



# Effect of size and oxidation state of size-controlled rhodium nanoparticles on the aqueous-phase hydrodechlorination of 4-chlorophenol

J.A. Baeza, L. Calvo\*, M.A. Gilarranz, J.J. Rodriguez

Sección Departamental de Ingeniería Química, C/ Francisco Tomás y Valiente 7, Universidad Autónoma de Madrid, 28049 Madrid, Spain

## HIGHLIGHTS

- PVP and methanol load had influence in size and oxidation state of Rh NPs.
- Size and oxidation state of the Rh NPs showed a significant influence on activity.
- The lower  $\text{Rh}^{n+}/\text{Rh}^0$  ratios led to the higher activity values.
- The crossed effect of size and  $\text{Rh}^{n+}/\text{Rh}^0$  ratio showed influence on selectivity.

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## ABSTRACT

Unsupported size-controlled Rh nanoparticles of different size and oxidation state were tested as catalysts models in aqueous phase hydrodechlorination (303–318 K, 1 atm) using 4-chlorophenol (4-CP) as target compound. A chemical reduction method was employed for the synthesis of the nanoparticles using methanol and poly(N-vinyl-2-pyrrolidone) (PVP) as reducing and capping agent, respectively. The size of Rh nanoparticles was in a narrow range (1.9–4.9 nm) whereas  $\text{Rh}^{n+}/\text{Rh}^0$  ratio values were found within a wide range (0.56–3.89).

High 4-CP conversion values (c.a. 100%) were achieved at low Rh concentration ( $2.45 \cdot 10^{-3} \text{ g L}^{-1}$ ). Phenol, cyclohexanone, cyclohexanol and traces of cyclohexane were identified as reaction products. A wide range of activity values ( $1.7\text{--}29.4 \text{ mmol g}^{-1} \text{ min}^{-1}$ ) were obtained, being equivalent to the measured in a previous work with unsupported Pd nanoparticles, in spite of the fact that Rh supported catalysts have generally been reported as less active than Pd ones in liquid phase hydrodechlorination. As the size of Rh nanoparticles decreased the activity increased reaching a maximum at 2.8 nm, lower size values leading to a significant decrease of activity. A remarkable dependence of activity on the  $\text{Rh}^{n+}/\text{Rh}^0$  ratio was found, thus a higher activity corresponded to a higher relative amount of zero-valent Rh in the nanoparticles samples. Regression models were developed in order to address the significance of nanoparticles size and oxidation state for the prediction of selectivity to cyclohexanone and cyclohexanol at varying reaction times. A crossed effect of particle size and  $\text{Rh}^{n+}/\text{Rh}^0$  ratio was identified as a significant factor influencing the selectivity.

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## 1. Introduction

Liquid phase catalytic hydrodechlorination (HDC) is considered as a feasible alternative to treat wastewater bearing chlorophenolic compounds [1,2]. This type of xenobiotic compounds are toxic and carcinogenic [3,4] and have no natural ways of remediation, so chlorophenols persist in the environment and can produce both

adverse ecological effects and severe impacts on public health [5]. The main advantages of HDC compared to other techniques of potential application have been reported in the literature [6–8] and can be summarized in the ability to treat a wide range of concentrations, the operation at mild conditions and the low reagents demand. Moreover, HDC shows a high selectivity towards less toxic by-products that could be recoverable, when waste valorization is possible, or safely delivered to a further biological treatment.

In spite of its high cost, Rh has been used in catalysis, it has been used for decades due to its exceptional features useful in a diversity of chemical reactions. Particularly, Rh has shown high catalytic

\* Corresponding author. Tel.: +34 914978774; fax: +34 914973516.

E-mail addresses: [josealberto.baeza@uam.es](mailto:josealberto.baeza@uam.es) (J.A. Baeza), [luisa.calvo@uam.es](mailto:luisa.calvo@uam.es) (L. Calvo), [miguel.gilarranz@uam.es](mailto:miguel.gilarranz@uam.es) (M.A. Gilarranz), [juanjo.rodriguez@uam.es](mailto:juanjo.rodriguez@uam.es) (J.J. Rodriguez).

## Nomenclature

$a$	catalytic activity (mmol/g <sub>cat</sub> min)	$r_{ph}$	phenol conversion rate (mmol/L min)
$C_{4-cp}$	4-CP molar concentration (mmol/L)	$r_{c-one}$	cyclohexanone conversion rate (mmol/L min)
$C_{ph}$	phenol molar concentration (mmol/L)	$r_{c-ol}$	cyclohexanol conversion rate (mmol/L min)
$C_{c-one}$	cyclohexanone molar concentration (mmol/L)	$S_{c-one}$	selectivity towards cyclohexanone
$C_{c-ol}$	cyclohexanol molar concentration (mmol/L)	$S_{c-ol}$	selectivity towards cyclohexanol
$C_{Rh}$	Rh nanoparticles concentration (g/L)	$S_i$	selectivity towards compound $i$ (%), defined as moles of compound $i$ per mole of 4-CP converted
$d_s$	surface-area-weighted average mean diameter (nm)	$S_{ph}$	selectivity towards phenol
$k_x$	rate constant (min <sup>-1</sup> )	$t$	reaction time (min)
$-r_{4-cp}$	4-CP conversion rate (mmol/L min)		

action on carbonylation, hydroformylation, oxidation, reduction and HDC reactions [9–11]. Rh has also a higher melting point than other active metals used in catalysis and exhibits high resistance to acid and base attack, so Rh-based catalysts can be singularly stable, even under severe reaction conditions [9]. An adequate study of the factors affecting the catalytic performances of the active phase, i.e. particle size, shape, oxidation state, interaction with the support [12,13], is needed to acquire an in-depth knowledge on each individual contribution and the possible interrelations between factors in structure-sensitive reactions.

Singularly, the particle size of the metallic phase is a key variable regarding the performance of the catalysts in structure-sensitive reactions. A number of authors have reported that HDC is a structure-sensitive reaction [14–16], but there is no general agreement on this point [17]. In general, it is accepted that a higher surface-to-volume ratio, associated to a lower nanoparticle size of the active phase, increases the catalytic activity, although some limit has been reported for this effect [16,18]. Furthermore, variations in size could change the adsorption energies and provoke quite different effects, from the poisoning of the catalyst to the activation of the substrate, according to the nature of the molecule-particle surface adsorption [19]. The oxidation state of metal nanoparticles has also been claimed as an important factor influencing catalytic activity in structure-sensitive reactions and some authors have linked it to particle size [13], but there is no conclusive agreement on whether there is a direct or inverse relationship between size and the relative amount of electrode deficient species [13,20], and therefore, further research is needed.

In spite of the influence of metal particle size on the activity, the catalysts commonly used in structure-sensitive reactions are not prepared with an accurate control of that feature. In the last few years, the methods of synthesis that allow obtaining nanoparticles in a narrow range of size have attracted much attention enabling the investigation on chemical and physical size-dependent properties. Thus, the studies on the preparation and application in nano-sized catalysts have increased significantly [21]. Different methods of synthesis addressed to obtain size-controlled nanoparticles have been reported [22–24]. Among them, chemical reduction has been frequently used due to its simple mechanism consisting on the reduction of a metal salt with a reducing agent (e.g. alcohols, potassium borohydride), using a capping agent (e.g. poly(N-vinyl-2-pyrrolidone), polyvinyl alcohol, dodecylamine) in order to prevent undesired particle growth and aggregation. A number of authors have prepared colloidal Rh nanoparticles of controlled size using a chemical reduction method to test their behavior as catalysts in different reactions [9,25–27]. However, the dependence of activity on the particle size is so far not clear in HDC, where Rh-based catalysts have shown highly active [11,28].

Therefore, the objective of the current work is to address the effect of both initial size and oxidation state of unsupported Rh nanoparticles, used as catalysts models, on the activity and

selectivity in 4-CP HDC in aqueous phase in order to gain an in-depth knowledge that could be useful for catalysts design. On the other hand, a direct comparison between the Rh nanoparticles synthesized in this work and those of Pd reported in our previous one [20] can provide a better understanding of the different behavior of both metals.

## 2. Experimental

### 2.1. Materials

Rh(III) chloride (98%, Sigma Aldrich Co.) was used as precursor salt to synthesize Rh nanoparticles. Methanol (99.5%, Panreac Quimica S.A.U.) was used as reducing agent and poly(N-vinyl-2-pyrrolidone) (PVP, average molecular weight: 40,000, Sigma-Aldrich Co.) was used as capping agent. Hydrogen (>99%, Praxair Spain, S.L.) was used to carry out catalytic HDC and for reducing Rh nanoparticles (sample 1 to sample 1R). NaHCO<sub>3</sub> (99.7%, Merck, GmbH) and Na<sub>2</sub>CO<sub>3</sub> (99.8%, Panreac Quimica, S.A.U) were used to prepare a carbonate-bicarbonate buffer for the HDC runs at basic pH (10.4). All the reagents were used as received without previous purification.

### 2.2. Synthesis and characterization of Rh nanoparticles

A  $2 \cdot 10^{-3}$  M Rh aqueous solution (pale pink color) was obtained by mixing RhCl<sub>3</sub> (0.5 mmol), HCl (1 mmol) and distilled water up to a final volume of 250 mL. An aliquot of 30 mL of the acidic  $2 \cdot 10^{-3}$  M Rh solution and 70 mL of methanol/water solution and PVP were mixed to obtain the colloidal synthesis of Rh nanoparticles. The mixture was refluxed in a flask connected to a Liebig condenser for 5 h at 363 K under atmospheric pressure. In the case of the samples of nanoparticles prepared with the lowest concentration of methanol (10%, v/v), it was necessary to increase the temperature from 363 to 368 K in order to achieve complete reduction of Rh. The colloidal suspension of nanoparticles (100 mL) was concentrated up to a final volume of approximately 10 mL in a rotary evaporator (Büchi). The synthesis of sample 1R was performed by reducing sample 1 under hydrogen flow (50 N mL min<sup>-1</sup>) at 363 K during 30 min. Different values of PVP/Rh ratio (5–35 mol/mol) and methanol concentration (10–40%, v/v) were used in the synthesis with the aim of obtaining Rh nanoparticles samples of different sizes and Rh<sup>III</sup>/Rh<sup>0</sup> ratios. Table 1 summarizes the working conditions used for the synthesis of nanoparticles and the corresponding nomenclature.

The size of Rh nanoparticles was measured by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) was used to determine the Rh<sup>III</sup>/Rh<sup>0</sup> ratio. TEM micrographs were obtained in a JEM-3000F + XEDS microscope at 300 kV (JEOL). ImageJ 1.44i software was used for data treatment of digital TEM

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