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Hydrogenation of phenol in aqueous phase with palladium on activated carbon catalysts

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Abstract

The hydrogenation of phenol in aqueous phase was studied in a continuous trickle bed reactor using commercial and some home-made Pd/activated carbon (AC) catalysts with the aim to explore a possible way for the treatment of phenolic wastewaters. The ranges studied for temperature, pressure and space-time (τ) were 110–170 °C, 2–9 bar and 0.5–3.1 kg_{cat} h/mol, respectively. The inlet concentration of phenol was always 1000 mg/L. High conversion values for phenol were obtained at 150 °C and 9 bar in the case of the commercial catalyst. This catalyst has shown a convenient chemical stability in long-term experiments, being Pd leaching almost negligible. Different home-made catalysts were prepared and the influence of Pd load and precursor as well as the preparation conditions on the activity and selectivity have been investigated. The highest phenol conversion values were obtained with the catalysts calcined at 250 °C and reduced in hydrogen atmosphere at 150 °C, using palladium chloride as precursor. Moreover, these conditions led to a higher selectivity towards cyclohexanol, the less toxic product of the reaction pathway. The introduction of oxygen groups on the surface of the activated carbon through oxidation with nitric acid also improved the selectivity to cyclohexanol, thus leading to a higher reduction of the ecotoxicity.

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Keywords: Phenol hydrogenation; Ecotoxicity; Palladium/activated carbon catalysts

1. Introduction

The adequate cleaning of industrial wastewaters is a problem of major concern nowadays. New and more stringent regulations are being imposed, which demand the need to develop and implement treatment technologies capable to deal with the hazardous pollutants present in many industrial waste streams. Phenol and phenolic compounds are starting and/or intermediate compounds in many industrial processes and are present in effluents from coke ovens, oil refineries, petrochemical units and polymers production. Wastewaters from these activities are characterized by variable concentrations of phenolic compounds (500–4000 mg/L) [1,2].

Among the techniques proposed and/or used for the treatment of phenolic wastewaters, incineration requires a high consumption of energy and becomes acceptable only for fairly high organic loads. Furthermore, it can produce trace amounts of highly harmful gaseous contaminants. Biological methods have been tested, but are excessively slow and ineffective at high concentrations [3]. Advanced oxidation processes such as wet air oxidation, Fenton, or photochemical processes have been studied extensively, showing some drawbacks or limitations such as relatively high temperatures and/or pressures, large amounts of reagents and complex equipment, respectively [4–6]. Catalytic hydrogenation of phenol is an emerging and promising alternative attending to environmental criteria since a biodegradable and much less toxic product can be obtained, cyclohexanol [7,8].

The hydrotreatment of phenol can follow two routes: hydrogenolysis or hydrogenation, depending on the reaction conditions. More severe conditions (temperatures and pressures higher than 200 °C and 10 bar, respectively) favour hydrogenolysis where C–OH bond is broken, yielding benzene, cyclohexene and cyclohexane [9]. Hydrogenation takes place under milder conditions, giving rise to the intermediate product cyclohexenol in a first step. This intermediate readily disappears by two routes, reacting with hydrogen to produce cyclohexanol or evolving via isomerization to cyclohexanone that can react with hydrogen to produce cyclohexanol too [10,11]. The distribution of products from phenol hydrogenation is highly dependent on the type of catalyst and the reaction conditions [12,13].

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Nomenclature

A_{BET}	BET surface area (m^2/g)
A_{ext}	external or non-micropore surface area (m^2/g)
AC	activated carbon
C-ol	cyclohexanol
C_i	concentration (mg/L) of compound *i*
EC_{50}	effective nominal concentration of toxicant that reduces the intensity of light emission by 50%
F_{Pho}	mass flow of phenol fed to the reactor (mol/h)
P	pressure (bar)
Ph	phenol
Q_{H2}	hydrogen flow rate (mL/min)
Q_{Ph}	phenol flow rate (mL/min)
S	selectivity defined as mol of product per mol of phenol converted
tos	time on stream (h)
T	temperature (°C)
T_{cal}	calcination temperature (°C)
T_{red}	reduction temperature (°C)
T.U.	toxicity units (ecotoxicity)
V_{mes}	mesopore volume (cm^3/g)
V_{mic}	micropore volume (cm^3/g)
W	catalyst weight (kg)
X	conversion

Greek symbol

τ	space-time (kg_{cat} h/mol) calculated as W/F_{Pho}

Hydrogenation of phenol has been studied extensively both in gas [14–18] and liquid phase [19], looking for a high selectivity towards cyclohexanone, an intermediate for caprolactam and adipic acid, monomers for nylon 6 and 66, respectively. Nevertheless, there is still a lack of information in the literature on the application of this technique in the wastewaters treatment field, where phenol concentrations range between low to moderate values and a high selectivity towards cyclohexanol is desirable since the ecotoxicity of this compound is lower than that of phenol and cyclohexanone and it is fairly more biodegradable [20,21].

Supported metal catalysts have been widely used for hydrogenation and dehydrogenation reactions because the supports ensure a better dispersion and stability of the metals in addition to influencing their catalytic properties through electronic interactions [22,23]. Activated carbons are attractive catalytic supports due to both their physical and chemical properties [24]. The surface chemistry plays an important role in the metallic dispersion and the catalytic behaviour [13,25]. Surface oxygen complexes can act as anchoring sites that interact with metallic precursors and metals improving the dispersion. The amount and nature of these groups on the activated carbon surface can be modified through oxidative treatments with HNO_3 [26,27], H_2O_2 [26] or $(NH_4)_2S_2O_8$ [27,28].

Results on phenol hydrogenation activity have been reported for catalyst based on Pd [14,17,19,29], Pt [7,9], Rh [30] and Ni [8,18]. From these studies Pd appears to be the most active metal. The metal precursor is a variable itself in the preparation of the catalysts and can play a significant role in their final properties [10]. The metal dispersion depends strongly on the precursor-support interactions as well as on the size of the precursor [23]. $Pd(CHCOO_3)_2$, $PdCl_2$, $Pd(NH_3)_4Cl_2$ and $Pd(NO_3)_2$ have been used to prepare Pd catalysts for phenol hydrogenation [2,10].

The aim of this work is to study the catalytic hydrogenation of phenol in aqueous phase with a commercial and some home-made Pd/AC catalysts, at a phenol concentration comparable to the commonly found in phenolic wastewaters. Our interest focuses not only in looking for a high catalytic activity but also for a high selectivity towards cyclohexanol, the less toxic product in the reaction pathway.

2. Experimental

2.1. Catalyst preparation

A 0.5% (w/w) commercial Pd/AC catalyst supplied by Engelhard (BET surface area: 899 m^2/g; total pore volume: 0.549 cm^3/g) was tested as well as several home-made Pd/AC catalysts with nominal Pd loadings in the range of 0.5–3% (w/w). These were prepared by incipient wetness impregnation using an activated carbon supplied by Merck (BET surface area ≈ 950 m^2/g; bulk density ≈ 0.5 g/cm^3; particle size ≈ 1.5 mm). The impregnation was carried out with three different precursors ($PdCl_2$, $Pd(NO_3)_2$ and $Pd(CH_3COO)_2$) which were dissolved in 0.1 M HCl, 0.1 M HNO_3 and 1 M HNO_3 aqueous solutions, respectively. The volume of solution exceeded by 30% the total pore volume of the activated carbon. Impregnation was followed by drying at room temperature for 2 h and overnight at 60 °C. Finally, the catalysts were calcined in air atmosphere at temperatures ranging from 150 to 350 °C and reduced at different temperatures between 110 and 190 °C under continuous H_2 flow. In some cases, the active carbon was subjected to an oxidative treatment with HNO_3 which was carried out by boiling 1 g of active carbon in 10 mL of a 6N solution for 20 min [26].

2.2. Catalyst characterization

The porous structure of the activated carbon and the catalysts was characterized by N_2 adsorption–desorption at 77 K (Autosorb-1 Quantachrome). The BET equation was used to obtain the surface area and the *t*-method for micropore volume. The external or non-micropore surface area was also obtained from the *t*-method. The difference between the volume of N_2 adsorbed at 0.95 relative pressures (as liquid) and the micropore volume was taken as the mesopore volume. The surface composition was studied by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics model 5700 apparatus with a MgKα X-ray excitation source (1253.6 eV). The precursors reducibility was analyzed by temperature programmed reduction (TPR) in a continuos flow system (Micromeritics Analyzer 2900). The samples were stabilized under a continuous flow of 5% of H_2

in Ar. The TPR profiles were registered while the samples were heated from room temperature to 400 °C, at a heating rate of 10 °C/min.

2.3. Experimental setup and procedure

Catalytic activity was tested in a trickle bed reactor consisting of a 9 mm i.d. stainless steel tube where 0.5 g of catalyst were placed. The reaction temperature and pressure were controlled by a thermocouple located in the catalytic bed and by means of a backpressure control valve, respectively. The liquid and the gas were passed through the bed in concurrent down-flow, controlled by mass flow controllers. The effluent was depressurized and stored in a steel phase separator where it was cooled up to 3 °C by means of a peltier cell and finally the samples were automatically collected by a fraction collector. An aqueous solution of 1000 mg/L of phenol was continuously fed to the reactor at different flow rates (0.25–1.5 mL/min). Hydrogen was introduced to the reactor at a flow rate of 60 N mL/min. Reaction temperatures from 110 to 170 °C were tested and the pressure was varied within the 2–9 bar range. In order to reduce the time required to reach the steady state, before each run the Pd/AC catalysts were saturated with phenol in the same experimental condition, except for the gas feed (N_2 instead of H_2). The absence of internal diffusion limitations was verified by running experiments varying the catalyst particle size within the range of 1.0–2.4 mm.

2.4. Analytical methods

Phenol and the reaction products were identified by GC/MS (Saturn 2100-T, Varian) using a 30 m long × 0.25 mm i.d. capillary column (Meta X5 Tracsil 5) and He as carrier gas. After 1 min holding at 60 °C, the column was ramped at 10 °C/min up to 280 °C. The temperature of the injector was fixed at 250 °C. Previous to the analysis, the aqueous samples were extracted with solid-phase cartridges (SEK-Pak Plus C_{18}, Waters) which were eluted with acetonitrile. These compounds were quantified by GC/FID (GC 3900 Varian) using a 30 m long × 0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and nitrogen as carrier gas. The following temperature program was used: starting temperature 130 °C, heating rate 8 °C/min and final temperature 210 °C. The temperature of the detector was always 300 °C. In order to verify the phenol concentrations, the samples were also analyzed by HPLC/DAD (Prostar, Varian) using a C_{18} as stationary phase (Valco Microsorb-MW 100-5 C_{18}) and a mixture of acetonitrile and water (1:1, vol.) as mobile phase. A wavelength of 280 nm was used. Samples from the reactor effluent were also analyzed by total reflection X-ray fluorescence (TXRF), using a TXRF EXTRA II spectrometer (Rich. Seifert & Co. Ahrensburg, FRG) to quantify the possible leaching of Pd.

Ecotoxicity determinations were carried out by the Microtox Acute Toxicity Test (SCI 500 Analyzer) using a freeze-dried preparation of the marine bacterium *Vibrio Fischery* as described in ISO 11348-3 (1998). The inhibition of the light emitted by the bacteria was measured after 15 min contact time.

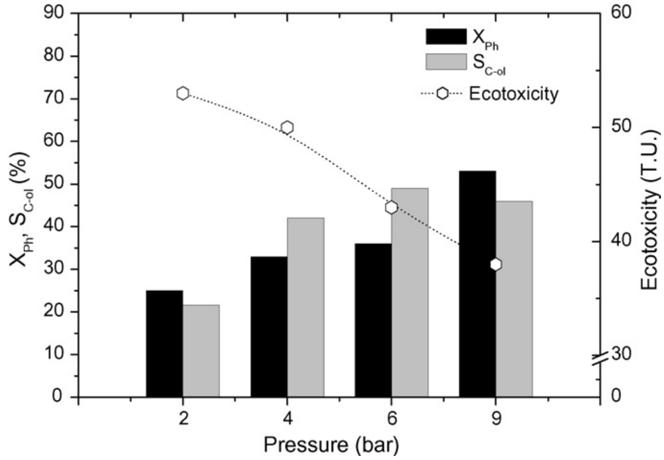

Fig. 1. Influence of pressure on phenol conversion (X_{Ph}), cyclohexanol selectivity ($S_{C\text{-}ol}$) and effluent ecotoxicity (T: 110 °C; τ: 1.5 kg_{cat} h/mol).

3. Results and discussion

The reaction products identified from phenol hydrogenation were cyclohexanone and cyclohexanol. The measured concentrations of these two species plus unconverted phenol matched in all the cases the mass balance close to a 95%.

3.1. Commercial Pd/AC catalyst

The effect of pressure was investigated in the range 2–9 bar at 110 °C. These conditions are less severe than the reported in other works [19] where the pressure was varied between 10 and 30 bar. Phenol conversion increases with pressure, as can be observed in Fig. 1. The product distribution was also found to depend on the pressure, the selectivity towards cyclohexanol increasing significantly when the pressure increases from 2 to 4 bar. Beyond this pressure, the effect on the selectivity becomes less significant reaching a saturation level. This beneficial effect of pressure can be explained as the result of a higher solubility of H_2 in the liquid phase which enhances the rate of the process giving rise to a higher phenol conversion at a given space-time and a higher extent of the reaction up to the final product (cyclohexanol). In agreement with this, the ecotoxicity of the effluent decreased at increasing pressure within the range investigated, as can be seen in Fig. 1.

Table 1 reports the EC_{50} values of the three pure compounds (phenol, cyclohexanol and cyclohexanone) and the equivalent ecotoxicities (in toxicity units, T.U.) of the corresponding 1000 mg/L aqueous solutions. As can be seen, cyclohexanol shows a lower ecotoxicity value than phenol but the other product from phenol hydrogenation, cyclohexanone, is even more

Table 1
Ecotoxicity values for phenol and the reaction products

Compound	EC_{50} (mg/L)	T.U. (1000 mg/L solution)
Phenol	15.9	63
Cyclohexanone	11.6	86
Cyclohexanol	18.5	54

toxic than phenol. Thus, it is important to reach a high phenol conversion but with a high selectivity towards cyclohexanol. The ecotoxicity values of Fig. 1 correspond to direct experimental measurements from the reactor effluent.

The effect of temperature on phenol conversion and cyclohexanol selectivity is shown in Fig. 2. As can be seen, phenol conversion increases with temperature up to around 150 °C where a maximum is observed. Beyond this temperature, a significant decrease of conversion takes place which can be attributed to an induced loss of catalytically active hydrogen from the catalyst surface [8,9,14]. This decrease of conversion is accompanied by a lower selectivity to cyclohexanol and an increase of the ecotoxicity, which nevertheless is still lower than that of the 1000 mg/L phenol solution fed to the reactor. The ecotoxicity of the effluent in the temperature range studied was also calculated from the values of the individual compounds (Table 1) and their exiting concentrations, according to the following expression used to calculate the toxicity of a mixture of compounds, which is based on the concept of concentration addition on the toxicity units [31]:

$$\text{T.U.}_{\text{mixture}} = \sum_i \frac{C_i}{\text{EC}_{50i}} \qquad (1)$$

The calculated ecotoxicity values are significantly higher than the directly measured ones, as can be seen in Fig. 2. This suggests the existence of antagonistic effects. Hoffmann et al. [32] tested mixtures of 10 chemicals in water to investigate possible synergistic, additive or antagonistic toxicity effects. The results indicated that most of the mixtures showed lower values than the expected from the pure toxicants, concluding that synergistic effects are rather unusual in combinations of toxicants.

Table 2 reports the results obtained at 150 °C and 9 bar working at different space-time values within the 0.5–3.1 kg_{cat} h/mol range. As can be seen, phenol conversion increases significantly with space-time and so does the selectivity to cyclohexanol. These results are consistent with a reaction scheme based on a series-parallel pathway where phenol gives rise to cyclohexanone and cyclohexanol and this second is also produced from cyclohexanone hydrogenation.

Table 2
Effect of space-time on phenol conversion and cyclohexanol selectivity (P: 9 bar; T: 150 °C)

τ (kg_{cat} h/mol)	X_{Ph} (%)	$S_{\text{C-ol}}$ (%)
3.1	87.8	56.4
1.5	68.8	45.2
0.8	35.6	33.8
0.5	34.7	22.6

To learn on the stability of the commercial Pd/AC catalyst, a long-term (96 h) run was carried out at 150 °C, 9 bar and a space-time of 1.5 kg_{cat} h/mol. The results are shown in Fig. 3, where it can be seen that phenol conversion decreased slightly during the initial 60 h from 70 to 64%. Beyond that time, phenol conversion remained practically constant. The trend in the selectivity towards cyclohexanol was quite similar than that of phenol conversion, but the decrease was more significant during the initial 20 h. Pd leached out from the catalyst during the 96 h, which could be also a cause of the slight deactivation, was lower than 0.03% of the initial Pd weight. TXRF analyses in the effluent showed the existence of small amounts of calcium leached from the catalyst. The high selectivity to cyclohexanone observed in most of the experiments can be explained by the presence of Ca in the commercial catalyst. This effect is well known in the case of industrial catalysts used for the hydrogenation of phenol to cyclohexanone [7,16,19,33].

3.2. Home made Pd/AC catalysts

The hydrogenation of phenol was also studied with some catalysts prepared in our lab with different palladium precursors in order to learn on the possible influence in the catalytic activity and on the reduction of the ecotoxicity of the effluent. The operating conditions of the runs were set at 9 bar, 150 °C and 1.5 kg_{cat} h/mol space-time. The Pd concentration in the impreg-

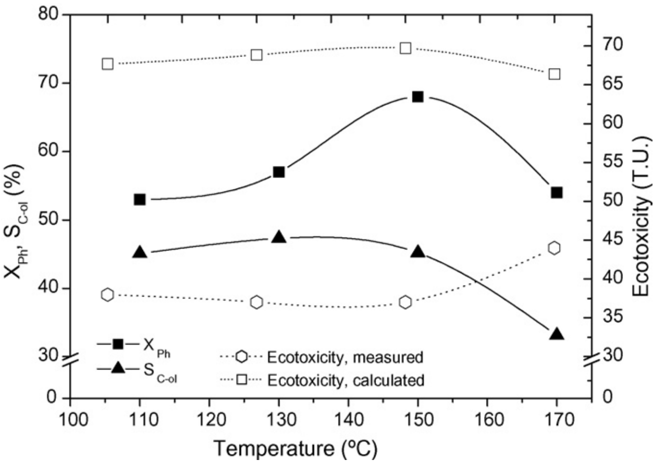

Fig. 2. Effect of temperature on phenol conversion, cyclohexanol selectivity and effluent ecotoxicity (P: 9 bar; τ: 1.5 kg_{cat} h/mol).

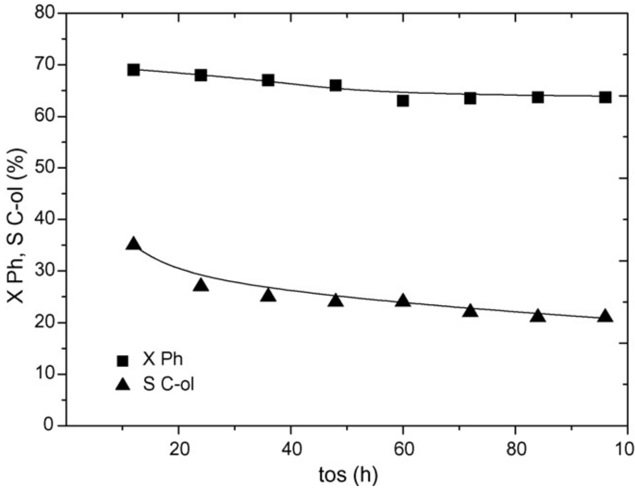

Fig. 3. Long-term experiment with the commercial Pd/AC catalyst (P: 9 bar; T: 150 °C; τ: 1.5 kg_{cat} h/mol).

Table 3
Characterization of the catalysts prepared with different palladium precursors (1% Pd w/w; T_{cal}: 250 °C; T_{red}: 150 °C; T: 150 °C; P: 9 bar; τ: 1.5 kg_{cat} h/mol) and results on phenol conversion and cyclohexanol selectivity

Precursor	Activity		Characterization				
	X_{Ph} (%)	$S_{C\text{-}ol}$ (%)	XPS	Adsorption–desorption isotherm			
			Pd (%, w/w)	A_{BET} (m^2/g)	A_{ext} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)
$PdCl_2$	86.8	68.2	0.8	917	117	0.203	0.118
$Pd(NO_3)_2$	8.0	11.7	2.5	950	85	0.299	0.112
$Pd(CH_3COO)_2$	20.1	46.4	1.3	935	87	0.277	0.127

nating solution was adjusted to obtain a 1% Pd w/w on the catalyst in all the cases. As can be observed in Table 3, phenol conversion was significantly influenced by the Pd precursor used to prepare the catalyst. A higher conversion was obtained with the catalysts prepared using $PdCl_2$ while $Pd(NO_3)_2$ lead to a very low catalytic activity, below 10%. The catalyst prepared with $Pd(CH_3COO)_2$ as precursor showed also a low conversion of phenol, about 20%. This fact is in contrast with the results reported in other works [10,17], where the Pd precursor did not seem to affect to phenol conversion. Moreover, the selectivity towards cyclohexanol reached higher values when using $PdCl_2$ as palladium precursor. In order to explain the differences in the activity and selectivity of the catalysts, characterization of the porous structure and XPS analyses were carried out, the results being summarized in Table 3. The use of different palladium precursors did not affect significantly to the porous structure whereas the XPS-measured palladium concentrations were fairly different. XPS provides the concentration of the elements in the most external layers of the solid, and thus a value of XPS-measured Pd concentration much higher than the nominal bulk Pd concentration (∼1%) indicates that the metallic active phase is deposited mainly in the external surface and suggests a poor distribution, which may be associated to a lower activity. This is the case when using $Pd(NO_3)_2$ as precursor whereas the opposite occurs with $PdCl_2$. Summarizing, the catalyst prepared with $PdCl_2$ as precursor led to both the higher catalytic activity and the higher selectivity towards the less toxic product of the chain reaction.

The influence of palladium loading was studied for the catalysts prepared with a $PdCl_2$ within the range of 0.5–3% (w/w) palladium. As can be seen in Fig. 4, increasing Pd loading increases phenol conversion and the selectivity towards cyclohexanol giving rise to a lower toxicity of the effluent. At 3% Pd phenol is almost completely converted to cyclohexanol and a very low toxicity value is achieved.

The temperature of calcination was also studied to analyze its influence on the activity and selectivity of the catalysts. In this sense, TPR experiments were carried out with two Pd/AC catalysts calcined at 200 and 400 °C. The results are shown in Fig. 5. The catalyst calcined at 400 °C did not show a significant consumption of hydrogen, suggesting a possible sintering of the metallic phase [34]. According to these results, hydrogenation of phenol was studied using catalysts calcined at temperatures between 150 and 350 °C. The results are summarized in Table 4. The effect of calcination temperature on phenol conversion was almost negligible within the 150–250 °C, range where conver-

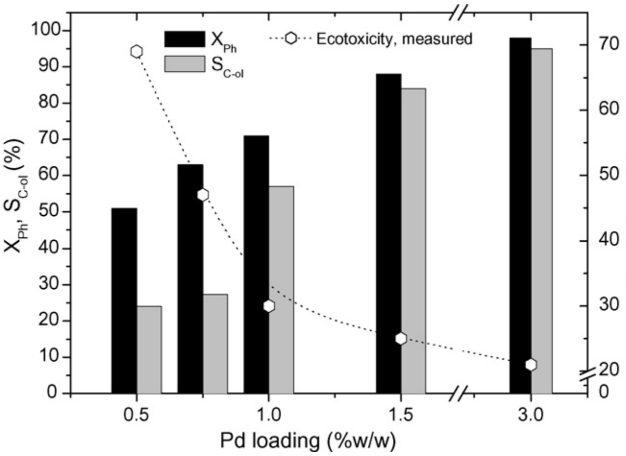

Fig. 4. Influence of Pd loading on phenol conversion, cyclohexanol selectivity and effluent ecotoxicity ($PdCl_2$, T_{cal}: 200 °C; T_{red}: 170 °C; P: 9 bar; T: 150 °C; τ: 1.5 kg_{cat} h/mol).

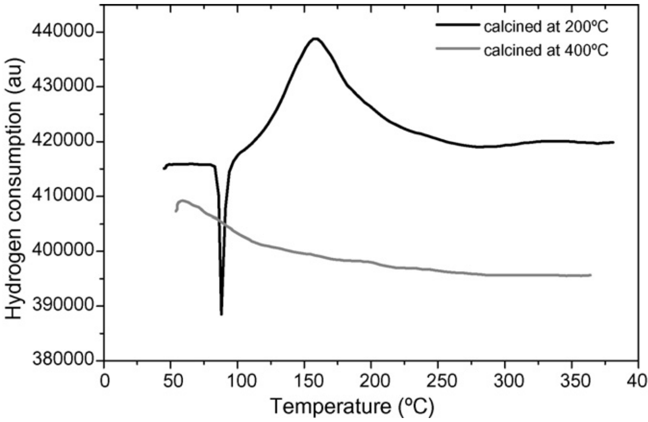

Fig. 5. TPR spectra of Pd/AC catalysts calcined at 200 and 400 °C.

Table 4
Effect of calcination temperature on phenol conversion and selectivity towards cyclohexanol (1% Pd w/w ($PdCl_2$); T_{red}: 150 °C; T: 150 °C; P: 9 bar; τ: 1.5 kg_{cat} h/mol)

Temperature (°C)	X_{Ph} (%)	$S_{C\text{-}ol}$ (%)
150	83.9	61.6
200	85.0	66.1
250	86.7	68.2
300	63.0	18.3
350	52.7	24.9

Table 5
Phenol conversion and selectivity towards cyclohexanol with catalysts reduced at different temperatures (1% Pd, w/w ($PdCl_2$); T_{cal}: 200 °C; T: 150 °C; P: 9 bar; τ: 1.5 kg_{cat} h/mol)

Temperature (°C)	X_{Ph} (%)	$S_{C\text{-}ol}$ (%)
110	84.2	63.6
130	84.0	57.8
150	85.0	66.1
170	71.1	54.3
190	75.9	48.4

sion values in the vicinity of 85% were obtained. Beyond 250 °C, phenol conversion decreased significantly, probably as the result of sintering of the active phase giving rise to a poorer Pd dispersion. Regarding to the selectivity towards cyclohexanol, it would be convenient to use Pd/AC catalysts calcined at 150–200 °C.

TPR studies were also performed to analyze the effect of the temperature used for catalyst reduction. The catalyst calcined at 200 °C showed two signals (Fig. 5). A broader band placed at 170–250 °C which is indicative of the reduction of palladium species and the reaction of hydrogen with the oxygen surface groups of the support. A negative peak near 100 °C was also seen, resulting from decomposition of the interstitial palladium hydride phase [34]. The results on phenol conversion and selectivity towards cyclohexanol obtained with the catalysts reduced at different temperatures are given in Table 5. No significant differences were found for reduction temperatures between 110–150 °C and increasing this temperature is detrimental for phenol conversion and selectivity towards cyclohexanol.

To learn on the possible influence of the surface composition of the activated carbon, it was subjected to an oxidative treatment with nitric acid. Phenol conversion did not show differences with respect to the catalyst prepared with the virgin carbon while the selectivity towards cyclohexanol increased significantly, giving rise to an important reduction of ecotoxicity. As it was reported in previous works [11,13], the nitric acid treatment produces modifications in the surface composition without significant changes of the porous structure. Thus, the differences in selectivity may be attributed to the increase of oxygen surface groups, which can act as anchorage sites for palladium favouring a more homogeneous distribution [29]. A higher dispersion is related with a deeper hydrogenation, leading to the end chain reaction product, cyclohexanol. Nevertheless, further work is required for a conclusive confirmation.

4. Conclusions

Catalytic hydrogenation of phenol with Pd/AC catalysts is a feasible method for the degradation of phenol in aqueous phase that can be coupled to a biological treatment once the toxicity of the wastewater has been reduced. The catalysts show a convenient stability in a long-term experiment, Pd leaching being negligible. The election of the catalyst is crucial to achieve a substantial reduction of ecotoxicity which is associated with a higher selectivity towards cyclohexanol. Higher phenol conversion and selectivity towards cyclohexanol were achieved using $PdCl_2$ as precursor, a calcination temperature of 250 °C and reducing the catalyst at 150 °C. The oxidation of the carbon support with nitric acid prior to impregnation could be an interesting option since the selectivity towards cyclohexanol was increased.

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