

# Nickel phosphide/silica catalysts for the gas-phase hydrogenation of furfural to high value-added chemicals

#### Carmen P. Jiménez-Gómez, Juan A. Cecilia, Ramón Moreno-Tost and Pedro Maireles-Torres\*

Abstract: A series of nickel phosphide-based catalysts, supported on a commercial silica, with a metallic Ni loading between 5-20 wt.% and initial P/Ni molar ratio 0-3, has been prepared by incipient wetness impregnation. Catalyst precursors were reduced and characterized by X-ray diffraction, CO chemisorption, NH<sub>3</sub>-TPD, N<sub>2</sub> adsorption-desorption at -196 °C and X-ray photoelectron spectroscopy, among other techniques and then tested in the furfural hydrogenation in gas-phase. Almost full furfural conversion and a 2methylfuran yield of 73% can be achieved with the Ni<sub>2</sub>P based catalysts with nickel content of 15 wt.%, at 190 °C after 5 h of TOS. The high selectivity towards 2-methylfuran is attributed to both the high hydrogenating capacity of metallic sites leading to furfuryl alcohol and the presence of reduced phosphorus species that favor hydrogenolysis process. However, catalysts undergo the deactivation along the catalytic test, due to formation of carbonaceous deposits in the form of coke and reactants and/or products.

#### Introduction

In the last century, the industrial development and the increase of the world population have caused the depletion of the fossil reserves. This fact together with more stringent environmental legislations have led to the search and development of alternative environmentally friendly energy sources to replace fossil fuels. Among them, biomass is emerging as an widely available source to produce energy and, excluding fossil fuels, is the only source that can provide liquid fuels and chemicals.<sup>[1]</sup> The lignocellulosic biomass is a non-edible source, which has been considered as the main biomass feedstock due to its high abundance and availability.<sup>[2]</sup> Generally, lignocellulosic biomass is composed by cellulose (40-50%), lignine (15-25%) and hemicellulose (20-35%).<sup>[1]</sup> The hemicellulose, formed by xylans and pentosans, has received much attention due to the synthesis of furfural through acid-catalyzed dehydration.<sup>[1,3]</sup>

Furfural is the second more produced chemical, after bioethanol, from the lignocellulosic biomass with an annual production about 280,000 Tm/year.<sup>[1]</sup> Itself, furfural is used in the resin and plastic production, in the pharmaceutical industry due to its fungicide and nematocide properties, and as extracting of lubricants.<sup>[2,4]</sup> The high interest for furfural is attributed to its chemical functionalities ( $\alpha$ , $\beta$ -unsaturated aldehyde with double C=O y

[a] C. P. Jiménez-Gómez (B.Ch.E), J.A. Ceclia (Ph.D.), R. Moreno-Tost (Ph.D.) and P. Maireles-Torres (Ph.D.)\* Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC) Universidad de Málaga Facultad de Ciencias, Campus de Teatinos, 29071 Málaga (Spain) E-mail: maireles@uma.es

Supporting information for this article is given via a link at the end of the document.

C=C bonds), which provide high reactivity, making it potentially interesting for the synthesis of a vast variety of high value-added chemicals.<sup>[1,3]</sup> In this sense, its catalytic hydrogenation is an important industrial route to obtain chemicals, such as furfuryl alcohol tetrahydrofurfuryl alcohol, 2-methylfuran, 2methyltetrahydrofuran, furan, tetrahydroduran and alkanes as products.<sup>[1]</sup> Furfuryl alcohol (FOL) is used in the synthesis of thermostatic resins or in the manufacture of vitamin C or lysine.<sup>[5]</sup> 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (2-MTHF) are products with high interest, being used as additives to increase the octane index of gasoline, in pharmaceutical industries or as solvents.<sup>[5,6]</sup> Furan is used as a starting point to other specialty chemicals as heterocycles.<sup>[7]</sup> Tetrahydrofuran (THF) has been also employed in the synthesis of polymers as well as adhesives PVC cements, vinyl films and cellophane.<sup>[5,8]</sup> The opening of the ring leads to the formation of butane or pentane which can be used for gasoline blending.<sup>[4]</sup>

Taking into account the great variety of products obtained from the furfural hydrogenation, the catalyst selection seems to be a key parameter for attaining high yields of the desired product. Copper chromite is the commercially used catalyst to obtain hydrogenated products without C-C cleavage,<sup>[9]</sup> while Pd/C is the commercial catalyst for furfural decarbonylation or furan ring opening.<sup>[5]</sup> However, the search of inexpensive catalysts, more resistant to deactivation and environmentally benign, has led to the development of new catalytic systems. Among them, Cu,<sup>[10]</sup> Co<sup>[11]</sup> and Ni<sup>[10c,12]</sup> based catalysts have shown to be active and highly selective. On the other hand, nickel phosphide (Ni<sub>2</sub>P) based catalysts have attracted great attention for hydroprocessing treatments, such as hydrodesulfurization (HDN)[13c,14] (HDS),<sup>[13]</sup> hydrodenitrogenation or hydrodeoxygenation (HDO),<sup>[15]</sup> due to the presence of phosphorous modifies the geometry and electronic density of nickel sites,<sup>[16]</sup> improving its hydrogen transfer properties.<sup>[17]</sup> In spite of their excellent catalytic behavior, Ni<sub>2</sub>P-based catalysts have not yet been evaluated in hemicellulose valorization.

The aim of the present work is the synthesis of nickel phosphide-based catalysts to be evaluated in the gas phase hydrogenation of furfural, at atmospheric pressure. Firstly, nickel phosphide loading was optimized, comparing their catalytic performance with that of nickel catalysts and the commercial catalyst used in the furfural hydrogenation (copper chromite). Then, the influence of the initial P/Ni molar ratio has been also studied, since it has been previously reported that phosphorous content is a key factor in the catalytic behavior in hydroprocessing.<sup>[13a,13c,18]</sup>

#### **Results and Discussion**

The identification of crystalline phases in catalysts reduced at 550 and  $620^{\circ}C$  for nickel and nickel phosphide based catalysts,

## WILEY-VCH

respectively, has been performed by X-ray diffraction (Figure 1). XRD patterns of catalysts with different Ni<sub>2</sub>P loadings reveal an increase in intensity of diffraction peaks located at  $2\theta = 40.7$ , 44.6, 47.4, 54.2 and 55.0° (Fig. 1A), which are ascribed to the Ni<sub>2</sub>P phase (PDF 01-089-4864), as the loading raises from 5 to 20 wt%. Consequently, the crystal size, as determined from the Williamson-Hall equation, also increases until a value of 29.1 nm for Ni<sub>2</sub>P-2-20 catalyst, although in the case of the Ni<sub>2</sub>P-2-5 catalyst, diffraction signals are barely visible.

The influence of phosphorus addition on the nature of crystalline phases was evaluated for the catalyst with 15 wt% Ni. Ni-15 catalyst (Fig. 1B) exhibits two diffraction peaks located at  $2\theta = 44.6$  and 51.8°, which are attributed to metallic nickel (Ni<sup>0</sup>) (PDF 01-070-1849). The modification of the phosphorus content causes a progressive decrease of the diffraction peaks intensity, but only signals associated to the crystalline Ni<sub>2</sub>P phase were detected. However, previous studies have demonstrated that the modification of the initial P/Ni molar ratio could lead to the formation of several crystalline phases: Ni<sub>5</sub>P<sub>4</sub>, Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>5</sub>P<sub>2</sub>.<sup>[18]</sup> The determination of the crystal size points out that the incorporation of phosphorus slightly decreases the crystal size from 20 nm for Ni-15 catalyst to 14 nm in the case of Ni<sub>2</sub>P-15-3 catalyst.



Figure 1. X-ray diffraction patterns of (A)  $Ni_2P$ -x-2 and (B)  $Ni_2P$ -15-y catalysts.

The amount of available Ni sites was evaluated by CO chemisorption, assuming that each CO molecule reacts with only one Ni site (Table 1). In the case of the catalysts with the same P/Ni ratio, i.e. P/Ni= 2, the CO chemisorption is irrespective of Ni loading up to 15 wt%; however, the incorporation of higher Ni content provokes a decrease of the CO chemisorption. This fact implies that metallic surface per mass unit of Ni and the dispersion decrease directly with the Ni loading. In spite of all nickel phosphide-based catalysts display Ni<sub>2</sub>P phase as the only crystalline phase, CO chemisorption data reveals that the incorporation of phosphorus in the catalytic system diminishes the amount of Ni species exposed on the catalyst surface. This fact involves a decrease of the metallic surface and the dispersion of the available Ni species.[17b,18] Concerning the influence of the P/Ni molar ratio, it is found a detrimental effect of the addition of phosphorous on metal dispersion and, consequently, on the metal surface area.

 Table 1. CO chemisorption data of nickel phosphide-based catalysts.

Comple	CO uptake (µmol g <sup>-1</sup> ) Dis	Metal	Metal sur	Particle	
Sample		Dispersion (%)	$m^2 g_{cat}^{-1}$	$m^2 g_{Ni}^{-1}$	(nm) <sup>a</sup>
Ni <sub>2</sub> P-5-2	39	4.55	1.52	30.31	-
Ni <sub>2</sub> P-10-2	41	2.43	1.61	16.18	10
Ni <sub>2</sub> P-15-2	39	1.52	1.55	10.33	15
Ni <sub>2</sub> P-20-2	18	0.53	0.72	3.60	29
-					
Ni-15	57	2.23	2.22	14.80	20
Ni <sub>2</sub> P-15-1	44	1.72	1.75	11.67	17
Ni <sub>2</sub> P-15-2	39	1.52	1.55	10.33	15
Ni <sub>2</sub> P-15-3	10	0.39	0.40	2.60	14

<sup>a</sup> Particle size, determined from Williamson-Hall method.

Textural properties of catalysts were evaluated by N<sub>2</sub> adsorptiondesorption at -196 °C (Table 2 and Fig. S1 in Supplementary Information). According to the IUPAC classification, the silica support and catalysts display Type II isotherms, typical of non porous or macroporous materials. This fact is attributed to the silica used as support, which is formed by solid nanospheres with a diameter of 200-300 nm, so BET surface area and pore sizes could be associated to interparticle voids. The incorporation of nickel and phosphorus on the surface of the support decreases the S<sub>BET</sub> values from 195 to 8 m<sup>2</sup> g<sup>-1</sup> due to the pore filling, as can be deduced from the corresponding pore size distributions (Fig. S1). In the same way, the textural properties also reveal that an increase of the phosphorus content also provokes a decrease of the S<sub>BET</sub> value and a shift of the pore sizes to higher values.

It is well known that acid/base properties can play an important role in furfural hydrogenation selectivity.  $^{\left[ 19\right] }$  The amount and

## WILEY-VCH

density of acid sites (Table 2) increase with both the nickel loading and the P/Ni molar ratio. The NH<sub>3</sub>-TPD profiles (Fig. S2) evidence a heterogeneous distribution of acid sites strength. Among the catalysts, the Ni<sub>2</sub>P-20-2 catalyst exhibits the higher amount of evolved ammonia at higher temperature, which demonstrates the existence of strong acid sites. It has been previously pointed out that unreduced phosphate species can provide Brönsted acid sites.<sup>[20]</sup> In addition, other authors have also established the existence of Lewis acid sites in the nickel phosphide-based catalysts due to nickel species bearing a small positive charge attributed to the electron transfer from nickel to phosphorus. The existence of Lewis acid sites can be also ascribed to unreduced Ni<sup>2+</sup> species and/or modification of the electronic density due to the metal-support interaction.<sup>[21]</sup>

	Table 2. Textural a	nd acidic properties	s of support and nickel
	phosphide-based ca	atalysts	
-			

	Sample	$(m^2 g^{-1})^{[a]}$	(cm <sup>3</sup> g <sup>-1</sup> ) <sup>[a]</sup>	Amount of acid sites (µmol g <sup>-1</sup> ) <sup>[b]</sup>	
-	SiO <sub>2</sub>	195	0.662	30	
	Ni <sub>2</sub> P-5-2	161	0.568	214	
	Ni <sub>2</sub> P-10-2	106	0.410	370	
	Ni <sub>2</sub> P-15-2	86	0.281	452	
	Ni <sub>2</sub> P-20-2	-	-	588	
	Ni-15	172	0.594	164	
	Ni <sub>2</sub> P-15-1	114	0.366	376	
	Ni <sub>2</sub> P-15-2	86	0.281	452	
	Ni <sub>2</sub> P-15-3	62	0.188	505	

[a] From N<sub>2</sub> adsorption-desorption isotherms at -196 °C

[b] From NH<sub>3</sub>-TPD measurements

Figure 2 displays the TEM micrographs of the Ni<sub>2</sub>P-15-y catalysts, where particles of spherical morphology can be observed, as was previously reported. The size of nickel particles decreases when phosphorus species are incorporated, which is in agreement with XRD data (Fig. 1). However, a high phosphorus content provokes the agglomeration of catalyst.

In order to get insights into the superficial composition of catalysts, XPS analysis was performed in the Ni 2p and P 2p regions. In all cases, the Ni  $2p_{3/2}$  core level spectra display three contributions. That located between 852.7 and 853.2 eV can be ascribed to reduced nickel species, although it cannot be discerned between Ni<sup>0</sup> and Ni<sup>5+</sup> species in nickel phosphide-based samples, since Ni<sup>0+</sup> is a quasimetallic oxidation state.<sup>[22]</sup> The second contribution at 856.6 eV is associated to unreduced Ni<sup>2+</sup>, <sup>[17b]</sup> while the third one (862 eV) is the typical *shake-up* satellite of the latter divalent species.<sup>[17b]</sup>



Figure 2. TEM micrographs of (A) Ni-15, (B)  $Ni_2P$ -15-1, (C)  $Ni_2P$ -15-2 and (D)  $Ni_2P$ -15-3 catalysts.

With regard to the P 2*p* core level spectra, the P 2*p*<sub>3/2</sub> region of all nickel phosphide-based catalysts shows the coexistence of two contributions: a lower binding energy value (129 eV) is assigned to reduced phosphorus (P<sup>δ-</sup>), in the form of phosphide,<sup>[22]</sup> while the band at 134 eV is attributed to oxidized phosphorus species (PO<sub>4</sub><sup>3-</sup> and HPO<sub>3</sub>H<sup>-</sup>).<sup>[17b]</sup>

Therefore, from XPS spectra (Figure 3), it can be inferred the coexistence of reduced and oxidized Ni and P species on the catalyst surface. In this sense, Ni<sup>2+</sup> species are responsible of Lewis acidity, whereas unreduced phosphorus species in the form of hydrogenphosphite could be associated to Brönsted acid sites. In addition, XPS data reveal that the proportion of oxidized P species is more important for the catalyst with the highest phosphorus content (Ni<sub>2</sub>P-15-3). These data agree with the information deduced from the NH<sub>3</sub>-TPD profiles, since this catalyst, with higher proportion of PO<sub>4</sub><sup>3-</sup> or HPO<sub>3</sub>H species, displays a higher acidity. The data obtained from XPS can also be related with the CO chemisorption (Table 1) inasmuch as the presence of a higher proportion of oxidized phosphorus species on the surface of catalyst could block the metallic sites for the CO chemisorption.

The surface atomic concentration data (Table 3) point out that both nickel and phosphorus contents on the surface increase with their loading, as expected, but with a higher proportion of phosphorus species in comparison to the nickel ones. The dispersion of Ni<sup>δ+</sup> species can be evaluated from their atomic concentrations and Ni<sup>δ+</sup>/Si molar ratio. These data indicate that higher nickel loading leads to an increase of Ni<sup>δ+</sup> content on the surface of the Ni<sub>2</sub>P-x-2 catalysts. On the other hand, the incorporation of phosphorus in the catalytic system (Ni<sub>2</sub>P-15-*y* catalysts) does not seem to affect the exposed Ni<sup>δ+</sup> on the

ChemCatChem

## WILEY-VCH

catalyst surface, while the phosphorus content, mainly in the

form of  $PO_x^{n-}$ , increases.



Figure 3. XPS spectra of the (A, B) Ni<sub>2</sub>P-x-2 catalysts and (C, D) Ni<sub>2</sub>P-15-y catalysts.

The presence of superficial Ni<sup> $\delta$ +</sup> species is favoured for higher Ni contents and P/Ni molar ratio in the case of the Ni<sub>2</sub>P-x-2 and Ni<sub>2</sub>P-15-y catalysts, respectively, whereas the amount of P<sup> $\delta$ +</sup>

doesn't follow a clear trend (Table 3). However, in most of catalysts, oxidized  $PO_x^{n}$  species are more abundant on surface

Table 3. XPS data of nickel and nickel phosphide-based catalysts (percentage in parentheses).

	Binding Energy (eV)					
Sample	Ni	2р	P	2р		
	Ni <sup>ŏ+</sup>	Ni <sup>2+</sup>	P <sup>δ-</sup>	PO <sub>x</sub> <sup>n-</sup>		
Ni <sub>2</sub> P-5-2	853.4 (50)	856.9 (50)	128.4 (28)	134.5 (72)		
Ni <sub>2</sub> P-10-2	852.9 (68)	856.0 (32)	129.1 (17)	134.7 (83)		
Ni <sub>2</sub> P-15-2	852.9 (73)	856.8 (27)	129.1 (39)	134.7 (61)		
Ni <sub>2</sub> P-20-2	853.0 (76)	856.0 (24)	128.6 (55)	134.2 (45)		
A						
Ni-15	852.9 (39)	856.6 (61)	-	-		
Ni <sub>2</sub> P-15-1	852.9 (52)	856.9 (48)	129.1 (18)	134.5 (82)		
Ni <sub>2</sub> P-15-2	852.9 (73)	856.8 (27)	129.1 (39)	134.7 (61)		
Ni <sub>2</sub> P-15-3	852.9 (77)	856.9 (23)	129.4 (10)	134.9 (90)		

The nickel phosphide-based catalysts have been evaluated in the furfural hydrogenation, in gas phase, at atmospheric pressure. In a preliminary test, cyclopentylmethyl ether (CPME), used as solvent, was fed without furfural under reaction conditions, being completely recovered after 5 h of time-onstream.

Several catalytic parameters were studied in order to elucidate their influence in both furfural conversion and selectivity pattern. Thus, the study of the nickel phosphide content, with a stoichiometric P/Ni molar ratio of 2, reveals that furfural conversion increases with the nickel content, achieving a complete furfural conversion for Ni<sub>2</sub>P-15-2 catalyst (Figure 4A), but a higher Ni<sub>2</sub>P content (20 wt% Ni) exerts a negative effect on furfural conversion (77%, after 1 h of TOS). This decrease can be ascribed to the presence of a lower amount of available metallic sites, as was inferred from CO chemisorption data (Table 1), which are involved in FUR hydrogenation. In any case, all nickel phosphide-based catalysts reach furfural conversion values higher than the reduced copper chromite (2CuO.Cr<sub>2</sub>O<sub>3</sub>)

catalyst, after 5 h of TOS. All catalysts undergo a progressive deactivation, which is less pronounced for the Ni<sub>2</sub>P-15-2 catalyst, that maintains a furfural conversion of 88% after 5 h of TOS.



**Figure 4.** Evolution of (A) Furfural conversion, (B) furfuryl alcohol yield, (C) 2methylfuran yield and (D) furan yield as a function of time-on-stream for Ni<sub>2</sub>P*x*-2 catalysts (Experimental conditions:  $m_{cat}$ = 150 mg, T= 210 °C, H<sub>2</sub> flow =10 mL min<sup>-1</sup>, Feed flow= 2.3 mmol FUR h<sup>-1</sup>).

Regarding yield data (Fig. 4), 2-methylfuran was the main product, reaching values between 76% (Ni<sub>2</sub>P-15-2) and 22% (Ni<sub>2</sub>P-5-2), after 1 h of TOS. However, the MF yield decreases along the TOS as a consequence of deactivation, as inferred from the evolution of FUR conversion, except in the case of the Ni<sub>2</sub>P-15-2 catalyst that still exhibits a MF yield of 72% after 5 h of TOS. The copper chromite catalyst, however, displays MF yields lower than 10%, being more selective toward FOL, although this catalyst suffers a severe deactivation along the TOS. The presence of furan is also noticeable for the catalyst with the highest catalytic activity, Ni<sub>2</sub>P-15-2, with a furan yield close to 25% after 1 h of TOS, which decreases until 13% after 5 h. Finally, the furfuryl alcohol yield is negligible for all the Ni<sub>2</sub>P-x-2 catalysts, being lower to 8%.

The influence of the phosphorus content was also evaluated in the furfural hydrogenation (Table 4). The incorporation of phosphorus does not seem to affect the catalytic behaviour since the conversion values are in the same range (88.9-92.4%) after 5 h of TOS, although the yield patterns differ between them. Thus, Ni-15 catalyst displays the highest FOL yield, attaining a yield close of 16.2 % after 1 h of TOS, and even increases along the TOS, reaching a yield of 25.6% after 5 h. The incorporation of phosphorus in the catalytic system leads to negligible FOL content. On the other hand, higher 2-MF yields are attained with both Ni<sub>2</sub>P-15-1 and Ni<sub>2</sub>P-15-2 catalyst, with values of 63.5 and 72.5%, respectively. Moreover, Ni-15 and Ni<sub>2</sub>P-15-3 catalysts reached high yields towards furan, 44.6 and 61.4%, respectively, whereas THF is only detected with Ni<sub>2</sub>P-15-3.

Table 4. Furfural conversion and furfuryl alcohol, 2-methylfuran, furan and
tetrahydrofuran yields after 1 h and 5 h of TOS (in parentheses) for Ni <sub>2</sub> P-15-y
catalysts (Experimental conditions: m <sub>cat</sub> = 150 mg, T= 210 °C, H <sub>2</sub> flow =10 mL
$min^{-1}$ , Feed flow= 2.3 mmol FUR $h^{-1}$ ).

Sample	Conv	Y(FOL)	Y(MF)	Y(F)	Y(THF)
	(%)	(%)	(%)	(%)	(%)
Ni-15	90.5	16.2	11.5	56.6	-
	(92.3)	(25.6)	(10.4)	(44.6)	(-)
Ni <sub>2</sub> P-15-1	97.9	-	67.5	24.3	-
	(88.9)	(0.12)	(63.5)	(23.3)	(-)
Ni <sub>2</sub> P-15-2	100 (88.4)	- (-)	75.4 (72.5)	24.5 (12.0)	- (-)
Ni <sub>2</sub> P-15-3	99.7	-	20.7	49.8	30.0
	(92.4)	(-)	(24.7)	(61.4)	(6.9)

Nickel-based catalysts has been largely reported for FUR hydrogenation in liquid phase, being scarce the number of papers dealing with the gas phase hydrogenation.[10c,12b-c] Concerning a plausible mechanism of FUR hydrogenation, besides the homolytic dissociation of H<sub>2</sub> molecules on the Ni surface, Sitthisa and Resasco<sup>[10c]</sup> established for a Ni/SiO<sub>2</sub> catalyst that Ni sites interact easily through the d orbital with a  $\pi$ acceptor orbital of the carbonyl group (Figure 5). This interaction takes place adopting a  $^{2}\eta$  (C,O)-aldehyde configuration, which is the most stable adsorption mode.<sup>[24]</sup> The hydrogenation process can occur via an hydroxyalkyl intermediate to form FOL, although this route is only favoured at mild temperatures. The use of high reaction temperatures modifies the conformation adopted by furfural molecules on the metallic surface, adopting a  $^{1}\eta$  (C)-acyl configuration that favours the decarbonylation of the hydroxyalkyl intermediate to form furan.<sup>[10c,25]</sup> The data reported for Ni-15 catalyst show the formation of F, FOL and MF, so the FUR adsorption might take place adopting both conformations. Previous works have pointed out that it is necessary the presence of weak acid sites to favour the hydrogenolysis reaction.<sup>[10d,26]</sup> In the case of Ni-15 catalyst, this acidity can only be provided by unreduced Ni2+ (Lewis acid sites), and since acidity of Ni-15 catalyst was low (Table 2), it was expected low MF yield. With regard to FOL yield, Ni-15 catalyst show an increase of yield along the catalytic test, which could be attributed to the loss of metallic sites by the decarbonylation reaction, as suggests the decrease of the furan yield.



Figure 5. Mechanisms of furfural hydrogenation with nickel-based catalysts (adapted from ref<sup>[1]</sup>).

The incorporation of phosphorus provokes a decrease of the Ni exposed to deactivation processes and also changes in the crystal structure.<sup>[17b]</sup> XRD data of the nickel phosphide-based catalysts revealed the presence of  $Ni_2P$  phase as the only crystalline phase. In this phase, the surface of Ni and P atoms are slightly polarized, such that Ni and P are partially charged.<sup>[27]</sup> The phosphorus atoms can act as stable adsorption sites for atomic hydrogen, the superficial phosphorus may also reduce the catalytic behaviour since P sites do not possess the same ability to promote the dissociative adsorption of H<sub>2</sub> molecules as  $\mathrm{Ni}^{0}$  sites.  $^{[28]}$   $\mathrm{Ni}_{2}\mathrm{P}$  crystals display an orthorhombic structure constituted by two kinds of Ni atoms denoted as Ni(1) and Ni(2) and two types of P atoms denoted as P(1) and P(2). Ni(1) atoms adopt an almost tetrahedral structure, while Ni(2) atoms exhibit a square pyramidal structure.<sup>[29]</sup> These authors have also pointed out that along (0001) direction of the Ni<sub>2</sub>P crystal, two stacked structures, Ni<sub>3</sub>P<sub>2</sub> and Ni<sub>3</sub>P, are formed (Figure 6).<sup>[29]</sup> However, it has been also established that  $\mathrm{Ni_3P_2}\text{-}\mathrm{terminated}$  surface can be involved in hydrodesulfurization<sup>[30]</sup>, hydrodeoxygenation,<sup>[31]</sup> hydrogen evolution<sup>[32]</sup> or water-gas shift reaction,<sup>[33]</sup> while the Ni<sub>3</sub>P-terminated surface is responsible of H<sub>2</sub> adsorption.<sup>[29a]</sup>

Considering these premises, it seems that H<sub>2</sub> are adsorbed on the Ni<sub>3</sub>P-surface, where proceeds its homolytic dissociation in atomic hydrogen, which can be adsorbed on P<sup> $\delta$ </sup> sites. The furfural molecule might be adsorbed on nickel sites of the Ni<sub>3</sub>P<sub>2</sub>-surface via an hydroxyalkyl intermediate. The catalytic results (Figure 4 and Table 4) reveal that FOL formation is negligible for all nickel phosphide-based catalysts in comparison with the nickel-based catalyst. This is attributed to the presence of a

higher amount of Brönsted acid sites (P-OH groups) (Table 2), which are involved in the dehydration reaction.<sup>[34]</sup> With regard to the furan yield, nickel phosphide-based catalysts prepared with an initial molar ratio P/Ni between 1 and 2 display values lower than the Ni-15 catalyst. This lower concentration of Ni sites in the Ni<sub>3</sub>P<sub>2</sub>-surface, in comparison to Ni-based catalysts, can lessen the interaction with the carbonyl group of furfural, disfavouring the furan formation. In the case of Ni<sub>2</sub>P-15-3 catalyst, the furan yield increases so it seems that the presence of higher amount of P-OH groups (Brönsted sites) may be involved in the decarbonylation of FUR.





In order to evaluate the changes of the active phase along the FUR hydrogenation, the used catalysts were recovered and kept in an inert solvent, and later characterized by XRD and XPS. XRD patterns of used catalyst (Fig. S3) are similar to those of the fresh catalysts, that indicating that  $Ni^0$  and  $Ni_2P$  crystalline phases are stable along the catalytic test. Thus, sintering of metal particles as cause of catalyst deactivation could be ruled

#### WILEY-VCH

out, which would be expected due to the reaction temperature is far from the reduction temperature.

The superficial modifications were studied by XPS (Figure 7). Both Ni 2p and P 2p core level spectra display the same contributions that were found for fresh catalysts, although the concomitant formation of MF is accompanied by the formation of a H<sub>2</sub>O molecule that could favour the oxidation of Ni species. The atomic concentrations of the used catalysts (Table S1) show that Ni and P content on the surface of the catalyst diminishes after the catalytic test as a consequence of the formation of carbonaceous deposits that could deactivate the active sites. In fact, it cannot be detected any contribution ascribed to the Ni 2p core level for the Ni<sub>2</sub>P-15-3 catalyst. On the other hand, the carbon concentration on the surface can be related with the acidity of the catalysts, and mainly with Brönsted acid sites associated to P-OH groups, in such a way that catalysts with a higher phosphorus content have greater tendency to form carbonaceous deposits.



Figure 7. XPS spectra of (A, B) Ni<sub>2</sub>P-x-2 catalysts and (C, D) Ni<sub>2</sub>P-15-*y* catalysts, after 5h of TOS. (Experimental conditions:  $m_{cat}$ = 150 mg, T= 210 °C, H<sub>2</sub> flow =10 mL min<sup>-1</sup>, Feed flow= 2.3 mmol FUR h<sup>-1</sup>).

In order to elucidate the chemical nature of these carbonaceous deposits, the C 1s core level spectrum of the spent catalyst with the higher carbon content (Ni<sub>2</sub>P-15-3) was analysed in detail (Figure 8). The deconvolution of the spectrum allows to discern

four components: a main contribution located at 284.8 eV attributed to the adventitious carbon and C-C bonds, a band about 286.3 eV, which can be ascribed to the existence of C-OH and/or C-O-C bands, at 287.9 eV could be assigned to C=O bonds and a high BE band at 288.8 eV due to carboxylate O-C=O groups.<sup>[35]</sup> The presence of these contributions suggest the adsorption of reagent of products on the surface of the metallic sites. In this sense, it has been reported Cu sites interacts strongly with FOL, and mainly FUR in the furfural hydrogenation,<sup>[10d]</sup> so it is expected a similar trend for nickel and nickel phosphide-based catalysts.



**Figure 8.** C 1s core level spectrum of Ni<sub>2</sub>P-15-3 catalyst after 5 h of TOS. (Experimental conditions:  $m_{cat}$ = 150 mg, T= 210 °C, H<sub>2</sub> flow =10 mL min<sup>-1</sup>, Feed flow= 2.3 mmol FUR h<sup>-1</sup>).

The Ni<sub>2</sub>P-15-2 catalyst, which displayed the highest MF yield, was chosen to test the effect of several catalytic parameters such as temperature and contact time. The furfural hydrogenation as a function of the reaction temperature (Table 5) shows an increase of the conversion with temperature, due to endothermic character of the hydrogenation process.[10d] However, higher temperatures could favour the desorption of reactants and/or products that interact strongly with metallic sites; however, the catalytic conversion above 210°C decays due to the polymerization of furfural and the formation of carbonaceous deposits which disable a high proportion of metallic sites.  $^{\rm [10e,f]}$  The FOL yield is negligible in all cases, since the reaction evolves easily towards MF, obtaining a MF yield of 72.5% at 190 °C after 5 h of TOS. This fact is attributed, as was mentioned previously, to the hydrogenolysis reaction, which is favoured by the existence of an excess of Brönsted acid sites. The increase of the reaction temperature improves the furan yield, obtaining a highest value close to 54.5%, which is agreement with those data reported in the literature for nickelbased catalysts,<sup>[10c]</sup> where the use of high temperatures favours the decarbonylation to furan. Moreover, it is detected a new hydrogenation product: tetrahydrofuran (THF), although only in the first few hours of reaction. The interaction between the delocalized  $\pi$ -electrons and the nickel metal sites favours the hydrogenation of the furanic ring to THF.<sup>[10c]</sup>

Finally, the study of the  $H_2$  flow reveals that FUR conversion increases for lower  $H_2$  flow values, that is, for long contact times (Figure 9). However, a lower contact time favours FOL formation. From these data, it can be deduced that a longer contact time

slightly prevents the hydrogenolysis step FOL  $\rightarrow$  MF, although MF continues being the main product in all cases. Thus, it could be inferred that the reaction mainly proceeds through the hydrogenation-hydrogenolysis route, while the decarbonylation route is favoured in the case of higher contact time (10 mL min<sup>-1</sup>).

**Table 5.** Influence of the reaction temperature on furfural conversion and product yields after 1 h and 5 h of TOS (in parentheses) for Ni<sub>2</sub>P-15-2 catalyst (Experimental conditions:  $m_{cat}$ = 150 mg, H<sub>2</sub> flow =10 mL min<sup>-1</sup>, Feed flow= 2.3 mmol FUR h<sup>-1</sup>).

Sample	Conv	Y(FOL)	Y(MF)	Y(F)	Y(THF)
	(%)	(%)	(%)	(%)	(%)
Ni₂P-15-2	33.5	2.5	26.0	3.5	-
(170 ⁰C)	(17.4)	(6.3)	(11.4)	(1.4)	(-)
Ni₂P-15-2	100	-	75.4	24.5	-
(190 ⁰C)	(88.4)	(-)	(72.5)	(12.0)	(-)
Ni₂P-15-2	100	-	15.8	44.7	38.4
(210 ⁰C)	(100)	(-)	(39.0)	(54.5)	(6.4)
Ni₂P-15-2	63.4	-	5.8	33.3	23.4
(230 ⁰C)	(14.6)	(-)	(3.7)	(8.7)	(2.0)



**Figure 9.** Influence of the H<sub>2</sub> flow on (A) Furfural conversion, (B) furfuryl alcohol yield, (C) 2-methylfuran yield and (D) furan yield as a function of time-on-stream for Ni<sub>2</sub>P-15-2 catalyst (Experimental conditions:  $m_{cat}$ = 150 mg, T= 210 °C, Feed flow= 2.3 mmol FUR h<sup>-1</sup>).

#### Conclusions

Nickel phosphide supported on a commercial silica catalysts have been synthesized, from Ni(OH)<sub>2</sub> and H<sub>2</sub>POH, characterized and tested in the furfural hydrogenation. Both nickel and nickel phosphide-based catalysts have shown to be active, with a maximum furfural conversion of 88 % with the highest 2methylfuran yield (73%), at 190 °C, for the nickel phosphidebased catalyst with a 15 wt% Ni. The furfural reaction takes place via hydrogenation of furfural to furfuryl alcohol; however, this product in only noticeable in the case of nickel-based catalyst. The incorporation of phosphorus species in the catalytic system causes a decrease of the metallic character of the Ni species, which must soften the interaction between the metallic sites and furfural, intermediates and products. Nonetheless, XPS data reported higher carbon content on the surface of the catalysts by the formation of coke and the strong interaction with molecules involves in the furfural hydrogenation, being the reason of the catalytic deactivation along the TOS. In addition, the presence of unreduced phosphorus species (-P-OH) generates Brönsted acid sites that favors the hydrogenolysis reaction of furfuryl alcohol to 2-methylfuran. In addition, it is noteworthy the presence of furan due to the decarbonylation of furfural is favored at higher temperature.

Among all possible products of furfural hydrogenation, 2methylfuran can be the most desirable product due to the interesting properties as fuel additive, as well as a model molecule of the desired reaction paths in bio-oil upgrading. Taking into account these results, nickel phosphide could be considered as an active phase with a high potential to obtain high value-added chemicals from lignocellulosic biomass.

## **Experimental Section**

For the use of nickel phosphide-based catalysts, a commercial silica (Sigma-Aldrich) with a diameter size of 200-300 nm was used. The reagents used to prepare nickel phosphide precursors were phosphorous acid (H<sub>2</sub>PO<sub>3</sub>H, Aldrich 99%), and nickel(II) hydroxide (Ni(OH)<sub>2</sub>, Aldrich 99%). In the case of the nickel based precursor nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O, Aldrich 99%) was employed, while the commercial copper chromite (2CuO Cr<sub>2</sub>O<sub>3</sub>, Aldrich).

Nickel phosphide-based catalysts were synthesized using an aqueous solution of nickel(II) dihydrogenphosphite (Ni(HPO<sub>3</sub>H)<sub>2</sub> prepared by mixing the stoichiometric amounts of H<sub>2</sub>PO<sub>3</sub>H and Ni(OH)<sub>2</sub> (a P:Ni molar ratio of 4:1). In order to evaluate the influence of the P/Ni molar ratio, the  $H_2PO_3H$  content was varied in the synthesis. The support was impregnated with aqueous solutions containing the desired amount of Ni and P precursors, and then were air dried at 60 °C for 24 h. Finally, the precursors were reduced to phosphide by temperature programmed reduction (H<sub>2</sub>-TPR) under H<sub>2</sub> flow of 60 mL min<sup>-1</sup>, with a rate of 3 °C min<sup>-1</sup> from room temperature to 610 °C, maintaining this temperature for 2 h, as was studied in previous research.<sup>[15b,c]</sup> Nickel-based precursor was prepared using an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O, which was used to impregnate the support. Then, the sample was air dried at 60 °C for 24 h and calcined at 500 °C for 4 h. Finally, the catalytic precursor was reduced to the metallic phase using a H<sub>2</sub> flow of 60 mL min<sup>-1</sup>, with a rate of 10 °C min-1 from room temperature to 550 °C, maintaining this

temperature for 2 h.<sup>[17b]</sup> The synthesized catalysts were labelled as Ni<sub>2</sub>P*x-y*, where *x* represents the weight percentage of nickel in catalysts and *y* the initial P/Ni molar ratio.

Powder X-ray diffraction (XRD) patterns were obtained in a PAN analytical X'Pert Pro automated diffractometer, in Bragg-Brentano reflection configuration, by using a Ge (111) primary monochromator (Cu K<sub>a</sub>1) and the X'Celerator detector with a step size of 0.017° (20), between 10 and 70° in 20 with an equivalent counting time of 712 s step<sup>-1</sup>. The crystallite size (D) was calculated by using the Williamson-Hall equation,<sup>[23]</sup> B cos  $\theta = (K \lambda / D) + (2 \epsilon \sin \theta)$ , where  $\theta$  is the Bragg angle, B is the full width at half maximum (FWHM) of the XRD peaks, K is the Scherrer constant,  $\lambda$  is the wavelength of the X ray and  $\epsilon$  the lattice strain.

CO chemisorption analyses were performed under static volumetric conditions using a Micromeritics ASAP 2020 apparatus. Samples were reduced ex situ and then transferred to an inert atmosphere. Prior to measurement, samples were reduced in situ in H<sub>2</sub> at 400 °C and evacuated at 25 °C for 10h. The chemisorption isoth erms were obtained by measuring the amount of CO adsorbed between 10 and 600 mmHg at 35 °C. After completing the initial analysis, the r eversibly adsorbed gas was evacuated and the analysis was repeated to determine only the chemisorbed amounts.

The textural parameters were evaluated from nitrogen adsorption-desorption isotherms at -196 °C, as determined by an automatic ASAP 2020 Micromeritics apparatus. Prior to measurements, samples were outgassed at 200 °C and 10<sup>-4</sup> mbar overnight. Specific surface areas (S<sub>BET</sub>) were determined by using the Brunauer–Emmett–Teller (BET) equation considering a nitrogen molecule cross section of 16.2 Å<sup>2</sup>. Pore size distribution was determined using the density functional theory (DFT).

X-ray photoelectron spectra were obtained using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K<sub>a</sub> radiation (300 W, 15 kV, 1253.6 eV) with a multi-channel detector. Spectra were recorded in the constant pass energy mode at 29.35 eV, using a 720 µm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.6 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. All recorded spectra were always fitted using Gaussian-Lorentzian curves to more accurately determine the binding energy of the different element core levels. All samples were stored in sealed vials with an inert solvent to avoid oxidation. The sample preparation was done in a dry box under a N<sub>2</sub> flow, where the solvent was evaporated prior to its introduction into the analysis chamber, and directly analyzed without previous treatment.

The vapor-phase hydrogenation of furfural was performed in a 1/4" tubular quartz reactor, by putting the pelletized catalyst (325-400 µm) at the center of the reactor tube, between two layers of glass beads and guartz wool. Prior to the catalytic test, catalysts were reduced in situ under a H<sub>2</sub> flow (60 mL min<sup>-1</sup>) at 550°C for 1 h in the case of nickel-based catalyst and 620 °C for the nickel phosphide-based catalysts. After reduction, catalysts were cooled down to the selected reaction temperature under a H<sub>2</sub> flow (10-60 mL min<sup>-1</sup>). After reaching this temperature, a flow of 3.87 mL h<sup>-1</sup> of a furfural solution in cyclopentyl methyl ether (CPME) (5 vol%) was continuously injected by means of a Gilson 307SC piston pump (model 10SC). The furfural was dissolved in CPME in order to avoid problems related to the use of pure furfural found in our equipment, such as blockage of the lines due to the polymerization of furfural. CPME is an environmentally friendly solvent that has been used in different organic reactions, thus demonstrating to be a green co-solvent for the selective dehydration of lignocellulosic pentoses to furfural.<sup>[36]</sup> The liquid samples were kept in sealed vials and subsequently analyzed by gas chromatography (Shimadzu GC-14B), with a flame ionization detector and a capillary column, CP Wax 52 CB. The furfural conversion, selectivity and yield were calculated and defined as follows:



#### Acknowledgements

The authors are grateful to financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2015-64226-C3-3-R project), Junta de Andalucía (P12-RNM-1565) and FEDER (European Union) funds.

**Keywords:** furfural; 2-methylfuran; biomass; nickel phosphide; hydrogenation

- R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López-Granados, *Energy Environ. Sci.* 2016, 9, 1144-1189.
- [2] J.P. Lange, E. van der Heide, J. van der Buijtenen, R. Price, *ChemSusChem* 2012, 5, 150-166.
- [3] S.T. Wettstein, D. Martin-Alonso, E.I. Gürbüz, J.A. Dumesic, Curr. Opin. Chem. Eng. 2012, 1, 218-224.
- KJ Zeitsch. The chemistry and technology of furfural and its many byproducts. Elsevier Science, 2000.
- [5] a) A. Corma, O. de la Torre, M. Renz, *ChemSusChem* 2011, 4, 1574-1577; b) A. Corma, O. de la Torre, M. Renz, N. Villandier, *Angew. Chem. Int. Ed.* 2011, *50*, 2375-2378; c) K. Yan, G. Wu, T. Lafleur, C. Jarvis, *Renew. Sustain. Energy Rev.* 2014, *38*, 663-676; d) W. Wang, N Li, S. Li, G. Li, F. Chen, X. Sheng, A. Wang, X. Wang, Y. Cong, T. Zhang, *Green Chem.* 2016, *18*, 1218-1223.
- [6] D.H. Brown Ripin, M Vetelino, *Synlett* **2003**, *15*, 2353-2353.
- [7] H.E. Hoydonckx, W.M. Van Rhijn, W. Van Rhijn, D.E. De Vos, P.A. Jacobs. (2005), *Furfural and Derivatives*. Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH, **2005**.
- [8] J.Kanetaka, T. Asano, S. Masamune, Ind. Eng. Chem. 1970, 62, 24-32.
- [9] R. Rao, A. Dandekar, R.T.K. Baker, M.A. Vannice, J. Catal. 1997, 1171, 406-419.
- [10] a) G. Seo, H. Chon, J. Catal. 1981, 67:424-429; b) B.M. Nagaraja, V.S. Kumar, V. Shasikala, A.H. Padmasri, B.D. Raju, K.S.R. Rao, Catal. Commun. 2003, 4, 287-293; c) S. Sitthisa, D.E. Resasco. Catal. Lett. 2011, 141, 784-791; d) S. Sitthisa, T. Sooknoi, Y. Ma, P.B. Balbuena, D.E. Resasco, J. Catal. 2011, 277, 1-13; e) C.P. Jiménez-Gómez, J.A. Cecilia, D. Durán-Martín, R. Moreno-Tost, J. Santamaría-González, J. Mérida-Robles, R. Mariscal, P. Maireles-Torres, J. Catal. 2016, 336, 107-115; f) C.P. Jiménez-Gómez, J.A. Cecilia, I. Márquez-Rodríguez, R. Moreno-Tost, J. Santamaría-González, J. Mérida-Robles, P. Maireles-Torres, Catal Today 2016, 279, 327-338.
- [11] M. Audemar, C. Ciotonea, L. de Oliveira Vigier, S. Royer S, A. Ungureanu, B. Dragoi, E. Dumitriu, F. Jérôme, *ChemSusChem* 2015, *8*, 1885-1891.
- [12] a) S. Sitthisa, W. An, D.E. Resasco, *J. Catal.* 2011, *284*, 90-101; b) Y.
   Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, *ChemCatChem* 2012, *4*, 1791-1797; c) T.P. Sulmonetti, S.H. Pang, M.T. Claure, S. Lee,

D.A. Cullen, P.K. Agrawal, C.W. Jones, Appl. Catal. A: Gen. **2016**, *517*, 187-196; c) M. Manikandan, A.K. Venugopal, K. Prabu, R.K. Jha, R.

Thirumalaiswamy, J. Molec. Catal. A: Chem. 2016, 417, 153-162; d) H.
 Jeong, C. Kim, S. Yang, H. Lee, J. Catal. 2016, 344, 609-615.
 a) S.T. Oyama, J. Catal. 2003, 216, 343-352; b) J.A. Cecilia, A.

- [13] a) S.T. Oyama, *J. Catal.* 2003, *216*, 343-352; b) J.A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, *J. Catal.* 2009, *263*, 4-15; c) A. Infantes-Molina, J.A. Cecilia, B. Pawelec, J.L.G. Fierro, E. Rodríguez-Castellón, A. Jiménez-López, *Appl. Catal. A: Gen.* 2010, *390*, 253-263.
- [14] a) M. Lu, A. Wang, X. Li, X. Duan, Y. Teng, Y. Wang, C. Song, Y. Hu, *Energy Fuels* **2007**, *21*, 554-560.
- [15] a) H.Y. Zhao, D. Li, P. Bui, S.T. Oyama, Appl. Catal. A: Gen. 2011, 391, 305-310; b) P. Bui, J.A. Cecilia, T.S. Oyama, A. Takagaki, A. Infantes-Molina, H. Zhao, D. Li, E. Rodríguez-Castellón, A. Jiménez López, J. Catal. 2012, 294, 184-198; c) J.A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, S.T. Oyama, Appl. Catal. B: Environ. 2013, 136, 140-149; d) N. Koike, S. Housokai, A. Takagaki, S. Nishimura, R. Kikuchi, K. Ebitani, Y. Suzuki, S.T. Oyama, J. Catal. 2016, 333, 115-126.
- [16] S.T. Oyama, T. Gott, H. Zhao, Y.K. Lee, *Catal. Today* 2009, 143, 94-107.
- [17] a) J. Chen, S. Zhou, D. Ci, J. Zhang, R. Wang, J. Zhang, *Ind. Eng. Chem. Res.* 2009, *48* 3812-3819; b) J.A. Cecilia, I. Jiménez-Morales, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, *J. Molec. Catal. A: Chem.* 2013, *368*, 78-87.
- [18] S.T. Oyama, X. Wang, Y.K. Lee, K. Bando, F.G. Requejo, J. Catal. 2002, 210, 207-217.
- [19] F. Dong, Y. Zhu, H. Zheng, Y. Zhu, X. Li, Y. Li, J. Molec. Catal. A: Chem. 2015, 398, 140-148.
- [20] I.I. Abu, K.J. Smith, Appl. Catal. A: Chem. 2007, 328, 58-67.
- [21] K. Li, R. Wang, J. Chen, Energy Fuels 2011, 24, 854-863.

- [22] J.A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, J. Phys. Chem. C 2009, 113, 17032–17044.
- [23] G.K. Williamson, W.H. Hall, Acta Metall. 1953, 1, 22-31.
- [24] V. Vorotnikov, G. Mpourmpakis, D.G. Vlachos, ACS Catal. 2012, 2, 2496-2504.
- [25] M. Mavrikakis, M.A. Barteau, J. Mol. Catal. A: Chem. 1998, 131, 135-147.
- [26] F. Dong, Y. Zhu, H. Zheng, Y. Zhu, X. Li, Y. Y. Li. J. Mol. Catal. A: Chem. 2015, 398, 140-148.
- [27] K. Edamoto, Appl. Surf. Sci. 2013, 269, 7-11.
- [28] H. Ariga, M. Kawashima, S. Takakusagi, K. Asakura. Chem. Lett. 2013, 42, 1481-1483.
- [29] a) S. Suzuki, G.M Moula, T. Miyamoto, Y. Nakagawa, K. Kinosthita, K. Asakura, S.T. Oyama, S. Otani, *J. Nanosci. Nanotechnol.* 2009, *9*, 195.201; b) Q. Yuan, H. Ariga, K. Asakura, *Top. Catal.* 2015, *58*, 194-200.
- [30] a) P. Liu, J.A. Rodriguez, T. Asakura, J. Gomes, K. Nakamura, *J. Phys. Chem: B*, **2005**, *109*, 4575-4583; b) D. Kanama, S.T. Oyama, S. Otani, D.F. Cox. Surf. Sci. Spectra **2001**, *8*, 220-224.
- [31] J.S. Moon, E.G. Kim, Y.K. Lee, J. Catal. 2014, 311, 144-152.
- [32] P. Liu, J.A. Rodriguez, J. Am. Chem. Soc. 2005, 127, 14871-14878.
- [33] P. Liu, J.A. Rodriguez, T. Takahasi, K. Nakamura. J. Catal. 2009, 262, 294-303.
- [34] V.O.O. Gonçalves, P.M.de Souza, v. T. da Silva, F.B. Norona, F. Richard. Appl. Catal. B: Environ. 2017, 205, 357-367.
- [35] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of Xray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Minnesota, 1992.
- [36] M.J. Campos-Molina, R. Mariscal, M. Ojeda, M. López-Granados, Bioresour. Technol. 2012, 126, 321-327.

## WILEY-VCH

## Entry for the Table of Contents

## FULL PAPER

**FULL PAPER** 



Nickel phosphide catalysts supported on silica have been evaluated in the furfural hydrogenation. The presence of reduced phosphorus diminishes the deactivation of nickel and the presence of phosphide favours the hydrogenolysis of furfuryl alcohol to obtain 2-methylfuran

C.P. Jiménez-Gómez, J.A. Cecilia, R. Moreno-Tost, P. Maireles-Torres\*

#### Page No. – Page No.

Nickel phosphide/silica catalysts for the gas-phase hydrogenation of furfural to high value-added chemicals