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Catalytic behavior of size-controlled palladium nanoparticles in the hydrodechlorination of 4-chlorophenol in aqueous phase

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ABSTRACT

Unsupported Pd nanoparticles of controlled size were tested as catalyst in liquid-phase hydrodechlorination (303–323 K, 1 atm) using 4-chlorophenol (4-CP) as target compound. The Pd nanoparticles were synthesized by chemical reduction, using ethanol and methanol as reducing agents and poly(N-vinyl-2pyrrolidone) (PVP) as capping agent. The size of the nanoparticles and the Pdⁿ⁺/Pd⁰ ratio decreased with increasing alcohol concentration and PVP/Pd ratio, both being lower for ethanol medium.

High 4-CP conversion values (80–100%) were achieved at low Pd concentration (2.45×10^{-3} g/L). Phenol was the only reaction by-product detected in contrast to the previous results with supported Pd catalysts, where the active phase–support interaction in 4-CP HDC led to obtain also cyclohexanone and cyclohexanol as by-products in equivalent experimental conditions. The smaller nanoparticles showed higher activity due to the higher available surface (m^2/g_{cat}). Thus, the smaller nanoparticles synthesized in ethanol medium ranged between 2.7 and 2.8 nm and yielded activity values between 16.7 and 39.1 mmol/g_{cat} min, whereas the smaller particles obtained in methanol medium were in the 3.1–4.2 nm range and exhibited activity values of 20.1–25.7 mmol/g_{cat} min. However, the large nanoparticles exhibited higher activity per unit of catalyst surface, for example, 0.34–0.43 mmol/min m² in the case of those synthesized in methanol medium. On the other hand, higher activity was observed for the nanoparticles synthesized in methanol medium when equivalent nanoparticle size was compared. Activation energy values around 100 kJ/mol were obtained for Pd nanoparticles of different characteristics, significantly higher than the value reported for supported Pd catalysts.

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1. Introduction

In the last years, catalytic hydrodechlorination (HDC) has received increasing attention for the treatment of wastewaters containing chlorinated organic compounds since it shows some advantages when compared to other techniques of potential application for these hazardous pollutants. HDC can operate at mild conditions [1–3], so that it does not require high temperatures and/or pressures as in the case of incineration or wet oxidation processes. Large amounts of reagents, such as in Fenton oxidation, are not needed and can be applied within a wide range of concentrations of chlorinated compounds, which is not the case of biological methods [4]. Though HDC does not provide the complete destruction of the pollutants, it can lead to a convenient transformation of them into substantially less harmful species [2,4,5].

Thus, HDC can be used as a detoxifying stage prior to a biological treatment.

Transition and noble metal-based catalysts have been commonly used in liquid-phase HDC [6-14]. Among those metals, Pd has been the most extensively used because of its singular catalytic properties [15] that lead to high dechlorination efficiencies [16-18]. These specific properties are affected by a number of factors such as the metallic particle size, shape, oxidation state and interaction with the support, among others [19–21]. Particularly, metal particle size is crucial for the performance of the catalyst in structure-sensitive reactions. A number of authors have concluded that HDC reaction is structure sensitive [22-28], although there is no general agreement with respect to this topic [29]. Thus, in order to design efficient catalysts, it is necessary a previous in-depth knowledge about how this factor affects the catalytic properties. In general, it is widely accepted that decreasing the particle size of the metallic phase increases the catalytic activity because of a higher surface-to-volume ratio although some limit has been claimed for this effect [30,31]. Moreover, the nature and the strength of bonding between the molecules adsorbed and the metal particles is affected by the number of particles surrounding a surface metal atom (electronic or ligand effect). Thus, adsorption



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Nomenclature							
a C _{4-cp} d _s k m _{pd}	catalytic activity (mmol/g _{cat} min) 4-CP molar concentration (mmol/L) surface-area-weighted average mean diameter (m) rate constant (min ⁻¹) Pd nanoparticles mass (g)	$-r_{4- ext{cp}}$ S_a t $ ho_{pd}$	4-CP conversion rate (mmol/L min) specific surface area (m ² /g) time (min) Pd density (g/m ³)				

energies could change with particle size, leading to poisoning of the catalyst or activation of the substrate, depending on the nature of the adsorption of the molecule on the particle surface [15]. It is important to remark that the catalysts commonly studied have their metallic phase dispersed at nanometric scale, but there is no precise control on the nanoparticle size upon the synthesis. Therefore, there is a remarkable interest in the literature in designing catalysts with controlled nanoparticle size and size distribution [32-35]. However, it must be emphasized that the influence of nanoparticle size on the catalytic activity is not well defined so far, since decreasing the particle size not always increases the reaction rates evaluated per unit mass of nanoparticle. Thus, when a certain minimum particle size is reached, an additional decrease produces an increase in the ionization energy and, as a result, an increase in the adsorption energy. The resulting stronger adsorption of intermediate species on the particle surface can provoke poisoning of active sites of the catalyst, which diminishes the catalytic activity [15,36].

Some research efforts have been focused on developing methods of synthesis of nanoparticles with the objective of controlling their size within a narrow distribution in order to investigate chemical and physical size-dependent properties [37-39]. Among the methods of synthesis of noble metals nanoparticles that have been reported in the literature, chemical [40,41], electrochemical [42], sonochemical [43] and microbial-based methods [44] are the most relevant. Chemical reduction is considered as a simple method based on the reduction of a metal precursor salt in the presence of a reducing agent (hydrazine, pyrogallol, potassium borohydride, ethanol, methanol, propanol) and a protective or capping agent (poly(N-vinyl-2-pyrrolidone), polyvinyl alcohol, dodecylamine). The last inhibits aggregation and is responsible for the controlled growth and shape of the particles. This method has been claimed in some works [45-48] for the design of size-controlled nanoparticles whose catalytic activities have been analyzed in different reactions. For example, Narayanan and El-Sayed [36] synthesized size-controlled Pd nanoparticles that were supported on activated carbon and tested them for the Suzuki reaction between phenylboronic acid and iodobenzene for producing biphenyl. In another related work, Joo et al. [48] studied the effect of particle size on CO oxidation over Ru nanoparticles catalysts. Nevertheless, investigation of size-controlled nanoparticles applications in other types of catalytic reactions is scarce, and thus, so far there is no still a comprehensive knowledge on how particle size influences the catalytic activity in reactions such as liquid-phase HDC.

The aim of this work is to address the effect of the synthesis conditions and the size of Pd nanoparticles on their activity in 4-CP HDC in aqueous phase. The Pd nanoparticles were prepared with poly(N-vinyl-2-pyrrolidone) (PVP) as capping agent and ethanol or methanol as reducing agent.

2. Experimental

2.1. Materials

Sigma–Aldrich PdCl₂ (99%) was used as Pd nanoparticles precursor. Poly(N-vinyl-2-pyrrolidone) (average molecular weight: 40.000, Sigma–Aldrich Co.) was used as capping agent to avoid uncontrolled growing and inhibit aggregation of Pd nanoparticles. Methanol (>99%) and ethanol (>99%), used as reducing agents, were purchased from Panreac Quimica S.A.U. and Merck KGaA, respectively. Hydrogen (>99%) was supplied by Praxair. All the reagents were used as received without further purification.

2.2. Synthesis and characterization of Pd nanoparticles

Pd (II) chloride (0.5 mmol), 0.2 N HCl (1 mmol) and distilled water (250 mL) were mixed to obtain a H_2PdCl_4 (2 × 10⁻³ M) pale-yellow aqueous solution. An aliquot of 30 mL of the 2 × 10⁻³ M H_2PdCl_4 solution was mixed with 70 mL of alcohol/ water solution and PVP. The mixture was refluxed in a 250-mL flask connected to a Liebig condenser for 3 h under atmospheric pressure [37]. The values of PVP/Pd ratio were varied between 5 and 40 (mol/mol), and different mixtures of alcohol/water (10–70%, v/v) were used in order to learn the effect of these variables on the size and size distribution of Pd nanoparticles. Finally, the colloidal dispersion of nanoparticles (100 mL) was concentrated up to a total volume of approximately 10 mL in a rotary evaporator (Büchi).

The Pd nanoparticles synthesized were characterized by transmission electron microscopy (TEM) at 400 kV (JEOL, mod. JEM-4000 EX). Samples were prepared placing a drop of colloidal Pd nanoparticles onto a carbon-coated copper grid and lefting it dry at room temperature. Software 'ImageJ 1.44i' was used for counting and measuring particles on digital TEM images (more than 200 nanoparticles were measured per image). Surfacearea-weighted mean diameters $(d_s = \sum n_i d_i^3 / \sum n_i d_i^2)$ and size distribution, characterized by the standard deviation ($\sigma_s =$ $\sqrt{\sum (d_i - d_s)^2/n}$, were calculated as described elsewhere [49]. Likewise, the catalysts were characterized by XPS (Physical Electronics, mod. ESCA 5701 equipped with a Mg K α X-ray excitation source, 1253.6 eV). Software 'Multipak v8.2b' was used for spectrograms deconvolution in order to determine both Pd electrodeficient and zero-valent species in the particle surface. The analysis procedure involved smoothing, a Shirley background subtraction and mixed Gaussian-Lorentzian by a least-square method curve fitting as described in a previous work [50]. C 1s peak (284.6 eV) was used as internal standard for binding energies corrections due to sample charging. Doublet separation for Pd 3d was 5.26 eV as described elsewhere [51]. Deconvoluted peaks showed binding energies in the range of 334.8-335.8 eV and 336.2-337.1 eV for Pd $3d_{5/2}$, which can be attributed to metallic Pd (Pd^{0}) and electrodeficient Pd (Pd^{n+}) , respectively. All these data values are in good agreement with those reported in NIST X-ray Photoelectron Spectroscopy Database [51]. A probing depth of several nanometers can be assumed; therefore, the surface Pd^{n+}/Pd^{0} ratio calculated should be essentially the same as the bulk ratio for the particles studied.

2.3. HDC experiments

Catalytic HDC runs were carried out during 4 h in a threenecked jacketed glass reactor where H_2 was continuously fed at 50 N mL/min flow rate under vigorous stirring (600–800 rpm) in order to facilitate hydrogen distribution through the 4-CP solution (150 mL). The reaction temperature (303–323 K) was controlled by a thermostatic bath connected to the reactor jacket. The system was equipped with a cold trap at the vent to check any possible stripping; no significant stripping was detected. The initial concentration of 4-CP was 100 mg/L, and the catalyst load was 2.45×10^{-3} g/L of Pd.

A sampling system consisting in a thin tube connected to a syringe allowed taking liquid samples (1 mL), which were collected through previous filtering (PTFE filter, pore size 0.45 μ m). The samples were analyzed by high-performance liquid chromatography (Varian Prostar equipped with a UV–VIS detector) using a C₁₈ column as stationary phase and a mixture of acetonitrile and water (1:1, v/v) as mobile phase. Cyclohexanone and cyclohexanol were analyzed by a GC/FID device (GC 3900 Varian) using a 30 m long \times 0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and nitrogen as carrier gas. The quantification of chloride ion was performed by ion chromatography (Metrohm 790 Personal IC). The carbon and chlorine balances matched always between 90% and 95%, respectively, at the least.

3. Results and discussion

3.1. Pd Particle size and size distribution

3.1.1. TEM characterization

Table 1 shows the mean diameters and size distributions of Pd nanoparticles prepared under different conditions. Fig. 1 shows, as representative examples, TEM images of four selected series. The nanoparticles appeared mostly spherical although some differences in shape were found in the case of the nanoparticles synthesized in 70% ethanol (series 4), with polyhedral shapes prevailing over spheres. These nanoparticles showed the largest size with a mean diameter of 22.1 nm.

3.1.2. Effect of the capping agent on nanoparticles size

The influence of the capping agent on the particle size can be observed in Fig. 2. When an intermediate concentration of 25% ethanol was used, an increase in the PVP/Pd molar ratio from 5 to 20 led to a reduction in both particle size and size distribution. The same trend was observed with a concentration of 10% methanol but within a wider range of the PVP/Pd molar ratio (5–35). At higher PVP/Pd molar ratios, no additional decrease in nanoparticle size and size distribution was found. It has been reported that the role of PVP is to act as a protecting agent, allowing controlled particles growth in a reactor of a nanosized water pool wrapped with PVP, preventing particles aggregation [52,53]. Increasing the PVP/Pd molar ratios favors the formation of micellar structures that surround the particles and control their growth.

3.1.3. Effect of the reducing agent

The alcohol used as reducing agent showed a crucial effect on the size of the nanoparticles, as can be seen in Table 1. Fig. 3 shows that, for a PVP/Pd molar ratio of 5, the ethanol concentration did not show a well-defined influence in the range of 10-40% where mean diameters and size distributions within 3.6-4.7 nm and 1.0-1.9 nm, respectively, were observed. However, a significant increase took place in 70% ethanol medium up to 22 nm mean particle diameter. A different behavior was observed with methanol as reducing agent. For a PVP/Pd molar ratio of 20, the nanoparticle mean diameter decreased when the methanol ratio increased from 10% to 40% where a minimum size of 3.8 nm was reached without any further decrease at higher methanol concentration. As reported in the literature [37], two main effects lead to the generation of smaller Pd nanoparticles in relation to the concentration of reducing agent. Firstly, a higher concentration of the reducing agent increases the reduction rate of $[PdCl_4]^{2-}$ to Pd⁰, provoking the generation of smaller nanoparticles because of the occurrence of a higher number of Pd nuclei. This effect seems to prevail at ethanol and methanol concentrations within 10-40% and 10-55%, respectively. Secondly, while PVP is dissolved in both alcohol and water, H₂PdCl₄ shows decreasing solubility at high alcohol concentration, so it does not disperse homogeneously in a mixed wateralcohol solution at the highest alcohol ratios tested. Therefore, nanoparticle mean diameter and size distribution become larger and wider, respectively, at high alcohol ratios. This seems to be the prevailing effect at alcohol concentrations beyond 40%.

The smallest nanoparticles were obtained at different alcohol ratios and PVP/Pd molar ratios for each of the alcohols used. As shown in Table 1, under identical synthesis conditions (alcohol concentration and PVP/Pd ratios), Pd nanoparticles synthesized with ethanol as reducing agent were smaller. The effect of the reducing agent on the particle size has been discussed in the literature. Teranishi et al. [37] suggested a faster reduction of $[PdCl_4]^{2-}$ by alcohols with higher boiling point, providing a higher number of Pd nuclei. Thus, alcohols of higher boiling point lead to Pd nanoparticles of lower size. Likewise, they indicated that ethanol can be oxidized more easily than methanol according to the hydrogenation enthalpies of the corresponding aldehydes. Our results are consistent with this explanation, since all of the nanoparticles

Table 1

Mean diameter (d_s), size distribution (σ_{sy} , Pdⁿ⁺/Pd⁰ ratio, specific surface area and activity (a) of the Pd nanoparticles prepared under different conditions

Pd nanoparticles series	Alcohol	Vol alcohol (%)	PVP/Pd (mol/mol)	$d_{s}(nm)$	σ_s (nm)	Pd ⁿ⁺ /Pd ⁰ ratio	Specific surface area (m^2/g_{cat})	a (mmol/g _{cat} min)
1	Ethanol	10	5	4.7	1.0		106	7.4
2	Ethanol	25	5	3.6	1.2	0.67	138	10.1
3	Ethanol	40	5	4.0	1.9	0.35	125	4.8
4	Ethanol	70	5	22.1	10.4	2.79	23	3.5
5	Ethanol	10	20	3.5	0.9	0.48	143	14.6
6	Ethanol	25	20	2.7	0.7		184	19.4
7	Ethanol	25	35	2.7	0.8	0.54	181	39.1
8	Ethanol	40	20	2.8	0.8		178	16.7
9	Ethanol	55	20	2.8	0.4		178	17.8
10	Methanol	10	5	12.9	7.0	1.46	39	16.8
11	Methanol	10	20	10.9	2.9	1.05	46	17.2
12	Methanol	10	35	3.1	0.6	0.48	161	25.3
13	Methanol	10	40	3.6	0.7	0.51	139	20.1
14	Methanol	25	20	8.5	4.6	1.03	59	19.8
15	Methanol	40	20	3.8	0.8	0.56	131	25.7
16	Methanol	55	20	4.2	1.2	0.39	119	23.7



Fig. 1. TEM images and size distributions of four samples of Pd nanoparticles prepared in ethanol (a and b) and methanol (c and d) water media.



Fig. 2. Mean diameter (\bullet) and size distribution (\bigcirc) of Pd nanoparticles obtained at different PVP/Pd ratios. (a) Ethanol 25 vol.% and (b) methanol 10 vol.%.



Fig. 3. Mean diameter (\blacksquare) and size distribution (\square) of Pd nanoparticles prepared with (a) ethanol (PVP/Pd ratio = 5 mol/mol) and (b) methanol (PVP/Pd ratio = 20 - mol/mol).

synthesized in ethanol medium were of lower size than those synthesized in methanol medium under the same synthesis conditions.



Fig. 4. XPS spectra of Pd nanoparticles of series 11 and 12 (Table 1).

3.2. XPS characterization

XPS was used to establish the oxidation state of Pd. The Pd^{n+}/Pd^{0} ratios obtained from the deconvolution of the XPS Pd 3d region spectra are summarized in Table 1. The presence of both Pd^{n+} and Pd⁰ was observed in all the Pd nanoparticles series analyzed. Gomez-Sainero et al. [54] reported that both electrodeficient and zero-valent species are required for carbon tetrachloride HDC on Pd/AC in gas phase, whereas catalysts with only one of the species $(Pd^{n+} \text{ or } Pd^{0})$ remained inactive. In this sense, they proposed a dual nature of Pd active sites by the association of both species, reaching a maximum of activity at a Pd^{n+}/Pd^{0} ratio close to 1. Other authors were also in agreement with the proposed dual nature of the Pd active sites in HDC in gas phase [50]. Fig. 4 shows the Pd 3d deconvolved spectra for the nanoparticles of series 11 and 12. Zerovalent Pd is the prevailing species in series 12, whereas quite similar proportions of electrodeficient and zero-valent Pd were found for series 11. As can be seen in Fig. 5, there is a relationship between the Pd^{n+}/Pd^{0} ratio values and the mean particle diameter. Three different patterns can be distinguished independently of the alcohol used as reducing agent. The smaller particles (2.7-4.2 nm) show Pdⁿ⁺/Pd⁰ ratios between 0.35 and 0.67, whereas for larger particles (8.5-12.9 nm), that ratio is between 1.03 and 1.46. Oversized particles (22.1 nm) show Pd^{n+}/Pd^{0} ratio value of 2.79. This observation is consistent with the previous results reported in the literature, where small particles had a lower $Pd^{n+/}Pd^{0}$ ratio than large ones [55]. The differences found in Pd^{*n*+}/Pd⁰ ratios can be related with the higher surface/volume ratio of smaller particles, which provides a higher surface per unit mass of Pd to be reduced by the reducing agent, thus leading to a lower Pd^{n+}/Pd^{0} ratio of small particles compared to larger ones. However, due to the difficulty to address where Pd^{*n*+} and Pd⁰ species are predominantly located in Pd nanoparticles, further research is needed.



Fig. 5. Pd^{n*}/Pd^0 ratio versus nanoparticle mean diameter: methanol (\blacksquare) and ethanol series (\bigcirc).

3.3. HDC activity of Pd nanoparticles

The HDC runs were carried out at variable concentrations of PVP in the reactor. Preliminary experiments carried out in the absence of catalyst proved that there was no reaction between PVP, 4-CP and H₂. Moreover, a control experiment was carried out adding to the reaction medium a dose of PVP ten times higher than that needed for the synthesis of the Pd nanoparticles with the aim of addressing the effect of the excess of PVP on the catalytic activity. The results showed no significant differences in activity between the series 10 of Pd nanoparticles (16.8 mmol/gcat min) and the same particles series in the control experiment (16.5 mmol/ gcat min). Thus, no synergistic or inhibitory effect of PVP was observed. These results are in good agreement with those reported by Hirai and Yakura [56] on the study of activity of Pd nanoparticles of different size protected by PVP layers of different thickness. These authors concluded that activity depends mainly on specific surface area and not on PVP concentration. Chemical control of the reaction has been checked experimentally by using different concentrations of catalyst in 4-CP HDC reaction; no significant differences in the HDC rates per unit mass of catalyst were observed.

Fig. 6 shows the evolution of 4-CP conversion upon reaction time with some Pd nanoparticles series. High 4-CP conversion values were achieved (80–100%) in all cases. Two different behaviors were observed in relation with the reducing agent used. In the case of Pd nanoparticles from the methanol series, changes in particle size were accompanied by small differences in activity. In contrast, in the ethanol series, the activity increased when decreasing the particle size.

The nanoparticle size affects the nature and strength of the interaction of 4-CP with the Pd surface since it determines the number of particles surrounding each surface metal atom. Moreover, the coordination of surface atoms depends on the particle size. Thus, smaller particles contain more surface atoms residing on the edges of the crystallographic planes or on edge junctions, increasing the number of active sites which could be accessible to the 4-CP molecules [15]. Additionally, Diaz et al. [57] indicated that structure sensitive appears as a determining factor on the HDC activity. The results reported suggested that a metal particle size within the 3-4 nm range can be considered as the optimum for Pd-based catalysts. Contradictory results have been found in the literature about the most favorable catalyst site (terrace vs. edges/corners) in HDC. A number of works have considered the edges/corners as the most favorable catalyst sites in HDC since a high activity seems to be related with the number of surface Pd



Fig. 6. HDC of 4-CP with Pd nanoparticles $(2.45\times 10^{-3}\,g/L)$ of: ethanol (a) and methanol series (b) (Table 1).

atoms of low coordination placed at the edges and corners of Pd particles [58–60], being such atoms more abundant in smaller particles. This interpretation has also been reported for other catalytic reactions such as Suzuki–Heck reaction [61,62]. Nevertheless, other authors have indicated that large ensembles or single atoms can be considered as the most favorable catalytic sites for HDC [63,64]. Although studies about the mechanism of liquid-phase HDC of 4-CP in the presence of Pd are not available, Orlov et al. [65] reported structure-dependent adsorption of 4-CP on a polycrystalline TiO₂ surface. Likewise, Solomon et al. [66] found differences in phenol adsorption varying from physical adsorption on clean Ag surface to chemisorption on oxygenated Ag surface. Thus, the adsorption pattern resulting from the different Pd arrangements may have an important role in catalytic activity.

A relevant result is that phenol was the only HDC product detected. Previous works in the literature showed high catalytic activities for supported Pd catalysts in the HDC of chlorophenols [67]. Previous works on the use of Pd on Al₂O₃ under mild conditions [68,69] and Pd on activated carbon at higher temperature [4] reported complete conversion of 4-CP, yielding cyclohexanone and cyclohexanol as reaction products in addition to phenol. The concentration of Pd used in those works was several times higher than ours. Thus, it is remarkable that, in the operating conditions tested, the Pd nanoparticles used in the current work did not show activity for phenol hydrogenation in contrast to the behavior reported for supported Pd catalysts. To learn more on this fact, some phenol hydrogenation experiments were carried out at the same experimental conditions than for 4-CP HDC, using a 100 mg/L phenol aqueous solution, and no detectable phenol hydrogenation was observed after 4 h reaction time. Thus, the support must play a key role in supported Pd catalysts, resulting in phenol hydrogenation to by-products, such as cyclohexanone and/or cyclohexanol. The support can affect the selectivity of reactions due to its interaction with the metallic active phase, provoking changes in the electronic density of Pd nanoparticles that can affect the strength of adsorption on the metal sites [69].

 Table 2

 Pseudo-first-order rate constant and apparent activation energies values (*Ea*) for 4-CP

 HDC with Pd nanoparticles

Pd nanoparticles series	Reaction temperature (K)	Rate constant (min ⁻¹)	r ²	Ea (kJ/mol)	r ²
2	303 308 313	0.026 ± 0.004 0.057 ± 0.007 0.090 ± 0.013	0.990 0.996 0.995	100 ± 15	0.953
3	303 310 313	0.011 ± 0.002 0.030 ± 0.002 0.042 ± 0.004	0.989 0.997 0.997	105 ± 6	0.994
12	303 310 313	0.072 ± 0.008 0.181 ± 0.020 0.278 ± 0.038	0.995 0.998 0.998	106 ± 3	0.998
11	303 313 323	0.026 ± 0.004 0.093 ± 0.010 0.310 ± 0.014	0.990 0.999 0.998	100 ± 1	0.999
15	303 308 310	0.058 ± 0.013 0.129 ± 0.025 0.261 ± 0.020	0.985 0.992 0.999	118±3	0.999

A simple pseudo-first-order kinetic equation was checked to describe the rate of 4-CP disappearance:

$$(-r_{4-cp}) = \frac{-dC_{4-cp}}{dt} = k \times C_{4-cp} \tag{1}$$

$$t = 0; \quad C_{4-cp} = C_0$$

Table 2 summarizes the results obtained by fitting the experimental 4-CP concentration-time curves. Besides the rate constants values, Table 2 includes the correlation coefficients and the apparent activation energy as calculated from the Arrhenius equation. Fig. 7 depicts, as representative example, the validation of the rate curves for Pd nanoparticles of series 11. Apparent activation energy values within the range of 100-118 kJ/mol were obtained and did not show dependence on nanoparticle size. These activation energy values are significantly higher than those reported in the literature for the HDC of chlorophenols with supported Pd catalysts (21-58 kJ/mol) [17,68,70,71]. This fact was also reported by Schwab [72], who indicated that activation energies for formic acid decomposition were significantly higher for bulk metals than for supported metals (Cu/MgO, Ag/MgO and Ni/Al₂O₃) due to an effect of metal-support electronic movement, even in supports with low conductivity. Therefore, the supports seem to play an important role in the HDC pathway that modifies not only the selectivity but also the activation energy.

The activity (a) of Pd nanoparticles was evaluated from the pseudo-first-order rate constant of 4-CP disappearance and was normalized taking into account the Pd dose used in each experiment:

$$a = k \times \frac{0.150L}{m_{pd}(g)} \tag{2}$$

The available catalytic surface was estimated from the specific surface area and the Pd dose used in each experiment. The specific surface area of Pd nanoparticles was calculated assuming spherical shape from the equation [3].

$$S_a = \frac{6}{d_s \times \rho_{pd}} \tag{3}$$

Table 1 shows the specific surface area and catalytic activity values of the Pd nanoparticles tested in the HDC runs. A decrease in nanoparticle size is associated with a higher surface area giving rise to a higher activity. Fig. 8 shows this relationship for the two series of nanoparticles prepared in ethanol and methanol



Fig. 7. Time evolution of (■) 4-CP and (○) phenol in 4-CP HDC with Pd nanoparticles series 11. Reaction temperature: (a) 303 K, (b) 313 K and (c) 323 K. Predicted curves in dashed lines.



Fig. 8. Catalytic activity of Pd nanoparticles versus mean diameter: (\blacksquare) methanol and (\bigcirc) ethanol series.

media. The particles synthesized in methanol medium showed a higher activity for equivalent particle size and also a less pronounced decrease with increasing size. Therefore, not only the particle size but also the synthesis conditions are relevant for activity. In this sense, the type of reducing agent seems to be an important factor.

Other additional effects reported in the literature in relation to particle size and catalytic activity are the differences in hydrogen solubility between larger (better solubility) and smaller (worse solubility) particles [73–75], and the better resistance of larger Pd particles to inhibition/poisoning by chlorine [30,64,76]. Thus, the higher activity per unit surface area of larger particles found in the present work could be related to a combination of these factors. Changes in coordination number with size should also be taken into account since larger particles could present higher coordination number, thus favoring the bonding strength of reactants



Fig. 9. Catalytic activity per unit surface area versus catalysts total available surface: (\blacksquare) methanol and (\bigcirc) ethanol series.

and products, avoiding the inhibition/poisoning by chlorine of the catalysts and taking advantage of the higher solubility of H_2 as well.

Fig. 9 shows that as a general trend, the nanoparticles of lower diameter, whose total available surface is higher, exhibit a lower catalytic activity per unit of surface area, the trend being more clear in the case of methanol series. Therefore, the nanoparticles of higher diameter seem to have a more active surface for HDC. The ethanol series did not show significant differences in catalytic activity per unit surface area; besides, such activity values were lower than for the methanol series. Moreover, as can be seen in Fig. 10, in the case of the methanol series, a positive effect of the increase in Pd^{n+}/Pd^{0} ratio on the catalytic activity per unit surface area can be observed. The values of Pd^{n+}/Pd^0 ratio of the particles with a higher activity per unit surface area were close to the optimum reported in the literature [5,54,77,78]. In the ethanol series, the synthesis method used provided Pd^{n+}/Pd^0 ratios far from that optimum. Thus, Pd nanoparticles with extreme values of Pdⁿ⁺/Pd⁰ ratio within the range studied presented a low activity per unit surface area. Although activity should peak in Fig. 10 according to the literature [54], the synthesis method used in this work did not allow obtaining a Pd^{n+}/Pd^{0} ratio within the range suitable to verify this relationship.

Therefore, the increase in activity per unit surface with increasing nanoparticle diameter in the case of the methanol series may be related to changes in the coordination of Pd atoms and to a lower interaction potential with reactants and products, which reduces adsorption strength.



Fig. 10. Catalytic activity per unit surface area vs. Pd^{n*}/Pd^0 ratio: (\blacksquare) methanol and (\bigcirc) ethanol series.

In the case of ethanol series, the influence of Pd^{n+}/Pd^{0} ratio was not so clearly observed, which can be attributed to the narrower Pd^{n+}/Pd^{0} ratio range provided by the Pd nanoparticles synthesis method based in the reduction with ethanol.

4. Conclusions

Pd nanoparticles have been synthesized and tested as catalysts in HDC of 4-CP at mild conditions (303-323 K, 1 atm). The load of PVP, the alcohol used as reducing agent and its concentration affect the particle size. Moreover, it seems that there is also a relationship between that particle size and Pd^{n+}/Pd^{0} ratio, the smaller particles showing Pd^{n+}/Pd^{0} ratios around 0.5. The Pd nanoparticles are fairly active for 4-CP HDC, but further phenol hydrogenation was not observed opposite to the reported for supported Pd catalysts. Decreasing particle size increases catalytic activity, which can be mostly attributed to the higher surface area. However, the larger particles showed a more active surface looking at the activity per unit surface area in the case of the methanol series. The higher activity per unit surface area of larger particles may be related to their Pdⁿ⁺/Pd⁰ ratio and to coordination of Pd atoms and lower strength adsorption of reactants and products onto them. At equal others synthesis conditions, the nanoparticles synthesized using methanol as reducing agent were larger than those prepared with ethanol and at similar particle size, and the former showed a higher activity. 4-CP disappearance upon HDC can be well described by a simple pseudo-first-order rate equation. Apparent activation energy values within the range of 100-118 kJ/mol were obtained for 4-CP disappearance, being significantly higher than the reported for supported Pd catalyst, indicating some important role of the supports on the reaction pathway.

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