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Synthesis and hydrodeoxygenation activity of Ni₂P/C – Effect of the palladium salt on lowering the nickel phosphide synthesis temperature

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1. Introduction

Many studies in the literature have shown the importance of residual biomass as a renewable source of biofuels and chemicals [1–8]. Through different processes, biomass may be converted into solid (bio-char), liquid (bio-oil) or gaseous (bio-gas) products. For biofuels production, bio-oil is of particular interest [9], but its high oxygen content does not allow its direct use as fuel. Different upgrading methodologies may be applied to reduce the bio-oil oxygen content [10–13], with hydrotreatment (HDT) being one of them. This technology is well developed and consolidated in oil industry, mainly for sulfur (hydrodesulphurization - HDS) and nitrogen (hydrodenitrogenation - HDN) removal. Despite this, its application in oxygen removal (hydrodeoxygenation - HDO) has received limited attention until concern about biomass-derived fuels arose. The interest in HDO started about 10 years ago, usually employing model oxygenated molecules as bio-oil representatives [14-18].

The main problem concerning HDO of bio-oil using conventional Co(Ni)-promoted Mo(W)S₂ HDT catalysts is that they present severe deactivation [19,20]. Therefore, several studies have been performed searching for alternative HDO catalysts [14,21,22]. Two works published during the 90s using metal phos-

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ABSTRACT

The effect of the nature of Pd salt (PdCl₂, Pd(NO₃)₂ or Pd(acac)₂) in lowering Ni₂P/C synthesis temperature and their effect on guaiacol hydrodeoxygenation reaction were investigated. Pd addition led to a partial lowering of Ni_xP_yO_z/C (precursor) reduction temperature. For each Pd salt, both the decrease in synthesis temperature and the degree of reduction of Ni_xP_yO_z were different. While the latter was related to Pd particle size (the bigger the particles were, the higher was the amount of Ni_xP_yO_z reduced), the former depends both on the contact between Pd and Ni_xP_yO_z (direct contact is needed) and on Pd particle size (the smaller the particles, the higher the decrease in synthesis temperature). Reaction data revealed that Pd addition suppressed guaiacol hydrogenation. Catalysts characterization revealed that the product distribution was dependent upon the relative proportion on the two types of Ni active sites of Ni₂P.

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phides as HDT catalysts caught the attention of the scientific community [23,24]. Among the different metal phosphides, nickel phosphide (Ni₂P) exhibits catalytic performances similar or superior to that of conventional HDT catalysts in HDS and HDN reactions [25–31]. Shu and Oyama [28] showed that carbonsupported nickel phosphide has a better performance for HDS and HDN reactions than silica-supported nickel phosphide and NiMoS/Al₂O₃ catalysts. Besides that, it has been shown that nickel phosphide presents good catalytic activity and has no deactivation issues when employed for the HDO of model molecules using high hydrogen partial pressures [20,32–35].

Despite being presented in the literature as a good alternative for conventional HDT catalysts, transition metal phosphides synthesized from the corresponding phosphates have a major disadvantage, which is their relatively high synthesis temperature ($\geq 650 \,^{\circ}$ C) when compared to the traditional HDT catalysts. Hence, many studies have been carried out in an effort to synthesize transition metal phosphides at lower temperatures [36–42]. Among them, Teixeira da Silva et al. [41] were able to lower the nickel phosphide synthesis temperature by approximately 200 $^{\circ}$ C through the incorporation of small amounts of PdCl₂ (0.1/0.5 / 1.0 wt.% Pd) to the silica-supported nickel phosphate precursor. The authors attributed the temperature lowering to the occurrence of hydrogen spillover and activation over Pd particles during reduction: the formed atomic hydrogen is more reactive than molecular hydrogen and is able to reduce phosphate particles at





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lower temperatures. Based on HDS catalytic activity data, they also proposed that Pd particles were covered by the as-formed Ni₂P phase and therefore had no participation at all in the reaction.

The main objectives of this work are therefore (1) to evaluate the effect of the Pd source (PdCl₂, Pd(acac)₂ or Pd(NO₃)₂) on lowering the synthesis temperature of carbon-supported nickel phosphide catalysts and (2) to evaluate the obtained catalysts in guaiacol HDO reaction as this phenolic molecule is often used as a representative of refractory oxygenated compounds present in bio-oils [20,43–51]. More precisely, the main reason for using guaiacol as a model compound lay on the fact that this molecule is a by-product of lignin degradation. It also presents two oxygenated functions (phenolic and methoxy) making it difficult to be completely deoxygenated.

2. Experimental

2.1. Synthesis

2.1.1. Ni_xP_vO_z/C

Ni₂P/C precursor (Ni_xP_yO_z/C) synthesis was based on a two-step procedure comprising: (1) an incipient wetness impregnation of activated carbon support (Merck, 772 m² g⁻¹, pore volume of 0.64 cm³ g⁻¹) with a solution prepared by dissolving adequate amounts of nickel nitrate and ammonium hydrogen phosphate salts and (2) thermal treatment of the impregnated sample under inert atmosphere (He) in order to have the nickel species transformed into nickel phosphate (Ni_xP_yO_z). For obvious reasons, *i.e.* activated carbon total oxidation, this thermal treatment could not be done under oxidizing atmosphere. Appropriate quantities were used to obtain catalysts with 30 wt.% Ni₂P after the reduction step.

Initially, 12.12 g of nickel(II) nitrate hexahydrate $(Ni(NO_3)_2 \cdot 6H_2O - Vetec, PA, 97\%$ pure) and 4.36 g of ammonium hydrogen phosphate $((NH_4)_2HPO_4) - Vetec, ACS, 98\%$ pure) were each solubilized in 20.5 mL of distilled water. Solution A $((NH_4)_2HPO_4)$ was then added dropwise to solution B $(Ni(NO_3)_2 \cdot 6H_2O)$ under magnetic stirring. After complete addition of solution A, approximately 4 mL of nitric acid $(HNO_3 - Vetec, PA, 65 wt.\%$ solution) was added dropwise under stirring in order to solubilize the precipitate formed after mixing solutions A and B. Thereafter, 7 g of the activated carbon support was impregnated with the prepared solution by means of successive impregnations (impregnations until wet point was reached intercalated with 1 h drying steps at 110 °C).

Once all the solution was incorporated into the carbon support, the sample was dried at 110 °C overnight. The obtained solid was then submitted to a thermal treatment at 500 °C/6 h in a quartz reactor under He flow (10 mL min⁻¹ He per gram of sample) (He – Linde, 99.995% pure). The obtained sample will be hereafter referred to as Ni_xP_yO_z/C.

2.1.2. $Pd(s) - Ni_x P_y O_z/C$

The palladium-containing samples $(Pd(s)-Ni_xP_yO_z/C)$ synthesis was also based on a two-step procedure comprising: (1) incipient wetness impregnation of $Ni_xP_yO_z/C$ sample with palladium solutions prepared from different salts (chloride, nitrate and acetylace-tonate) and (2) thermal treatment under inert atmosphere. The amount of palladium added was such in order to obtain a 1 wt.% Pd loading after the reduction step.

Due to solubility issues, different solvents (water, acetone and hydrochloric acid) were used for each Pd salt. Palladium nitrate (Pd(NO₃)₂·xH₂O – Aldrich, PA) was solubilized in distilled water, palladium acetylacetonate (Pd(C₅H₇O₂)₂ – Aldrich, PA) in acetone ((CH₃)₂CO – Vetec, PA, 99.5% pure) while palladium chloride (PdCl₂ – Aldrich, PA, 99% pure) was dissolved with hydrochloric acid (HCl

– Vetec, PA, 37% solution) and distilled water. $Pd(NO_3)_2$ and Pd (acac)₂ were easily dissolved in water and acetone, respectively, while $PdCl_2$ was solubilized employing the procedure described elsewhere [41].

Once each Pd source solution was prepared, they were used to impregnate Ni_xP_yO_z/C. Successive impregnations followed by 1 h drying steps at 110 °C were performed until all the solution was used. The impregnated sample was then dried overnight at 110 °C. In order to decompose the impregnated Pd salts, each sample was submitted to thermal treatment at 350 °C/2 h under pure He flow (10 mL min⁻¹ He per gram of sample). Since it has been concluded in previous studies done by our group that at 350 °C each one of the palladium salts is totally decomposed, this temperature was used. The obtained samples were labeled as Pd(s)–Ni_xP_y-O_z/C, where (s) stands for the employed Pd source: (C) for PdCl₂, (A) for Pd(acac)₂, and (N) for Pd(NO₃)₂.

2.1.3. 30 wt.% Ni₂P/C and 1 wt.% Pd(s) 30 wt.% Ni₂P/C

Promoted and non-promoted nickel phosphide catalysts were obtained by temperature-programmed reduction of their precursors under pure hydrogen flow (H₂ – Alphagaz, 1 mL min⁻¹ H₂ per mg of precursor) and 1 °C min⁻¹ heating rate up to 650 °C/0 h (Ni_xP_yO_z/C) or 550 °C/1 h (Pd(s)–Ni_xP_yO_z/C). After reduction, catalysts were cooled to room temperature in inert atmosphere using either helium (He – Alphagaz, <5.5 ppm total impurities) or argon (Ar – Alphagaz, <5.5 ppm total impurities). Reduced samples with and without Pd were labeled as Pd(s)–Ni₂P/C and Ni₂P/C, respectively, with (s) denoting the palladium salt employed.

Due to the Ni₂P pyrophoric nature, all reduced samples were passivated for 2 h at room temperature under 50 mL min⁻¹ of a 2% (v/v) O₂/Ar gas mixture before ex situ characterization. After the passivation step, all samples could be manipulated in air and stored for further characterization.

2.2. Characterization

2.2.1. Temperature programmed reduction (TPR)

TPR analyses were carried out in a tubular quartz reactor in line with a VG 40 Thermo quadrupole mass-spectrometer. For each test, the reactor was loaded with 0.05 g of either $Ni_xP_yO_z/C$ or Pd (s)– $Ni_xP_yO_z/C$. Analysis conditions were the same for all cases: a flow of 50 mL min⁻¹ of pure H₂ and a heating rate of 1 °C min⁻¹ up to 650 °C.

The signal due to water (m/z = 18) was recorded during TPR to follow the reduction process. Other mass to charge (m/z) signals were also recorded: 2 (H₂), 12 (C), 14 (N), 16 (CH₄), 28 (CO and/ or N₂), 31 (P), 32 (O₂), 34 (PH₃), 44 (CO₂), 62 (P₂). Water formation profiles were deconvoluted using Peak Fit 4 software and each contribution was simulated by means of Gauss-Lorentz functions (65/35 Gaussian/Lorentzian weight).

2.2.2. X-ray diffraction (XRD)

XRD analyses of precursors and reduced catalysts (in the passivated form as detailed in Section 2.1.3) were performed using a D8 Bruker diffractometer equipped with a Ni filter (Cu K α_1 radiation, $\lambda = 1.542$ Å). Powder patterns were recorded in the 4° < 2 θ < 90° range with steps of 0.020°. PDF4 (2013) database was used to identify the observed crystalline phases. Rietveld refinement was also applied to calculate Ni₂P crystallite size using Topaz software.

2.2.3. High resolution transmission electron microscopy (HR-TEM)

HR-TEM analyses of non-reduced samples were performed in a JEOL JEM-2100 microscope at 200 kV. Energy Dispersive X-ray (EDX) analysis was performed using Oxford Instruments X-Max^N analyzer and Aztec software. Samples were prepared by dispersion

in methanol with sonication before supporting on holey carbon film copper grids.

2.2.4. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

ICP was used to determine the Ni, P and Pd contents in reduced solids. Samples were first dissolved in $H_2SO_4 + aqua regia$ (Pd containing samples) or $H_2SO_4 + HNO_3$ (sample without Pd) at 250–300 °C and the obtained solutions were analyzed using an ACTIVA – Horiba Jobin Yvon spectrometer.

2.2.5. In situ CO chemisorption and CO temperature-programmed desorption (TPD)

In situ CO chemisorption and TPD analyses were carried out in a homemade multipurpose unit. A four channels Type 247 MKS mass flow meter was used to select the gas to be used in each analysis and the exit gases were analyzed by a QME 200 Pfeiffer mass spectrometer.

In a typical test, a quartz reactor was loaded with 0.2 g of the sample to be analyzed and connected to the multipurpose unit. After reduction using the procedure described in Section 2.1.3, H₂ flow was changed to He (50 mL min⁻¹) and the reduced catalyst was cooled to room temperature. Once all signals were stabilized at ambient temperature, CO (2.4 mL of a 20% (v/v) CO/He mixture) was pulsed into the reactor until 3 successive peaks presented the same intensity denoting complete saturation of the sample. CO uptake (µmol g_{cat}⁻¹) was calculated using Eq. (1):

$$CO_{UPTAKE} = \frac{n_{CO} \cdot \sum_{i=1}^{n_{pulses}} \left(1 - \frac{A_i}{A_{CO}}\right)}{m_{cat}}$$
(1)

where n_{CO} (µmol) is the amount of CO injected per pulse, A_i is the area of the m/z = 28 peak obtained for the *i*th pulse, A_{CO} is the area of m/z = 28 peak after stabilization (no CO chemisorption) and m_{cat} (g) is the weight of catalyst after reduction.

Once the CO signal reached stabilization, the reactor was heated up to 1000 °C using a 15 °C min⁻¹ heating ramp in order to acquire the CO TPD profile of the analyzed catalysts. The signal evolution of m/z = 28 was then deconvoluted using the Peak Fit 4 software. Based on literature data [52], it was assumed that Ni₂P presents 2 different types of active sites and both components were simulated by means of Gaussian functions.

2.3. HDO catalytic activity tests

Guaiacol (Acros Organics, 99%) HDO was carried out in a 300 mL Parr autoclave reactor. The reaction mixture consisted of 3 mL of guaiacol, 300 μ L of hexadecane (Sigma–Aldrich, 99%) used as internal standard and 100 mL of dodecane (Sigma–Aldrich, 99%). All experiments were performed at 300 °C and 30 bar (H₂) during 6 h and with a catalyst weight of approximately 0.15 g.

In a typical experiment, 0.2 g of catalyst precursor was reduced in a U-shaped quartz reactor with stopcock valves, using the conditions described in Section 2.1.3. Once reduction was completed and the sample cooled to room temperature, the stopcock valves were closed and the reactor containing the reduced sample was transferred to an inert glove box constantly fed with argon flow and equipped with a precision balance. The autoclave and the reaction mixture were also transferred to the glove box and the purging with argon was performed over 30 min to remove residual oxygen from the inert glove box. Thereafter, the reduced catalyst was weighed and loaded into the autoclave. After that, the autoclave was filled with the reaction mixture, taken out from the inert box and connected to the Parr reactor system. After a new purging procedure with nitrogen to remove oxygen from the dead volume of the reactor, stirring (800 rpm) was initiated and an initial liquid sample was collected, corresponding to reaction time zero t_{00} at room temperature. Thereafter, heating was started and a new liquid sample was collected when the reaction temperature (300 °C) was reached, corresponding to reaction time zero t_0 . These two time zero reaction samples were collected in order to verify whether there was guaiacol conversion either at room temperature or during the heating step. Thereafter, hydrogen was introduced in order to reach a pressure of 30 bar of H₂ while reaction time measurement was started. Liquid samples were collected after 20 min (t_1) and then hourly up to 6 h of reaction (t_2 - t_7). All collected samples were analyzed in a Hewlett Packard 5890 SERIES II gas chromatograph (GC) equipped with a flame ionization detector (FID) and a DB-5MS column (30 m × 0.32 mm × 0.25 µm). Response factors for each of the identified products were taken from the literature, allowing quantitative analysis of the products.

Given that guaiacol is a molecule with 2 oxygenated groups and an aromatic ring, it can be transformed into different compounds. oxygenated or not. Therefore, conversion is expressed in this work either as total conversion (X_T) or as HDO conversion (X_{HDO}) . The former is defined as the sum of all of the products obtained during the test divided by the initial guaiacol, while the latter is defined as the sum of totally deoxygenated products divided by the initial guaiacol. Selectivity values were calculated by the ratio between the molar fraction of each formed product (y_i) and the total conversion X_T . According to this definition, selectivity for time zero of reaction cannot be mathematically calculated because X_T is null at the beginning of the reaction. However, extrapolating the selectivity curves to time zero allows to determine whether the primary products are being formed through parallel (finite values of selectivity for the primary products) or sequential reactions (zero selectivity for secondary products).

Turnover frequency (TOF) values were calculated as the ratio between guaiacol reaction rates ($r_{GUA} - \text{mol } \text{g}_{cat}^{-1} \text{s}^{-1}$) and the number of active sites determined by CO chemisorption (CO_{UPTAKE} – mol g_{cat}^{-1}). For each test, the CO uptake was experimentally determined (Section 2.2.5) while reaction rates were calculated by Eq. (2):

$$r_{\rm GUA} = \frac{n_{\rm GUA}^0 \cdot S}{m_{\rm cat}} \tag{2}$$

where n_{GUA}^0 is the amount of substance of guaiacol at reaction time zero (mol), *S* is the slope of $X_T vs$. time curve at $t_0 (s^{-1})$ and $m_{\text{cat}} (g)$ is the weight of catalyst.

3. Results

3.1. Precursor characterization

Water formation profiles obtained during TPR of the samples Pd $(s)-Ni_xP_yO_z/C$ are presented in Fig. 1. While the Pd-free phosphate displays one large and asymmetrical reduction peak with maximum at 550 °C, Pd-promoted samples show an extra reduction peak in the 350-450 °C temperature range. The additional peak is too intense and at too low a temperature to be solely attributed to the reduction of cationic or partially oxidized Pd (1 wt.%) so it is reasonable to attribute this to the lowering of the $Ni_x P_y O_z$ reduction temperature as a result of the noble metal presence/or the promotional effect of the noble metal. Contrary to what was observed for the reduction of Pd-Ni_xP_yO_z/SiO₂ [41], in which only one single peak was found, data in Fig. 1 show that the Pd effect on lowering the reduction temperature on carbon-supported samples is only partial. Moreover, depending on the Pd salt used, the first reduction peak is observed at different temperatures and has different intensities. It is noteworthy that during the TPR of the pure support (results not presented) no water formation was



Fig. 1. Water formation profiles during TPR of $Ni_xP_yO_z/C$ and $Pd(s)-Ni_xP_yO_z/C$ (reduction conditions: $1 \degree C \min^{-1}$ up to 650 $\degree C$).

observed, only CO, CO₂ and CH₄ formation at temperatures around 680, 450, and 670 °C, respectively. While CO and CO₂ formation is due to the decomposition of the superficial groups of the support, CH₄ formation results from carbon methanation. Consequently, the water profiles observed in Fig. 1 are solely related to nickel phosphate reduction.

Deconvolution of the TPR profiles is presented in Fig. 1, where it can be seen that the reduction profile of the non-promoted $Ni_x P_v O_z / C$ catalyst presents three contributions. The first one can be related to a surface reduction of the nickel phosphate particles leading to the formation of a partially reduced nickel phosphate layer that slows down hydrogen diffusion thus resulting in the second and third contributions represented by the high temperature reduction peaks. For Pd-promoted Ni_xP_yO_z/C samples, the first peak shifts to lower temperatures depending on the nature of the Pd source and its relative area (shown in Table 1) changes according to the type of Pd precursor. The shift of the maximum of the first reduction peak follows the order Pd(N) > Pd(A) > Pd(C) while the change in relative area increases according to $A_{Pd(A)} < A_{Pd(N)} < A_{Pd(C)}$. Therefore, Pd particles derived from Pd(NO₃)₂ led to highest shift in the synthesis temperature while Pd particles resultant from PdCl₂ were able to reduce a bigger amount of phosphate.

XRD patterns of the different precursors are presented in Fig. 2 and all of them present a large and broad peak around 26° and small one at 45°, which are attributed to the carbon support. Moreover, the absence of any peak due to nickel phosphate indicates that this species was present as an amorphous phase (nickel

Table 1Temperature of the maxima and relative area of the deconvoluted water formationprofiles of Fig. 1 (peaks were fitted using Gauss-Lorentzian functions).

Sample	1st Peak		2nd Peak		3rd Peak	
	T (°C)	A _{rel.} (%)	T (°C)	A _{rel.} (%)	T (°C)	A _{rel.} (%)
Ni _x P _y O _z /C Pd(C)-Ni _x P _y O _z /C Pd(A)-Ni _x P _y O _z /C Pd(N)-Ni _x P _y O _z /C	463 443 430 420	15.0 32.7 22.3 23.2	508 490 483 491	25.9 23.0 19.8 18.3	546 533 540 535	59.1 44.3 57.9 58.5



Fig. 2. XRD patterns of Ni_xP_yO_z/C and Pd(s)–Ni_xP_yO_z/C samples.

orthophosphate – Ni₃(PO₄)₂) in all samples as seen in other works from the literature [41]. Because phosphorous excess was used in the synthesis to guarantee Ni₂P formation, then it can be assumed that the Ni_xP_yO_z is composed mainly of amorphous Ni₃(PO₄)₂ and small amounts of P₂O₅. In this way, the water formed during reduction is essentially due to the orthophosphate reduction. On the other hand, Pd-promoted samples presented an additional peak at $2\theta = 40^{\circ}$ attributed to metallic Pd particles. This result suggests that all of the different palladium salts were decomposed during thermal treatment under He and underwent reduction most probably due to the reducing nature of the carbon support. Moreover, the data show that the Pd particle size changes depending on the salt employed. Considering the change in intensity and width of the peak at $2\theta = 40^{\circ}$, Pd particle size increased in the order *Pd*(*A*) < *Pd*(*N*) \ll *Pd*(*C*).

HR-TEM micrographs of the non Pd-promoted Ni_xP_yO_z/C and Pd (s)–Ni_xP_yO_z/C are presented in Fig. 3. The Ni_xP_yO_z particles exhibit a single morphology corresponding to agglomerated quasi-spherical clusters over the "orange peel" type morphology typical of poorly crystalline or amorphous carbon (Fig. 3a inset). Pd-containing samples presented a similar morphology but upon impregnation particles of palladium can be seen intimately mixed within the Ni_xP_yO_z/C support (Fig. 3b–d). As seen in the XRD (Fig. 2) the particle sizes increase in the order $Pd(A) < Pd(N) \ll Pd(C)$ with larger Pd particles clearly apparent in the Pd(C)–Ni_xP_yO_z/C catalyst prepared from PdCl₂ (Fig. 3d).

Elemental EDX mapping results for the non-promoted and Pdpromoted samples are presented in Fig. 4. In all cases, Ni, P and O elements are well dispersed all over the carbon support. However, C maps show that carbon-rich regions are present in some areas of the Pd(s)–Ni_xP_yO_z/C samples implying that the carbon surface was not fully covered by the Ni_xP_yO_z particles. Additionally, Pd EDX mapping images suggest that the Pd dispersion increases in the order $D_{Pd(C)} \ll D_{Pd(N)} < D_{Pd(A)}$, which is in accordance with the XRD results concerning the Pd particle sizes (*i.e.*, the smaller the particles, the higher the dispersion). A comparison between Pd and C maps also indicates that some noble metal particles are deposited directly on the Ni_xP_yO_z phase while the rest is on the carbon support. It is also noteworthy that EDX analysis of sample Pd (C)–Ni_xP_yO_z/C revealed the presence of chlorine in concentrations of *c.a.* 0.5 wt.% (see Fig. A1 in the Supplementary Material).

3.2. Catalysts characterization

Elemental analysis (Table 2) showed the actual Ni, P and Pd concentrations to be close to the theoretical values. The small excess of



Fig. 3. Ni_xP_yO_z/C HR-TEM micrographs obtained at different magnifications showing (a) Ni_xP_yO_z/C, (b) Pd(N)-Ni_xP_yO_z/C, (c) Pd(A)-Ni_xP_yO_z/C, (d) Pd(C)-Ni_xP_yO_z/C.

phosphorous observed was expected because a surplus was used to prepare the solution. In fact, it is well known from the literature [53] that if a stoichiometric P/Ni molar ratio of 0.5 is used an Nirich phase (Ni₁₂P₅) is formed, which is inactive for HDT reactions. To avoid the formation of this undesired phase, a 0.8 P/Ni molar ratio was employed in this work. TPR data show the formation of PH₃ and P₂ in small amounts during reduction (see Fig. A2 in Supplementary Material), thus explaining why the phosphorous excess reported in Table 2 is smaller than the expected one. Moreover, Pdpromoted samples presented lower P excess than the nonpromoted Ni₂P/C sample.

XRD results are presented in Fig. 5 and the crystallite sizes calculated using the Scherrer equation are shown in Table 3. As observed in Fig. 5, all of the diffraction peaks are characteristic of the Ni₂P phase (JCPDS file number 03-0953) indicating that Pd addition did not modify the nature of the nickel phosphide phase formed. Moreover, in comparison with the non-promoted catalyst, Ni₂P crystallite sizes were smaller for Pd-promoted samples when Pd(NO₃)₂ and Pd(acac)₂ salts were used. Strikingly, the use of PdCl₂ leads to a Ni₂P crystallite size similar to the non-promoted sample. This result shows that there is a direct relationship between the Pd particle size in the Pd(s)–Ni_xP_yO_z/C samples and the final Ni₂P particle size. This implies a direct influence of the Pd particle size on the final dispersion of the nickel phosphide active phase.

In order to confirm Pd effect in lowering Ni₂P synthesis temperature, the evolution of the crystalline phases as a function of the reduction temperature was studied. Ni_xP_yO_z/C and Pd(C)–Ni_xP_yO_z/ C samples reduced at 400, 450, and 500 °C were analyzed by XRD and the results are presented in Fig. A3 of the Supplementary Material. The results show, as previously reported for the Pd(C)– $Ni_xP_yO_z/SiO_2$ system [41], that palladium addition indeed promotes a decrease in synthesis temperature of nickel phosphide.

CO chemisorption and desorption data are presented in Table 3 and Fig. 6, respectively. The analysis of the table and the figure shows some differences in terms of surface sites properties among the reduced samples. As shown in Table 3, CO uptake values for Pd (A)–Ni₂P/C and Pd(C)–Ni₂P/C are smaller when compared to those obtained for Pd(N)–Ni₂P/C and Ni₂P/C. The small CO uptakes and large crystallite sizes reported in Table 3 have been reported in the literature [28,54,55] for systems containing high loadings of nickel phosphide and weak interactions with the support as it is the case with carbon. However, despite these observations the important point is that palladium addition has promoted a decrease of 100 °C in synthesis temperature as seen in Fig. 1.

It could be argued that it is too luxury to add 1 wt.% Pd without increasing the CO uptake. However, in a previous work [41] it has been shown that smaller amounts of palladium such as 0.1 or 0.5 wt.% are able to reduce the synthesis temperature of nickel phosphide with the CO uptake being similar for the different samples. The low CO uptake is related to the fact that the final synthesis temperature (550 °C) is still high enough to promote the active phase sintering.

CO desorption data (Fig. 6) reveal that all profiles are composed of a broad peak that can be deconvoluted in two peaks: a low temperature one (A_1) presenting a maximum in the 99–105 °C temperature range and another peak at higher temperature (A_2) with maximum in the range 149–160 °C. Moreover, the area of the low temperature peak is higher whatever the sample considered. It can also be seen from Fig. 6 that the A_1/A_2 ratio is higher in Pd (s)–Ni₂P/C catalysts than in Ni₂P/C.



Fig. 4. $Ni_x P_y O_z/C$ and $Pd(s)-Ni_x P_y O_z/C$ EDX maps showing element distribution in selected particles.

Table 2					
Elemental	analysis	data of	all re	educed	catalysts.

Sample	Content (wt.%)		.%)	Ni ₂ P content ^d (wt.%)	P excess ^e (wt.%)
	Ni ^a	P ^b	Pd ^c		
Ni ₂ P/C	26.3	7.4	-	33.2	0.4
Pd(C)-Ni ₂ P/C	27.5	7.5	0.9	34.7	0.2
$Pd(A)-Ni_2P/C$	26.5	7.2	1.3	33.5	0.2
Pd(N)-Ni ₂ P/C	28.3	7.7	1.1	35.7	0.2

^a Theoretical value: 23.7%.

^b Theoretical value: 6.3%.

^c Theoretical value: 1.0%.

^d Assuming that all Ni is as Ni₂P.

^e Theoretical value: 3.8%.



Fig. 5. XRD patterns of Ni₂P/C and Pd(s)-Ni₂P/C samples.

Table 3

Ni₂P crystallite sizes and CO uptake values of Ni₂P/C and Pd(s)-Ni₂P/C samples.

Sample	Ni ₂ P crystallite size (nm) ^a	CO uptake (μ mol g ⁻¹ _{cat})
Ni ₂ P/C	45	19
$Pd(C)-Ni_2P/C$	48	12
$Pd(A)-Ni_2P/C$	38	15
Pd(N)-Ni ₂ P/C	35	19

^a Calculated using Rietveld refinement.

3.3. HDO catalytic activity evaluation

Reaction rates (r_{GUA}) and TOF values were calculated for the guaiacol HDO reaction and are presented in Table 4. It is noteworthy that independently of the sample, the TOF values are essentially the same if one takes into consideration the experimental error associated with the CO chemisorption and conversion measurements. In fact, comparison of the reaction rate values shows a levelling off effect between Pd-promoted samples and Ni₂P/C, with $Pd(N)-Ni_2P/C$ presenting a reaction rate 20% higher than that of the Ni₂P/C. However, taking into account that reaction rate values were calculated using the total conversion of guaiacol (X_T) and that some products can be only partially deoxygenated or not deoxygenated at all, it is necessary also to compare the results in terms of HDO activity. Considering this fact, X_T and X_{HDO} were compared during the reaction course for each catalyst and the obtained data are presented in Fig. 7. Since X_{HDO}/X_T curves are almost superimposed for all samples, it can be concluded that the HDO activity follows essentially similar tendencies to those observed for the total conversion.

Main products selectivity data obtained for all catalysts are presented in Fig. 8 (selectivity data of products below 10% are presented in Fig. A4 in Supplementary Material). Benzene and cyclohexane appear as the main final products with phenol, anisole and methoxycyclohexanol (*cis* and *trans* isomers) are the primary products as their initial selectivity values (extrapolation to zero conversion) leads to finite values. It should also be noted that the selectivity ratio anisole/phenol tends to decrease when going from Pd(C)-Ni₂P/C to Pd(A)-Ni₂P/C and finally Pd(N)-Ni₂P/C showing a progressive higher relative tendency to demethoxylation, particularly for Pd(N)–Ni₂P/C. Finally, methanol, which is a primary product formed from the demethoxylation of guaiacol can also be formed in other steps of the reaction network (as will be discussed later) and because of this presents a steady selectivity value. For low conversion values methanol is not identified in the reaction mixture probably due its adsorption on activated carbon. All the remaining identified products had selectivity values below 10% and are presented in Fig. A4 of the Supplementary Material.

Comparing the Ni₂P/C selectivity data with those of Pdpromoted catalysts, a strong decrease in the methoxycyclohexanol and cyclohexanol formation is observed, which was accompanied by an increase in selectivity for benzene and anisole. In order to verify if the observed changes in selectivity was due to a parallel reaction of guaiacol over Pd sites, a 1 wt.% Pd/C catalyst (reduced in the same conditions as those used for Pd promoted samples) was evaluated for guaiacol HDO. As may be seen in the Supplementary Material (Fig. A5), the total conversion after 6 h was only 3.6% and this catalyst presented a completely different product distribution with formation of only catechol, methoxycyclohexanol, phenol and cyclohexanol.

4. Discussion

As shown in Fig. 1, the effect of Pd in decreasing the Ni₂P synthesis temperature was only partial, contrary to what was reported in the literature for silica-supported systems [41]. Comparing both cases, the most probable explanation for such a change in behavior is the difference in the specific surface area values of the supports: while the activated carbon used in the present work has a specific surface area of 772 m² g⁻¹, the specific surface area of the silica support used in Ref. [41] was 205 m² g⁻¹. Since the Ni₂P loading is 30 wt.% in both studies, it is reasonable to assume that due to the differences in specific surface area, the surface coverage by the Ni_xP_yO_z particles prior to the reduction step is different in both works, being lower in the present study.

If one considers the specific surface areas values of the carbon support of this study (772 m² g⁻¹) and of silica (205 m² g⁻¹) [41], the Ni₂P loading necessary to form a theoretical monolayer in each of the supports can be determined. While this value corresponds to 34 wt.% for SiO₂, a 66 wt.% Ni₂P loading would be necessary for C. Given that both catalysts have the same nickel phosphide loading (30 wt.%), then it can be concluded that while for SiO₂ the surface covering by Ni₂P was almost complete, for the carbon support the covering was only partial. This hypothesis is confirmed by the EDX data presented in Fig. 4. In fact, EDX mapping shows the presence of high carbon concentration regions for all samples confirming the hypothesis that the covering was not complete. Since the SiO₂ surface of the work from literature [41] is almost completely covered, it may be assumed that in this case all Pd particles were in direct contact with $Ni_x P_y O_7$. However, the same assumption cannot be made for C-supported systems because palladium distribution is random with some Pd particles being deposited on top and/or in close contact with the $Ni_x P_y O_z$ phase, while others are deposited on the exposed carbon surface and without contact with the nickel phosphate particles. EDX data support this description: a comparison between Pd and C maps shows that Pd particles are present on both carbon-poor regions (i.e., Pd in on top and/or in close contact



Fig. 6. CO temperature-programmed desorption profiles of Ni₂P/C and Pd(s)-Ni₂P/C samples. Each profile was deconvoluted into two contributions, A₁ and A₂. The A₁/A₂ ratio is given for each sample.

Table 4

TOF values and reaction rates (r_{GUA}) for Ni₂P/C and Pd(s)–Ni₂P/C samples during the guaiacol HDO reaction at 300 °C and 30 bar (H₂).

	Sample	TOF (s^{-1})	$r_{\rm GUA} (10^{-6} { m mol} { m g}_{\rm cat}^{-1} { m s}^{-1})$
Ni ₂ P/C 0.22 4.18	Ni ₂ P/C	0.22	4.18
Pd(C)–Ni ₂ P/C 0.37 4.44	$Pd(C)-Ni_2P/C$	0.37	4.44
Pd(A)–Ni ₂ P/C 0.30 4.50	$Pd(A)-Ni_2P/C$	0.30	4.50
Pd(N)–Ni ₂ P/C 0.26 4.94	$Pd(N)-Ni_2P/C$	0.26	4.94



Fig. 7. HDO conversion (X_{HDO}) and total conversion (X_T) relationship for guaiacol reaction for Ni₂P/C and Pd(s)–Ni₂P/C samples. Tendency lines are added only to guide the eye.

with $Ni_xP_yO_z$) and carbon-rich regions (*i.e.*, Pd in contact with C support). Taking into account TPR and EDX data and comparing SiO₂ and C supported systems, the present data suggest that Pd and $Ni_xP_yO_z$ particles need to be in close contact in order for the noble metal to be able to efficiently lower the synthesis temperature of Ni₂P.

Data reported in Table 1 show that both the temperature decrease and the amount of $Ni_x P_y O_z$ reduced at lower temperature

due to Pd addition were directly affected by the nature of the Pd salt. Analysis of respectively XRD and EDX allows to conclude that the Pd crystallite size increases in the order $Pd(A) < Pd(N) \ll Pd(C)$, while the noble metal dispersion trend is $Pd(C) \ll Pd(N) < Pd(A)$.

Analyzing the amounts of $Ni_xP_yO_z$ reduced and the maxima of the first water formation peak for each of the Pd salts incorporated into the $Ni_xP_yO_z/C$ two clear trends are observed. The first one clearly shows that the smaller the noble metal particle size, the higher the lowering in the maximum of the first reduction peak; and the second trend shows that the bigger the palladium particles, the higher the amount of phosphate reduced at lower temperatures.

In fact, as shown in Table 1, the first peak relative area (*i.e.*, the relative amount of $Ni_x P_y O_z$ reduced) increases in the order Pd(A)< Pd(N) < Pd(C), which follows the increase of the Pd crystallite size. It is proposed in the literature [41] that the lowering of the reduction temperature of $Ni_x P_y O_z$ due to addition of palladium takes place in two steps: (1) hydrogen spillover and its activation over Pd particles, which would decrease $Ni_x P_y O_z$ reduction temperature and (2) the covering of Pd particles by Ni_2P phase during reduction (or noble metal migration to the interior of Ni₂P), which would stop the hydrogen spillover and activation with the consequent decrease in phosphate reduction. Taking these hypotheses into account and considering the observed relationship between Pd particle size and the $Ni_x P_y O_z$ amount reduced by addition of Pd, it is clear that the reduced amount of phosphate seems to be dependent on how long noble metal particles remain exposed during the reduction step. Assuming that the proposed model is also valid in the present study, it would be reasonable to expect that bigger Pd particles would take longer to be covered. Consequently, the bigger the Pd particles, the longer the spillover effect would last resulting in a higher amount of $Ni_x P_y O_z$ reduced at lower temperatures.

The differences in temperature maxima observed for the first reduction peak as presented in Fig. 1 may be explained if Pd particle size and the degree of contact between Pd and $Ni_x P_y O_z$ particles are considered. If it is accepted that the palladium particles promote hydrogen activation and spillover, then the formed atomic hydrogen has to come into contact with the phosphate in order to reduce it to phosphide. Recombination of atomic hydrogen into



Fig. 8. Main products selectivity data as a function of total conversion (X_T) for Ni₂P, Pd(C)-Ni₂P/C, Pd(A)-Ni₂P/C and Pd(N)-Ni₂P/C.

molecular hydrogen directly depends on how far palladium is from the phosphate particle leading, in extreme cases, to a complete absence of the effect on the reduction temperature. In other words, palladium and phosphate particles have to be in close contact in order to be possible to observe an effect on the reduction temperature. Since the Pd loading is the same for all of the samples studied in this work, a better dispersion implies that smaller particles were formed and, consequently, that a larger number of Pd particles were obtained. The probability for one of these Pd particles to be in direct contact with $Ni_x P_y O_z$ is consequently higher, thus explaining why PdCl₂, with the lowest dispersion, was a less effective precursor in terms of temperature lowering. This also seems to directly influence the final Ni₂P particle size since a higher dispersion of Pd leads to a lower Ni₂P particle size. Finally, one should note that if the noble metal dispersion was homogeneous on the overall exposed surface (C surface + $Ni_xP_yO_z$ surface), contact degree would be directly related to noble metal dispersion and particle size. However, depending on the respective Pd interaction with both C and $Ni_x P_y O_z$, a preferential deposition over one surface or another would be possible depending on the Pd salt used. This last hypothesis may explain why $Pd(NO_3)_2$ presents the best temperature lowering while Pd(acac)₂ shows the best dispersion. A schematic representation summarizing the Pd effect on lowering the $Ni_x P_y O_z/C$ reduction temperature is presented in Fig. 9.

With respect to the reaction data, a significant difference was observed in products selectivity. A general scheme for the guaiacol HDO reaction over Ni_2P/C is proposed in Fig. 10, based on selectivity data reported in Fig. 8. Basically, guaiacol may be initially con-

verted via three different routes: (1) demethoxylation (DMO) to phenol, (2) direct deoxygenation (DDO) to anisole and (3) hydrogenation (HYD) to methoxycyclohexanol. In subsequent steps, different additional routes would lead to the formation of benzene and cyclohexane as the main final products and to some additional compounds in minor amounts (selectivity below 10%). For Ni₂P/C, guaiacol was initially converted via DMO, DDO and HYD in similar proportions and cyclohexanol appeared as a significant additional intermediate. With addition of Pd, the observed decrease in selectivity to methoxycyclohexanol and cyclohexanol showed that the HYD route was remarkably suppressed on the route forming these compounds. This fact was followed by an increase of the selectivity for anisole and benzene, showing that the DDO route was herein favored at the expense of the HYD pathway for Pd-containing samples.

Considering that benzene and cyclohexane are guaiacol main HDO final products, the evaluation of the benzene/cyclohexane ratio is a simple way to compare the hydrogenating character of the different catalysts. As shown in Fig. 11, benzene/cyclohexane ratios are higher for Pd promoted samples than for the non-promoted catalyst, thus confirming the assumption that Pd addition really suppressed the Ni₂P/C hydrogenating character. Besides, the benzene/cyclohexane ratios presented in Fig. 11 show that for low guaiacol conversion the formation of benzene for Ni₂P/C is zero allowing to conclude that for this catalyst the HYD route through *cis/trans* methoxycyclohexanol formation is favored. On the other hand, reaction on the palladium containing catalysts seems to be favored through the guaiacol DDO or DMO pathways forming



Fig. 9. Schematic representation of the Pd effect on lowering the $Ni_xP_yO_z/C$ reduction temperature: smaller particles promote a more extensive decrease in synthesis temperature while bigger particles promote a higher reduction.



Fig. 10. Proposed reaction scheme for guaiacol HDO over Ni₂P/C and Pd(s)-Ni₂P/C. Guaiacol is represented in green, main reaction products are represented in red and additional main products for the non-promoted sample are represented in purple.



Fig. 11. Benzene/cyclohexane molar ratios in function of the total conversion for Ni_2P/C and $Pd(s)-Ni_2P/C$ catalysts for the HDO of guaiacol.

anisole and phenol, respectively. Subsequently, anisole and phenol lead to benzene formation through DMO and DDO reactions as depicted in Fig. 10. It is noteworthy that with the increase in conversion the benzene/cyclohexane ratio decreases for the palladium containing catalysts suggesting that the hydrogenation pathway occurs with increasing extent. It could be argued that the participation of Pd active sites in guaiacol HDO reaction could be the cause for the benzene/cyclohexane ratios observed in Fig. 11 for the palladium containing catalysts. However, this hypothesis can be excluded because the catalytic test using 1 wt.% Pd/C leads to a final conversion below 4% and the selectivity to either anisole or benzene was null (see Fig. A4 in Supplementary Material). Contrary to some reports from the literature [56,57,50] that show that Pd/C is a good catalyst for the guaiacol HDO reaction, the very low conversion attained by the 1 wt.% Pd/C in this work can be explained by the very high reduction temperature employed (550 °C/1 h). This temperature was employed to allow the direct comparison with the palladium containing catalysts that were reduced in this condition.

If palladium had any role on the activity of the noble metal containing catalysts, then one would expect to find catechol (intermediate product obtained by demethylation of guaiacol) in the reaction products. Because this compound was not detected, then the hypothesis that Pd particles in direct contact to $Ni_xP_yO_z$ are covered during TPR seems to be in fact possible. Supposing that isolated Pd particles are not recovered, one could expect catechol formation in Pd(s)–Ni₂P/C catalytic tests. However, because the obtained conversion with 1 wt.% Pd was too low, the remaining (non-covered) amount of Pd probably presented an even lower activity. Consequently, products due to non-covered Pd in Pd(s)– Ni₂P/C samples, if produced, were below the detection range. Based on Ni₂P crystalline structure and EXAFS data, Oyama and Lee [52] reported the existence of two types of Ni sites on Ni₂P:

- Ni(1), which are quasi-tetrahedral sites surrounded by 4 nearest-neighbor P atoms and 8 s-nearest neighbor Ni atoms and;
- Ni(2), which are square pyramidal sites surrounded by 5 nearest-neighbor P atoms and 6 next-nearest neighbor Ni atoms.

Ni(1) has a lower coordination number and was believed to be the site related to direct desulphurization (DDS) route in HDS, while Ni(2) presents a higher coordination number and was the site associated with the HYD route. The authors also reported that Ni/P molar ratios after reduction were smaller for samples containing more Ni(2) sites.

Deconvolution of the CO TPD profiles (Fig. 6) resulted in two peaks, each one related to different active sites. In all cases, the active sites associated with CO desorption at lower temperatures were more abundant than those associated with CO desorption at higher temperatures. This result is quite important because it implies that by using a relative simple technique as CO desorption is possible to determine the relative proportion between Type 1 and Type 2 sites.

The differences in CO desorption temperature may be interpreted as being due to differences in the active site - CO bonding strength. In fact, metal - CO bonding is complex and involves charge donations between CO molecular orbitals and metal orbitals [58,59] and it can be approximated as a charge donation from the CO 5σ molecular orbital to the metal *d* orbital and to a charge backdonation from the metal *d* orbital to the CO $2\pi^*$ molecular orbital. Therefore, it would be reasonable to expect that active sites having more electrons (sites less positively charged) would promote charge backdonation in a greater extent and, consequently, would bond more strongly with the CO molecule. Taking this into account, it may be suggested that the first desorption peak in CO TPD profiles is related to Ni sites more positively charged (Ni(1)) while second desorption peak is associated with Ni sites less positively charged (Ni(2)). If Ni(1) type sites are weaker than Ni(2) type sites, then it may be proposed that they are related to the first and second desorption peaks of the CO TPD profiles, respectively.

Oyama and Lee [52] reported that the amount of Ni(1) and Ni(2) depends on the particle size, with the former being predominant in bigger particles and the latter prevalent on small particles. The fact that all of the CO TPD profiles present two desorption peaks suggests that all samples have particles with different sizes, small and big. In fact, TEM results of the reduced and passivated Ni₂P/C catalyst reveal that there are particles in a wide range of sizes (please see Fig. A6 of the Supplementary Material). This broad distribution in particle size is quite common in nickel phosphide catalysts with high loadings [54,60,61].

Fig. 6 shows that Pd addition induces a slight increase in the relative quantity of Ni(1) sites. This assumption is in accordance with the small decrease observed in P excess after TPR, once Ni(1) sites present a lower coordination number. Finally, if Ni(1) sites are associated with the DDS route in HDS reactions, they could also be considered by analogy to be related to the DDO route in HDO reactions. In other words, CO TPD profiles and elemental analysis data suggest that Pd addition increases the relative amount of Ni sites associated with the DDO route at the expense of the HYD route, which is in accordance with the strong suppression of the hydrogenating character observed for Pd-promoted catalysts. Note, however, that the significant low signal to noise ratio in Fig. 6 does not allow to precisely compare changes in the benzene/cyclohexane ratio among the different Pd(s)–Ni₂P/C catalysts. The "two-active-site" model proposed here cannot be used to explain the differences in selectivity between anisole and phenol since these compounds result respectively from DDO and DMO steps directly from guaiacol. The two types of nickel sites observed by Oyama and Lee [52] were considered to be responsible for changes in the hydrogenating character of nickel phosphide catalysts and can be envisaged here for the only real significant hydrogenation step occurring on all catalysts (containing or not Pd) and corresponding to the benzene-cyclohexane transformation.

It is also clear that the deconvolution into two components of the CO TPD sites remains quite approximate due to the relatively low signal to noise ratio in Fig. 6. Therefore, the change of the A_1/A_2 ratio from 1.68 to 1.73 for the different Pd(s)–Ni₂P/C catalysts cannot be considered as enough significant to finely correlate these data with the changes of the benzene/cyclohexane ratio in Fig. 11. However, the change of the A_1/A_2 ratio going down to 1.55 for Ni₂P/C explains in a satisfactory way the more marked modification of the benzene/cyclohexane ratio when comparing Ni₂P/C with the series of Pd(s)–Ni₂P/C catalysts.

5. Conclusions

The present study about the effect of Pd on lowering the synthesis temperature of Ni₂P shows that both the contact degree between Pd and $Ni_x P_y O_z$ particles and the Pd particle size are of fundamental importance to understand how Pd promotes the lowering in synthesis temperature of nickel phosphate. In this respect, Pd is able to decrease the $Ni_x P_y O_z$ reduction temperature only if the noble metal and the phosphate are in close contact. Moreover, depending on the nature of the Pd salt, a change in Pd particle size is observed and this parameter directly influences Ni_xP_yO_z reduction conditions. The change in Pd particle size has opposite effects on the temperature lowering for obtaining Ni₂P and on the reduced amount of $Ni_x P_y O_z$: while the increase in Pd particle size improves the amount of $Ni_x P_y O_z$ reduced by Pd addition, it leads to a lower shift of the synthesis temperature. The effectiveness in decreasing reduction temperatures also directly influences the Ni₂P particle size and then the intrinsic catalytic activity of nickel phosphide. Pd addition also modifies selectivity properties. A strong suppression of HYD route intermediates (methoxycyclohexanol and cyclohexanol) was observed on Pd-promoted catalysts. Taking into account CO temperature-programmed desorption and elemental analysis data, the change in selectivity could be associated with an increase of Ni(1) sites, which are responsible for the HDO route.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.05.016.

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