phase cartridges (C$_{18}$, Waters), which were eluted with acetonitrile. Chloride ion and formic acid concentration were determined by means of ion chromatography (Metrohm 790 Personal IC).

3. Results and discussion

In a first approach, a series of batch experiments were conducted to learn about the role of the catalyst. Thus, a first series of experiments were carried out in the absence of catalyst within the whole range of HCOOH/4-CPhOH molar ratios to evaluate the possible occurrence of homogeneous reaction between formic acid and 4-CPhOH. In these conditions, negligible conversion values of 4-CPhOH were obtained, which allows to neglect the contribution of homogeneous reaction. On the opposite, when the batch experiments were carried out in the presence of the Pd/C catalyst, hydrodechlorination of 4-CPhOH was observed, being phenol and HCl the main reaction products identified, the rest being detected only at trace levels. The presence of the catalyst was also found essential for the hydrodechlorination of chlorophenols using molecular hydrogen [1], but in the current case the catalyst also seems to contribute to the decomposition of formic acid to yield hydrogen [16].

In a further series of batch experiments the decomposition of formic acid over the Pd/C catalyst in absence and in the presence of 4-CPhOH was studied in the range of 25–75 °C. The concentration of formic acid was fixed at 0.4 M, corresponding to a HCOOH/4-CPhOH molar ratio of 500, based on a 100 mg/L initial concentration of 4-CPhOH. The results are shown in Fig. 1, where it can be seen that
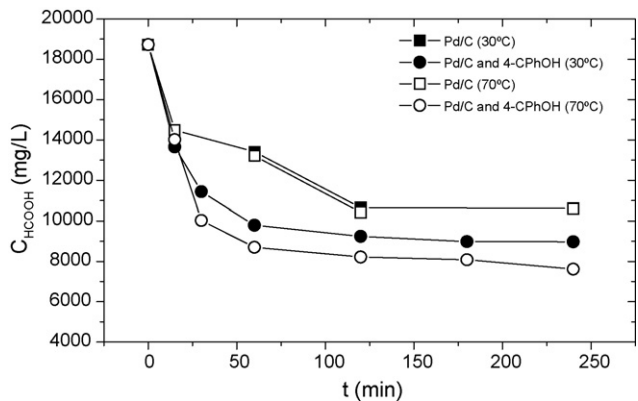
Fig. 1. Decomposition of formic acid over Pd/C catalyst in the presence and absence of 4-CPhOH (HCOOH/4-CPhOH molar ratio: 500; 500 mg cat./L).

the rate of formic acid decomposition is higher in the presence of 4-CPhOH. This observation is in agreement with the results reported by Kopinke et al. [16] for the hydrodechlorination of chlorobenzene with formic acid, and must be due to a displacement of the equilibrium of formic acid decomposition thanks to the consumption of hydrogen by the hydrodechlorination reaction. The hydrogen generated upon formic acid decomposition would be chemisorbed in the catalyst surface and would saturate the palladium active sites in the absence of 4-CPhOH leading to the inhibition of that decomposition reaction. Thus, the decomposition of formic acid in the presence of 4-CPhOH is faster at 70 °C due to faster hydrodechlorination and hydrogen consumption. The reaction scheme given below [16] shows that the dehydrogenation of both formic acid and formiate anion can take place, although the HCl released in hydrodechlorination reactions and formic acid itself provide an acidic reaction medium. The dehydrogenation of formic acid is much more favoured from a thermodynamic point of view than dehydration [15], which can help to minimize poisoning of the catalyst by CO:

$$HCOOH \leftrightarrow HCOO^-$$

$$HCOOH \leftrightarrow CO + H_2O$$

$$HCOOH \leftrightarrow CO_2 + H_2$$

$$HCOO^- \leftrightarrow CO + OH^-$$
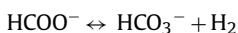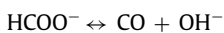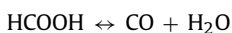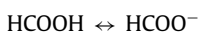
$$HCOO^- \leftrightarrow HCO_3^- + H_2$$

Fig. 2 shows the results of the runs carried out to investigate the influence of the HCOOH/4-CPh molar ratio on 4-CPhOH conversion
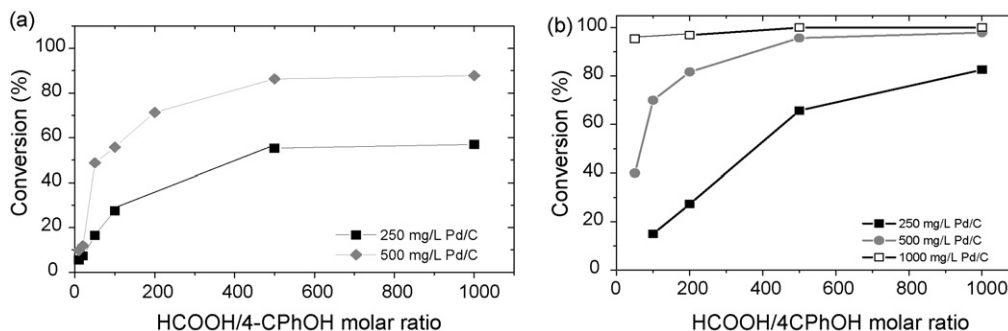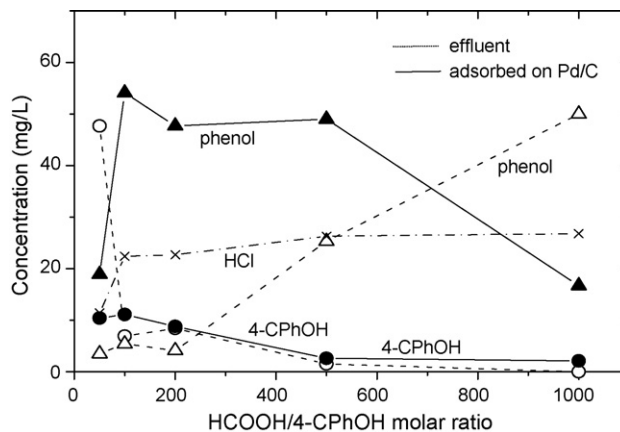

Fig. 3. Phase distribution of 4-CPhOH and phenol at different HCOOH/4-CPhOH molar ratios (50 °C, 500 mg cat./L).

at different catalyst concentrations and temperatures. It can be seen that when the hydrodechlorination experiments were performed using a HCOOH/4-CPhOH molar ratio within the 10–50 range the conversion values achieved were always lower than 10% regardless the concentration of catalyst. On the contrary, the conversion of 4-CPhOH increased dramatically when the HCOOH/4-CPhOH molar ratio was increased from 50 to 100. The increase was more important for the set of experiments carried out with a catalyst concentration of 500 mg/L. The benefit of the use of a high concentration of catalyst can be observed in the experiments at 50 °C, where conversion values over 95% were obtained even for the lower HCOOH/4-CPhOH molar ratio (50). When using a catalyst concentration of 500 mg/L at 50 °C, a HCOOH/4-CPhOH molar ratio as high as 500 was needed to achieve conversion values equivalent to those obtained with a catalyst load of 1000 mg/L. Lowering the catalyst concentration to 250 mg/L conversion values below 80% were always obtained, even at the highest HCOOH/4-CPhOH molar ratio tested.

The distribution of reaction products between the liquid phase and the surface of the catalyst was also found to be dependent on the HCOOH/4-CPhOH molar ratio, as it can be observed in Fig. 3. The mass balance closures for the experiments shown ranged between 88 and 99%. These experiments were performed with a catalyst concentration of 500 mg/L and it can be seen that the concentration of phenol in the treated water increased by 33% when the molar ratio was increased from 500 to 1000. In this range, the conversion only increased by 2%, which indicates that the increase of phenol concentration in the liquid phase was caused mainly by a lower adsorption on the catalyst surface. The lower adsorption of phenol may be caused by the competitive adsorption with formic acid and by the lower interaction of phenol with formic acid in the liquid
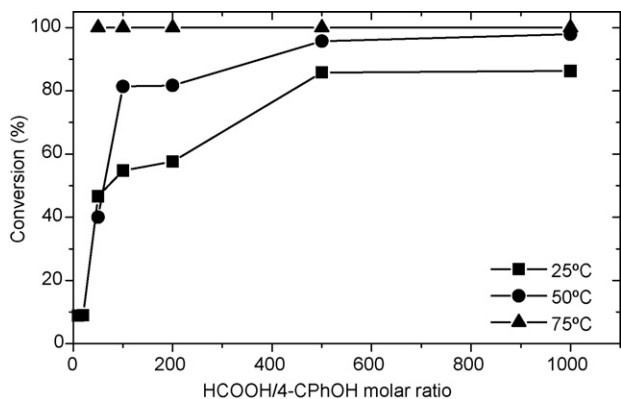

Fig. 2. Influence of the HCOOH/4-CPhOH molar ratio on the conversion of 4-CPhOH: (a) 25 °C and (b) 50 °C.

Fig. 4. Influence of temperature on 4-CPhOH conversion (500 mg cat./L).

phase. These changes in the adsorption behaviour also affected to the reaction pathway and products distribution. Thus, an oxidation product of phenol, 1,2,4-trihydroxybenzene, was detected as one of the species adsorbed on the catalyst for the experiments carried out at HCOOH/4-CPhOH molar ratios lower than 500. The occurrence of this compound may be promoted by a higher phenol uptake by the catalyst.

Increasing the reaction temperature enhances 4-CPhOH conversion (Fig. 4), being higher the influence at lower HCOOH/4-CPhOH molar ratios. It can be seen that at 75 °C, 4-CPhOH was removed almost completely within the whole range of HCOOH/4-CPhOH molar ratios whereas at the lowest temperature tested, 25 °C, a HCOOH/4-CPhOH molar ratio of at least 500 is needed to reach a good hydrodechlorination efficiency. The effect of temperature on the distribution of the main reaction product, phenol, between the treated water and the catalyst can be seen in Fig. 5. The concentration of phenol in the treated water increased significantly with temperature both for a catalyst load of 250 and 500 mg/L. On the contrary, the amount of phenol adsorbed on the catalysts remained practically constant with temperature and even a monotonical decrease was observed in the experiments carried out with a catalyst load of 500 mg/L.

As expected, the catalyst load also shows a high influence on the 4-CPhOH conversion achieved, as it can be seen in Fig. 6. For a catalyst load of 250 mg/L, the conversion value remained at a value of 80% even when the HCOOH/4-CPhOH molar ratio was increased to 1000. A substantial increase of conversion was observed when a catalyst load of 500 mg/L was used, and conversion values higher than 90% were obtained. No significant differences of conversion were observed within the range of catalyst load of 500–1000 mg/L

in the whole range of HCOOH/4-CPhOH molar ratios tested. However, for a load of 1000 mg/L most of the phenol generated was adsorbed on the catalyst.

From the results of the batch experiments a main conclusion arises in the sense that high HCOOH/4-CPhOH molar ratios were needed to obtain acceptable 4-CPhOH conversion values. Besides, no additional conversion of 4-CPhOH was observed after a reaction time of 4 h in spite of the fact that a significant concentration of formic acid is still remaining (Fig. 1). This may be attributed to an equilibrium state. Therefore, continuous runs were performed to test the behaviour of the catalytic system and to explore the possibility of converting phenol to more hydrogenated and less toxic products. The initial operating conditions were chosen basis on previous works where it was found that the hydrodechlorination of 4-CPhOH with molecular hydrogen on Pd/C catalysts can lead to high conversions [17,18]. Thus, the treatment was firstly carried out at 2.5 bar, 50–75 °C and 21.4 kg$_{cat}$ h/mol space–time, being the results summarized in Table 1. Reasonably high conversion values were obtained for 4-CPhOH at the lowest HCOOH/4-CPhOH molar ratios (50–100). Beyond that molar ratio no further improvement of conversion was achieved and even a slight decrease was observed in some experiments. These HCOOH/4-CPhOH molar ratios are fairly lower than the required in the batch runs to reach comparable conversion values for 4-CPhOH, which is an advantage from an economical point of view. Besides, it is interesting to point out that now phenol is not the only reaction product generated, since a more hydrogenated product, cyclohexanone, was detected in the effluent, which indicates additional hydrogenation of phenol in contrast to the results obtained in batch experiments. Thus, for a HCOOH/4-CPhOH molar ratio of 50, at 100 °C, around 21% of the phenol resulting from hydrodechlorination is converted to cyclohexanone. The selectivity to cyclohexanone increased to 36% at 75 °C. The occurrence of cyclohexanone is expected to be the result of phenol hydrogenation, as it has been reported for the hydrodechlorination of 4-CPhOH in the presence of molecular hydrogen.

In the continuous runs, 4-CPhOH conversion exhibited a linear dependence with temperature, as it can be seen in Fig. 7. In the runs carried out at a HCOOH/4-CPhOH molar ratio of 100 the conversion increased by about 25% when the temperature was risen from 35 to 75 °C. The influence of temperature is fairly similar at both HCOOH/4-CPhOH molar ratios (50 and 100).

Fig. 8 shows the influence of space–time on the 4-CPhOH conversion. In this figure two different regions are observed: for space–times in the range of 10.7–21.4 kg h/mol, the conversion increases significantly with space–time, whereas beyond that range a further modest improvement of conversion was obtained. The products distribution was also found to depend on the space–time and HCOOH/4-CPhOH molar ratio, as it is shown in Fig. 9. When
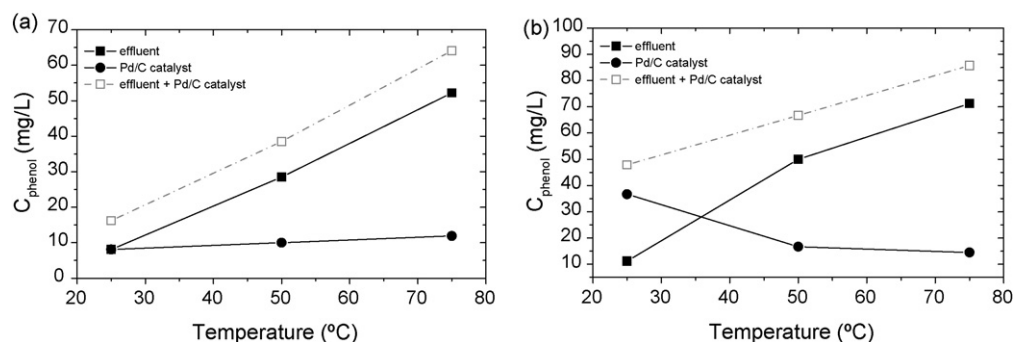

Fig. 5. Influence of the temperature on the phase distribution of phenol: (a) 250 mg cat./L and (b) 500 mg cat./L (HCOOH/4-CPhOH molar ratio: 1000).
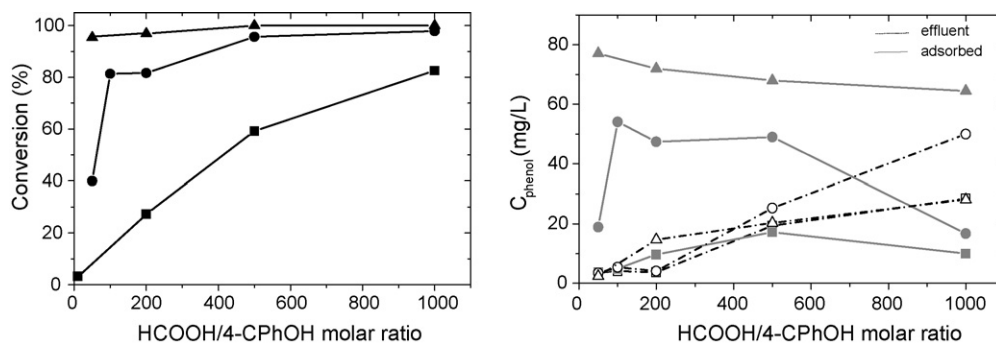
Fig. 6. Influence of the catalyst load on 4-CPhOH conversion and phenol production at 50 °C ((■) 250 mg/L Pd/C; (●) 500 mg/L Pd/C; (▲) 1000 mg/L Pd/C).

Table 1
Conversion of 4-CPhOH and products distribution in the continuous hydrodechlorination runs (21.42 kg$_{cat}$ h/mol; P = 2.5 bar)

HCOOH/4-CPhOH molar ratio	Conversion (%)		Phenol yield[a] (%)		Cyclohexanone yield[a] (%)	
	50 °C	75 °C	50 °C	75 °C	50 °C	75 °C
50	70	78	53	62	3	3
100	80	92	76	84	7	12
200	76	93	60	85	3	6
2000	76	81	62	68	3	3

[a] Yield is defined as the ratio between the product in the effluent and the initial concentration of 4-CPhOH.
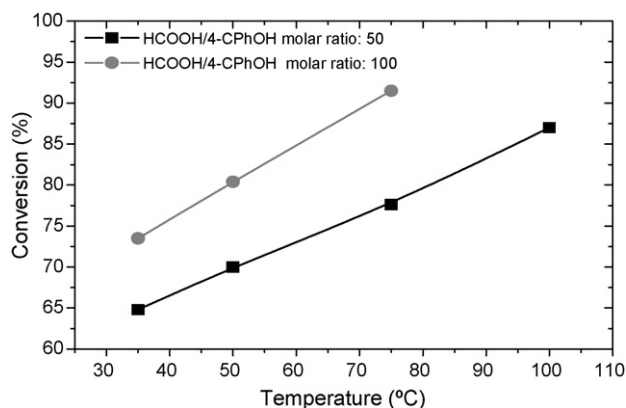

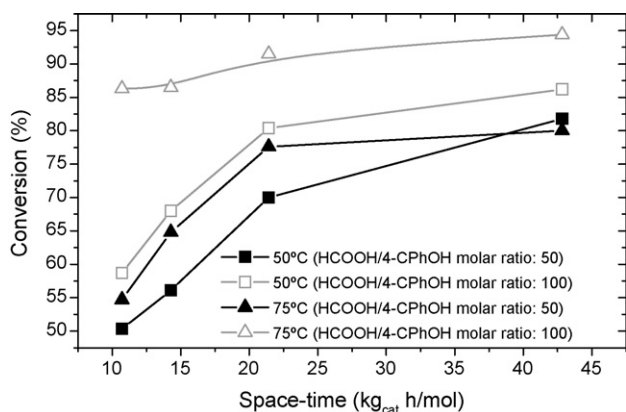**Fig. 7.** Conversion of 4-CPhOH vs. temperature (τ = 21.42 kg$_{cat}$ h/mol; P = 2.5 bar).

Fig. 8. Influence of space–time and temperature on 4-CPhOH conversion at 2.5 bar.

increased by more than 4 and 5.5 times at HCOOH/4-CPhOH molar ratios of 100 and 200, respectively. In spite of that increase of selectivity, the yield of cyclohexanone remained at a relatively low value.

These results prove the feasibility of hydrodechlorination of 4-CPhOH with formic acid. The operation in a continuous reactor makes possible to reduce strongly the amount of formic acid needed, although further efforts to reduce more the consumption of this agent would be advisable. Another issue that should be considered is the attack of formic acid to the metallic phase of the catalyst. Thus, in order to evaluate the stability of the catalyst, a long-term experiment (100 h) was carried out at 50 °C. As can be seen in Fig. 10, during the initial 20 h the conversion of 4-CPhOH remained practically constant, whereas beyond that time, a gradual loss of activity was observed. Further research would be needed to learn on the factors that cause catalyst deactivation and the ways to prevent it.
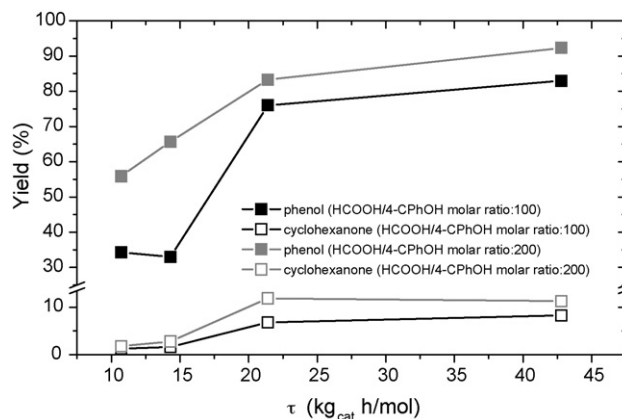

Fig. 9. Influence of space–time and HCOOH/4-CPhOH molar ratio on the phase distribution of reaction products (T = 50 °C; P = 2.5 bar). Yield is defined as the ratio between the product concentration in the effluent and the initial concentration of 4-CPhOH.
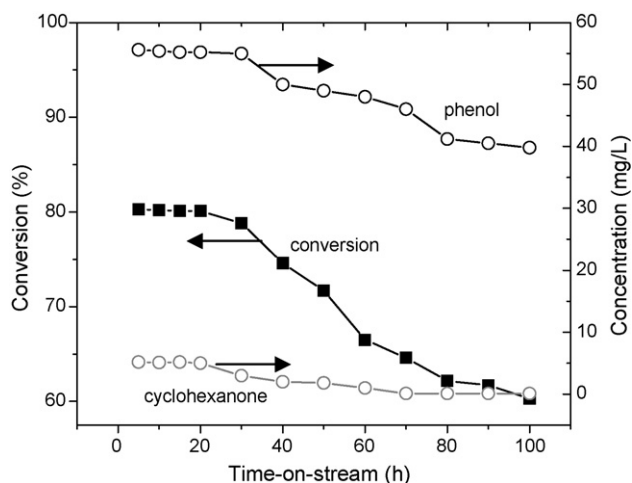
space–time increased from 10.7 to 21.4 kg h/mol, the phenol and cyclohexanone yield increased significantly. The most noticeable increase in selectivity was observed for cyclohexanone, thus in the range of space–time studied, the generation of this compound

Fig. 10. Evolution of 4-CPhOH conversion and reaction products upon time-on-stream (21.42 kg_{cat} h/mol; $T = 50\,^\circ$C; $P = 2.5$ bar).

4. Conclusions

The catalytic hydrodechlorination of 4-CPhOH with Pd/C catalyst using formic acid has been studied in order to test its feasibility as a treatment for chlorophenols-bearing wastewaters. The Pd/C catalyst decomposes formic acid, releasing hydrogen for the hydrodechlorination reaction. The rate of decomposition of formic acid increases in the presence of 4-CPhOH, most probably due to equilibrium displacement because of H_2 consumption for hydrodechlorination. A conversion value of 4-CPhOH above 99% was achieved in batch experiments at $50\,^\circ$C with 500 mg/L of catalysts and a HCOOH/4-CPhOH molar ratio of 500. Phenol and HCl were the main reaction products identified in those batch runs, though most of phenol generated was adsorbed by the catalyst. Therefore, continuous runs were performed to evaluate the efficiency of the catalyst at lower HCOOH/4-CPhOH molar ratios and to explore the possibility of further conversion of phenol to more hydrogenated products. The use of a fixed bed reactor allowed a reduction in both the amount of catalyst and formic acid needed, resulting in a more economic alternative. Conversion values of 4-CPhOH close to 95% were obtained. Phenol was not the only reaction product generated in the continuous runs, since a more hydrogenated product, cyclohexanone, was detected in the effluent, as a consequence of additional hydrogenation of phenol in contrast to the behaviour observed in batch experiments. In order to evaluate the stability of the catalyst, a long-term experiment was carried out at 21.42 kg_{cat} h/mol space–time, $50\,^\circ$C and 2.5 bar, showing a decline in the activity of the catalyst after 20–30 h. Further research is needed focusing on the stability of the catalyst.

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