



# Exploring the catalytic properties of supported palladium catalysts in the transfer hydrogenolysis of glycerol



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## ABSTRACT

The transfer hydrogenolysis of glycerol promoted by supported palladium catalysts is reported. The reactions were carried out under mild conditions (453 K and 5 bar of N<sub>2</sub>) in absence of added hydrogen by using the reaction solvent, 2-propanol, as hydrogen source. The catalytic results are interpreted in terms of metal (Pd)–metal (Co or Fe) interaction that modifies the electronic properties of palladium and affords bimetallic PdM sites (M = Co or Fe), thus enhancing the catalytic properties of the systems in the conversion of glycerol as well as in the selectivity to 1,2-propanediol and 1-propanol. The transfer hydrogenolysis mechanism is here elucidated and involves the glycerol dehydration to 1-hydroxyacetone and the subsequent hydrogenation of 1-hydroxyacetone to propylene glycol.

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## 1. Introduction

The use of renewable biomass for bulk chemicals production provides a viable route for the modern chemical industry to alleviate its historical dependence on fossil resources and to reduce, at the same time, CO<sub>2</sub> emissions [1]. Among several catalytic processes for upgrading biomass derived compounds, “bio”-hydrogenolysis has gained a lot of attention bearing the potential to bridge available technologies and future refinery concepts [2]. Surely, one of the main targets is currently to make the hydrogenolysis a self-sustainable process and to reduce the costs related to hydrogen purchase, transport and storage and to minimize safety problems in industrial hydrogenation processes. Catalytic transfer hydrogenolysis (CTH) reactions [3] represent an interesting alternative to the direct use of molecular hydrogen. Together with traditional hydrogen donors (cyclohexane, hydrazine, formic acid and formates), simple alcohols can be used in CTH reactions with secondary alcohols generally more active than primary alcohols due to the higher electron-releasing inductive effect.

Glycerol is the major by-product in the industrial production of biodiesel and it is also a model molecule for biomass derived polyols keeping the potential to become a new primary building block [4]. Indeed, glycerol can be converted, through the hydrogenolysis reaction [5], into valuable products such as 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO) and ethylene glycol (EG), widely used in the synthesis of polyester fibers and resins, pharmaceuticals, cosmetics, flavors and fragrances, antifreeze, among others.

While several active metals and metal oxides supports [6] have been widely studied in the hydrogenolysis of glycerol, palladium has not been investigated significantly. In recent years, the coprecipitated palladium on iron oxide (Pd/Fe) catalyst, has been deeply tested showing superior performance in a number of reactions such as: aqueous-phase reforming of ethylene glycol [7], ethylene glycol dehydroxylation [8], aliphatic carbonyl reduction [9] and glycerol hydrogenolysis [10]. Furthermore, the same Pd/Fe catalyst can be used in the CTH of glycerol [11] and in the sequential transfer hydrogenation/hydrogenolysis of furfural and 5-hydroxymethylfurfural [12].

It is generally accepted that coprecipitated catalysts are characterized by an intimate interaction between the active metal and the oxide-support; however, mixture of single/mixed oxides phases and not uniform distribution of the active metal do also occur [13]. This complexity, by itself, does not allow to fully understand the role of the different components in coprecipitated catalysts. In this context, a comparison between the catalytic activity of palladium catalysts supported on iron oxide and cobalt oxide prepared both

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by coprecipitation and impregnation techniques should be widely welcome.

The present study aims to clarify the effect of individual parameters such as surface area, metal particle size, oxidation state of palladium, role of the support and presence of bimetallic clusters which may affect the catalytic properties of palladium catalysts in the transfer hydrogenolysis of glycerol. More fundamental understanding might, in fact, help a further and more rational optimization of the synthesis parameters in order to drive the catalytic properties of coprecipitated catalysts. Therefore, X-ray diffraction (XRD), transmission electron microscopy (TEM), CO chemisorption ( $S_{\text{act}}$ ), temperature-programmed reduction by  $\text{H}_2$  ( $\text{H}_2$ -TPR) and X-ray photoelectron spectroscopy (XPS) were performed to characterize structures and surface properties of palladium catalysts.

The catalytic conversion of glycerol to 1,2-propanediol, 1-propanol and ethylene glycol was carried out in absence of additional  $\text{H}_2$  with the reaction solvent (2-propanol) being the source of the necessary hydrogen. The comparison of results involves, on one hand, coprecipitated Pd/Co and Pd/Fe catalysts and, on the other hand, impregnated Pd/ $\text{Co}_3\text{O}_4$ , Pd/CoO, Pd/ $\text{Fe}_2\text{O}_3$  and Pd/ $\text{Fe}_3\text{O}_4$  samples as well as a model catalyst such as commercial Pd/ $\text{SiO}_2$ . This broad set of Pd catalysts was chosen to get a wide framework of the factors that characterize the catalysts behavior.

The relationship between the physico-chemical properties of palladium based catalysts and their catalytic performance is elucidated. The final aim is to draw up a deep insight on the key factors which make coprecipitated palladium systems very peculiar and unique in affording glycerol CTH. The correlation of the physico-chemical properties of the investigated Pd-based catalysts with the catalytic tests on glycerol CTH suggests that the catalyst preparation method plays a crucial role in determining the electronic properties of palladium and in affording bimetallic PdM sites ( $M = \text{Co}$  or  $\text{Fe}$ ) so that unusual catalytic properties can derive.

Furthermore, an insight on the ability of palladium catalysts to dehydrogenate 2-propanol, thus supplying the hydrogen necessary for the CTH reaction to occur, is included. A thorough examination of the reaction mechanism with hydroxyacetone (AC) being the key-intermediate is finally proposed.

## 2. Experimental

### 2.1. Catalysts preparation

All chemicals were purchased from Sigma–Aldrich and used without further purification.

Supported palladium catalysts, with a nominal palladium loading of 5 wt%, were obtained by using two different techniques: coprecipitation and impregnation.

Pd/Co and Pd/Fe catalysts were prepared by using the coprecipitation technique and were obtained from aqueous solutions of the corresponding inorganic precursors. Anhydrous palladium chloride (Fluka, purum, 60% palladium) was dissolved in HCl and cobalt(II) nitrate hexahydrate (Fluka, purity  $\geq 99\%$ ) or iron(III) nitrate nonahydrate (Fluka, purity  $\geq 98\%$ ) were added. The obtained aqueous metal salt solutions were added dropwise into a 1 M aqueous solution of  $\text{Na}_2\text{CO}_3$ . After filtration, samples were washed until complete removal of chloride ions, dried for 1 day at 353 K under vacuum and further reduced at 473 K for 2 h under a flow of hydrogen.

Catalysts prepared by incipient wetness impregnation (Pd/ $\text{Co}_3\text{O}_4$ , Pd/CoO, Pd/ $\text{Fe}_3\text{O}_4$  and Pd/ $\text{Fe}_2\text{O}_3$ ) were obtained by adding a solution of palladium(II) acetylacetonate (Aldrich, purity 99%) dissolved in acetone to commercially available supports  $\text{Co}_3\text{O}_4$  (Aldrich,  $S_{\text{BET}} = 40\text{--}70 \text{ m}^2 \text{ g}^{-1}$ ), CoO (Aldrich,  $S_{\text{BET}} = 7 \text{ m}^2 \text{ g}^{-1}$ ),  $\text{Fe}_2\text{O}_3$  (Sigma–Aldrich,  $S_{\text{BET}} = 4 \text{ m}^2 \text{ g}^{-1}$ ) and  $\text{Fe}_3\text{O}_4$  (Aldrich,  $S_{\text{BET}} = 60 \text{ m}^2 \text{ g}^{-1}$ ). After impregnation, samples were dried

for 1 day under vacuum at 353 K and reduced at 473 K for 2 h under a flow of hydrogen.

In order to determine the exact amount of Pd on our supports an X-ray fluorescence (XRF) analysis was carried out and the results are reported in Table 1.

### 2.2. Catalysts characterization

XRD data were acquired at room temperature on a Philips X-Pert diffractometer by using the Ni  $\beta$ -filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). Analyses were performed on samples reduced at 473 K for 2 h and registered in the  $2\theta$  range of  $10\text{--}80^\circ$  at a scan speed of  $0.5^\circ \text{ min}^{-1}$ . Diffraction peaks were compared with those of standard compounds reported in the JPCDS Data File.

The particle size and the relative morphology of investigated catalysts were analyzed by performing Transmission Electron Microscopy (TEM) measurements using a JEM-2100F (JEOL, Japan) operating at an acceleration voltage of 200 kV and directly interfaced with a computer controlled-CCD for real-time image processing. The specimens were prepared by grinding the reduced catalyst powder in an agate mortar and then suspending it in 2-propanol. A drop of the suspension, previously dispersed in an ultrasonic bath for 1 h, was deposited on a copper grid coated by a holey carbon film. After evaporation of the solvent, the specimens were introduced into the microscope column. Particle size distributions were obtained by counting several hundred particles visible on the micrographs on each sample. From the size distribution, the average diameter was calculated by using the expression:  $d_n = \sum n_i d_i / n_i$  where  $n_i$  is the number of particles of diameter  $d_i$ .

$\text{H}_2$ -TPR measurements were performed using a conventional TPR apparatus. The dried samples (50 mg) were heated at a linear rate of  $10 \text{ K min}^{-1}$  from 233 to 1273 K in a 5 vol% of  $\text{H}_2/\text{Ar}$  mixture at a flow rate of  $20 \text{ cm}^3 \text{ min}^{-1}$ . The  $\text{H}_2$  consumption was monitored with a thermal conductivity detector (TCD). A molecular sieve cold trap (maintained at 193 K) and a tube filled with KOH, placed before the TCD, were used to block water and  $\text{CO}_2$ , respectively. The calibration of signals was done by injecting a known amount of  $\text{H}_2$  into the carrier.

The active surface areas ( $S_{\text{act}}$ ) were determined by CO-pulse chemisorption technique using a Micromeritics ChemiSorb 2750 system at room temperature. Samples were first reduced with  $\text{H}_2$  at 25 stp ml/min using a  $10 \text{ K min}^{-1}$  ramp up to 473 K, then cleaned with He at 25 stp ml/min for 15 min and finally cooled to room temperature. CO pulses (0.64 stp ml, 5% CO/He –  $1.29 \mu\text{mol CO}$  each injection) were injected until saturation.  $S_{\text{act}}$  values were calculated by assuming a CO/Pd stoichiometry of 1 and a surface area of  $7.87 \times 10^{-20} \text{ m}^2$  per Pd atom [7].

XPS measurements were performed on a JPS-9010MC photoelectron spectrometer using an Al  $\text{K}\alpha$  (1486.6 eV) radiation source. After the reduction treatment, samples (denoted as “reduced”) were introduced into the XPS chamber, avoiding exposure to air. In order to obtain the XPS spectra, the pressure in the analysis chamber was maintained at  $5 \times 10^{-9} \text{ mbar}$ . All spectra were recorded at room temperature, and the binding energies (BE) were set taking the C 1s peak at 284.6 eV as reference. XPS spectra of reduced catalyst samples were also recorded after an additional “in situ reduction” condition (denoted as “in situ-reduced”) in an auxiliary reaction chamber at 473 K under 100 Pa  $\text{H}_2$  for 4 h.

Peak deconvolution and fitting analyses were performed using the peak-fitting software “SPECURF, JEOL” including the spin-orbit splitting and relative intensities of the spin-orbit components fixed.

### 2.3. Catalytic tests

Hydrogenolysis reactions were performed in a 250 ml stainless steel autoclave at a stirring speed of 500 rpm. The reactor was first

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