

Journal Pre-proofs

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PII: S0021-9517(20)30269-4
DOI: <https://doi.org/10.1016/j.jcat.2020.06.036>
Reference: YJCAT 13807

To appear in: *Journal of Catalysis*

Received Date: 2 April 2020
Revised Date: 25 June 2020
Accepted Date: 28 June 2020

Please cite this article as: A. Garcia-Ortiz, J. Diego Vidal, S. Iborra, M. José Climent, J. Cored, D. Ruano, V. Pérez-Dieste, P. Concepción, A. Corma, Synthesis of a hybrid Pd⁰ / Pd-carbide / carbon catalyst material with high selectivity for hydrogenation reactions, *Journal of Catalysis* (2020), doi: <https://doi.org/10.1016/j.jcat.2020.06.036>

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Synthesis of a hybrid Pd⁰ / Pd-carbide / carbon catalyst material with high selectivity for hydrogenation reactions

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ABSTRACT

We present a highly selective and active Pd carbon catalyst prepared by an easy hydrothermal synthesis method. This synthetic procedure allows the stabilization under mild conditions of interstitial carbon atoms on the surface of a Pd⁰ carbon catalyst. The so formed Pd carbide phase appears on the upper surface layers of the Pd carbon catalyst, as demonstrated by X-ray photoelectron depth profile analysis using variable synchrotron X-ray energies. The presence of carbon in the palladium carbide species modifies the electronic state of surface Pd atoms, resulting in more electron positive Pd species (Pd^{δ+}). This influences the adsorption of reactants and reaction intermediates during the hydrogenation of alkynes, dienes and imines, resulting in high selectivities at practically 100% conversion.

Keywords

Palladium carbide, selective hydrogenation, reductive amination, synchrotron XPS, hydrothermal synthesis

1. Introduction

Currently, selective hydrogenation of conjugated double carbon-carbon bonds in dienes and trivalent carbon-carbon bonds such as alkynes to achieve partial hydrogenation products is a highly desirable and challenging process in the field of chemical production.^[1-2] A variety of heterogeneous and homogeneous catalysts based on transition metals for the partial hydrogenation of dienes and alkynes have been reported, being Pd the most widely used. In fact, it is observed that Pd-based catalysts can selectively hydrogenate triple into double C-C bonds. On this base, it is possible to remove acetylene from ethylene streams for the manufacture of polymer grade ethylene. The high selectivity of Pd to hydrogenate mixtures of alkyne and alkene hydrocarbons has been explained on the base of the weaker adsorption energy of the alkene with respect to the alkyne on Pd.^[3] Recent spectroscopic studies based on operando X-ray absorption spectroscopy^[4,5] combined with X-ray powder diffraction and theoretical simulation of the X-ray absorption near-edge structure (XANES) spectra using a Monte-Carlo approach,^[6] as well as near ambient X-ray photoelectron spectroscopy,^[7] have shown the tendency of Pd to form carbides and hydrides under reaction conditions, which markedly affects the adsorption of olefins and alkynes, influencing accordingly the selectivity to the alkene. It has been experimentally and theoretically found^[8] that bulk dissolved hydrogen in Pd, resulting in the formation of β -hydride phase, is considerably more energetic than the hydrogen adsorbed on the surface and can emerge from the bulk to the surface, enhancing total hydrogenation of acetylene.^[9] On the other hand, when no subsurface hydrogen exists, the hydrogen on the surface of the metallic nanoparticles is more selective toward partial hydrogenation of acetylene to ethylene. By studying binding energy maps, Tescher et al.^[10] proposed that the distribution of hydrogen in Pd is affected by the presence of dissolved carbon species within the metal nanoparticles, decreasing the population of hydrogen in the subsurface region. In this case the binding energy of hydrogen on the surface is strongly reduced and its population decreases leading to the selective hydrogenation of the alkyne into the

corresponding alkene. ^[11] These carbon species are formed *in situ* during the reaction from the fragmentation of carbon containing feed molecules, being their amount strongly dependent on the reaction conditions such as reaction time, pressure and temperature. ^[4-6,11,12] The formation of metal-C species in the absence of carbon species in the feed have been also detected by dispersing small metal clusters onto a carbon support, resulting in a high degree of metal-carbon interaction, specifically at defects sites of the support ^[13] with the diffusion of carbonaceous species from the support into the Pd lattice. ^[13,14] While the incorporation of carbon into the Pd lattice has been proven to be beneficial for catalyst selectivity, the controlled synthesis of palladium based catalysts containing interstitial carbon atoms has been scarcely reported. To the best of our knowledge, there are only few reports dealing with the efficient incorporation of C atoms in Pd catalysts. Between these studies, Okitsu et al., ^[15] reported a sonochemical reduction of a palladium salt in the presence of an organic additive. However, the radical nature of the synthesis results in important compositional changes of the final material depending on the synthesis conditions, hampering the scalability of the method. In another approach Guo et al, ^[16] described a method for the synthesis of palladium carbide (PdC_x) nanocubes, starting from Pd nanocube seeds, glucose and oleylamine stirred at 200 °C for a certain time. The method requires the initial synthesis of Pd nanocubes using a surfactant mediated method and the use of amines, which are not desirable from an environmental perspective. However, it has been shown the possibility to control the C/Pd atomic ratio by simply adjusting the reaction time. On the other hand, Beltzung et al. ^[17] reported a KOH activated high temperature (900 °C) pyrolysis procedure of a polyacrylonitrile polymer containing Pd nanoparticles, resulting in partial carburization of the Pd nanoparticles. The method uses harsh conditions and has drawbacks of accessibility of the reactants to the active sites. On the basis of these outcomes, the possibility to employ a sustainable method using mild conditions for the synthesis of Pd catalysts containing dissolved carbon atoms would be very interesting from a point of view of eco-efficiency. On the other hand, the effect of carburization on the catalytic performance of Pd

catalysts in other reactions than alkyne semihydrogenation has not been yet investigated, being matter of interest. Thus, the goal of our work is to state an efficient and facile approach of effective incorporation of carbon atoms in the Pd lattice and study their influence on the catalytic behaviour of highly demanding selective hydrogenation reactions.

The hydrothermal synthesis methodology has been successfully employed for the synthesis of carbon materials ^[18] and mono and bimetallic carbon coated catalysts, with applications in many catalytic processes, ^[19-22] however in none of these studies metal carburization has been reported. Recently, we demonstrated the formation of ruthenium carbide species stabilized in the upper surface layers of a ruthenium carbon catalyst, using a hydrothermal approach. ^[23] Inspired on this finding and based on the high affinity of Pd to carbon, we tried to use the same approach for the synthesis of Pd carbide containing catalysts. The herein employed hydrothermal synthesis procedure involves an aqueous solution of a palladium salt (i.e. $\text{Pd}(\text{NO}_3)_2$), an organic compound as carbon source (i.e. Na_2EDTA) and a water-methanol mixture, heat-treated under autogenous pressure at 200 °C for 24 h. This synthesis method is very easy, reproducible and cost-efficient in comparison to the previous methods found in the literature for the controlled synthesis of palladium based catalysts containing interstitial carbon atoms. The method can also be applied using glucose instead of Na_2EDTA as carbon source, and water as solvent, rendering as a “green” alternative to the actual synthesis procedure.

2. Materials and methods

2.1. Synthesis of PdHT catalyst

The PdHT-EDTA catalyst was prepared through a hydrothermal process using $\text{Pd}(\text{NO}_3)_2$ as the metal precursor and Na_2EDTA as organic compound. The pH of the synthesis gel was 13. In detail, 3.50 g $\text{Pd}(\text{NO}_3)_2$, 1.8 g Na_2EDTA and 0.38 g NaOH were dissolved in 8.1 mL H_2O and 4 mL MeOH, resulting in a black suspension. The solution was transferred into a 35 mL stainless steel

autoclave and heated at 200 °C for 24 h. After cooling to room temperature, the solid was precipitated, filtered and washed with deionized water and acetone several times followed by air-drying at 25 °C.

The PdHT-Glucose catalyst. 120 mg of glucose (Aldrich) was dissolved in 7 mL of deionized water and stirred at room temperature for 0.5 h. Then 0.1 g of RuO₂ (Aldrich, 99.9%, particle size 32 nm determined by XRD) is added and mixed under ultra-sonication (Branson 3510 operating at 40 Hz) for 0.5 h, obtaining a black suspension. The so obtained suspension was transferred into a Teflon-coated stainless steel autoclave of 12.5 mL and heated at 175 °C for 18 h under static conditions. After cooling, the content of the autoclave was filtrated under vacuum conditions, recovering a black solid. The solid was washed five times, first with water and later with acetone. Then it was dried in an oven at 60 °C for 12 h.

2.2. Characterization methods

Power X-ray diffraction patterns (XRD) were collected using a Panalytical CUBIX diffractometer with a monochromatic Cu K α radiation ($\lambda=0.15406$ nm) at 45 kV and 40 mA. The angle (2θ) was measured in a scan range of 2.00–90.038 in steps of 0.04018 with a counting time of 34.92 s. The crystal size was calculated from the main peaks (40.3, 46.9, 68.3, 82.3, 86.8; 2θ) using the Scherrer equation and assuming a shape factor 0.9. TEM images of the catalyst were taken with a JEOL JEM 2100F electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. Raman spectra were obtained with a “Reflex” Renishaw spectrometer, equipped with an Olympus microscope and a CCD detector. Spectra were acquired using a 514 nm laser. The laser power on the sample was 10 mW, taken 10 acquisitions for each spectra. Synchrotron X-ray Photoelectron Spectroscopy experiments were performed at the NAPP end-station of CIRCE BL24 at the ALBA Synchrotron Light Source Facility. The data were acquired with a Phoibos 150 NAP electron energy analyser, pass energy of 10 eV and

beamline exit slit of 20 μm . The beam spot size at the NAPP sample position was 100 $\times$ 30 (H $\times$ V) μm^2 . Incident photon energies of 500, 700, 950 and 1386 eV for Pd 3d were used, allowing to probe sample depths between 1.9 nm and 4.7 nm. The probing depth was obtained according to the inelastic mean free path (IMFP) data. ^[24] The sample (80-100 mg) was pelletized and mounted onto the sample holder using a resistive button heater for sample heating and a K-type thermocouple in direct contact with the sample for temperature monitoring. In the *in situ* H₂ reduction experiments, 1 mbar H₂ was dosed into the analysis chamber using leak valve, and the temperature raised from 25 to 250 °C. Shirley type background and Lorentzian type curves have been used in the spectra fitting. The surface area of palladium in Pd catalysts was estimated from CO adsorption using the double isotherm method on a Quantachrome Autosorb-1C equipment. Prior to adsorption, the samples, except the PdHT, (300 mg with a pellet size of 0.8-1.1 mm) were reduced *in situ* in flowing pure hydrogen (25 mL/min) at the same reduction temperature applied before catalysis, that is 100 °C for 1 h (10 °C/min rate). The PdHT sample was treated in a helium flow at 100 °C (2 h). After activation, the samples were degassed at 1333 $\times$ 10⁻³ Pa for 2 h at 100 °C, and then the temperature lowered at 25 °C (1 hour for cooling down the sample to adsorption temperature). Then, pure CO was admitted and the first adsorption isotherm (i.e. the total CO uptake) was measured. After evacuation at 25 °C, the second isotherm (i.e. the reversible CO uptake) was taken. The amount of chemisorbed CO was obtained by subtracting the two isotherms. The pressure range studied was 0.5-11 $\times$ 10⁴ Pa. The dispersion of Pd (D %) was calculated from the amount of irreversibly adsorbed CO assuming a stoichiometry of Pd/CO=1 as was used by other authors. ^[25] The mean Pd⁰ diameter (d) was determined from chemisorption data assuming spherical geometry for the metal particle according to the procedure described by Anderson. Equations used for metal dispersion and metal diameter determination are shown below.

$$D (\%) = \frac{Nm * Fs * M * 100}{L} * 100$$

N_m: chemisorption uptake expressed in mol of CO per gram of sample. F_s: adsorption stoichiometry. M: molecular weight of the supported metal. L: percent loading of the supported metal.

$$d = \frac{L * 6}{ASA * Z * 100}$$

d: mean metal diameter (m). Z: density of the supported metal (g/m³). ASA: active surface area (m²/g_{sample}) calculated from the following equation:

$$ASA = N_m * F_s * A_m * N_A$$

A_m: cross-sectional area occupied by each active surface atom. N_A: Avogadro's number.

Temperature programmed desorption (TPD) of phenylacetylene and styrene adsorbed on PdHT and Pd/C samples were done using a quartz reactor connected to a Balzer mass spectrometer (QMG 220M1). Phenylacetylene and styrene were adsorbed on the sample by wet impregnation, followed by drying in vacuum at 25 °C. For the TPD experiments, the sample was submitted to a flow of argon and the temperature increased from 25 °C up to 200 °C at a rate of 2 °C/min.

2.3. Catalytic studies

Phenylacetylene reduction: The reactions were carried out in a schlenk reactor. The catalyst (5 mg) was placed under vacuum at room temperature. Then, a solution of 1 mmol of phenylacetylene in 10 mL of ethanol was added. The system was purged with H₂ and the reaction was left under 1 bar of H₂ using a balloon. The reaction was followed by taking samples at regular periods, that were analyzed by gas chromatography using a flame ionization detector and a capillary column (HP5, 30 m x 0.25 mm x 0.25 mm), using dodecane as external standard.

Hydrogenation of 1,5-cyclooctadiene: The hydrogenation of 1,5-cyclooctadiene was performed in a stainless steel high-pressure reactor. 1,5-Cyclooctadiene (2 mmol), 4 mL of n-octane and

catalyst (14 mg) were introduced into the reactor, purged with N₂ and H₂, pressurized with H₂ and finally heated at 50 °C under stirring (1000 rpm). The reaction was followed by taking samples at regular periods that were analyzed by gas chromatography using a flame ionization detector and a capillary column (HP5, 30 m x 0.25 mm x 0.25 mm), using dodecane as external standard. The identification of the products was performed by using a GC-MS spectrometer.

Reductive Amination of Furfural: The reaction was performed in a stainless steel high-pressure reactor. Furfural (2 mmol), aniline (2 mmol) in 2 mL of TFT, and the catalyst (20 mg) were introduced into the reactor, purged with N₂ and H₂, and then heated at 100 °C under stirring (1000 rpm). Finally, the reactor was pressurized at 4 bar of H₂ (pressurization was set as t=0). The products were analyzed on Agilent GC-7980A gas chromatograph equipped with a capillary column HP-5 (30 m × 0.25 μm × 0.25 mm) and FID detector. The identification of the products was performed by using a GC-MS spectrometer.

In all cases the initial reaction rates r^0 [mol·h⁻¹] were calculated for the corresponding compounds at conversions below 20%.

3. Results and discussion

3.1. Synthesis of Pd samples

The samples have been prepared under autogenous pressure in a stainless steel autoclave heated in an oven at 180-200 °C for 18-24 h. The synthesis gels contains a palladium salt, an organic compound and water and/or methanol solution. Details are given in the experimental section. The as prepared samples are labelled as PdHT-EDTA (when using Na₂EDTA as carbon source) and PdHT-Glucose (when using glucose as carbon source). The metal loading in both samples is ~20 wt % Pd, according to ICP analysis.

3.2. Spectroscopic characterization of the as prepared PdHT sample

Independent on the carbon source used in the synthesis, TEM, EDS and XRD of the as prepared PdHT samples show the presence of Pd⁰ particles with an average size of ~27 nm surrounded by a carbon matrix (Figure 1, and Figures S1, S2a).

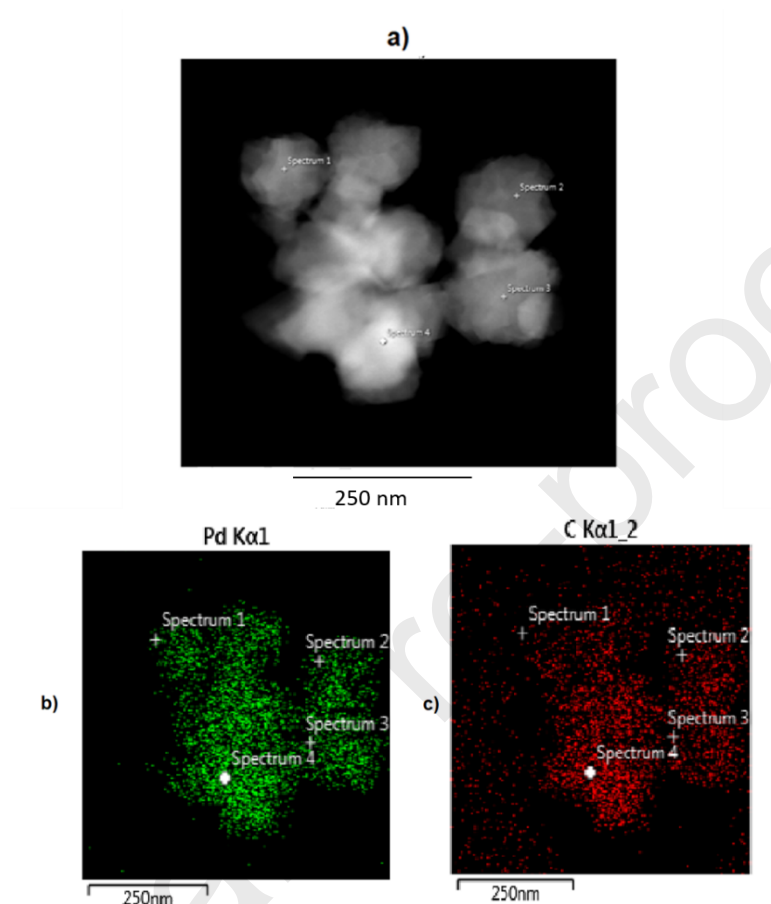


Figure 1. (a) TEM image of PdHT-EDTA sample, (b) Palladium EDS and (c) Carbon EDS analysis of the PdHT sample.

Raman spectra show two main bands at 1575 and 1371 cm⁻¹ corresponding to graphitic sp² carbon and disordered type graphitic carbonaceous species respectively, together with a small component at 1500 cm⁻¹ corresponding to amorphous carbon species (Figure S3).^[26] In addition, very weak bands at around 767 and 685 cm⁻¹ corresponding to PdO_x.^[27] In contrast to the results obtained using bulk type characterization tools where only Pd⁰ and a small amount of PdO_x are detected, high-resolution synchrotron photoelectron spectroscopy working under high surface sensitivity conditions (i.e. 500 eV x-ray excitation energy) shows the presence of an additional

palladium phase beside Pd^0 and PdO_x , ascribed to palladium carbide (PdC). Indeed, three components at 335.0, 335.5 and 336.0 eV BE are clearly detected using 500 eV excitation energy (Figure 2a) contributing ~33%, 60% and 7% respectively to the total peak intensity in the PdHT-EDTA sample. These species correspond to Pd^0 , palladium carbide (PdC) and PdO_x respectively. [7,28] To verify that PdC species are located on the upper layers of the Pd particle, depth profile analysis using variable synchrotron X-ray excitation energies was performed and the corresponding Pd $3d_{5/2}$ spectra are displayed in Figure 2. The concentration profile of the PdC phase among different atomic layers is given in Table 1. This result confirms the effective incorporation of C atoms into the uppermost surface layers of a bulk Pd metal catalyst prepared under the hydrothermal synthesis conditions described above. Similar profile of interstitial carbon is observed in the PdHT-Glucose sample when glucose is used as carbon source (Fig. S4 and Table S1). The effective stabilization of the PdC phase represents an interesting way to modulate the surface electronic properties of bulk metal catalysts and, accordingly, as will be shown below, their reactivity.

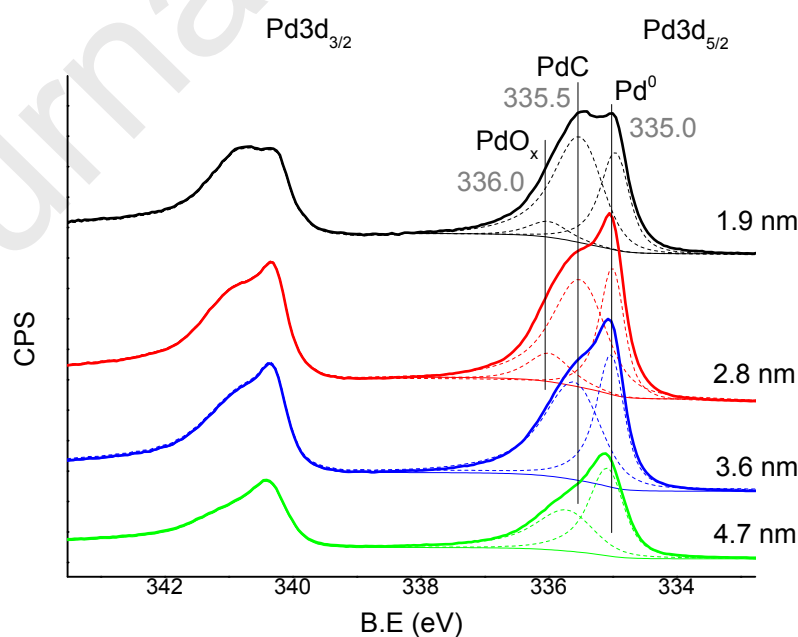


Figure 2. Pd 3d XPS spectra of the as prepared PdHT-EDTA sample acquired under UHV at variable X-ray excitation energy (h ν) corresponding to different sample depth: h ν =500 eV (1.9 nm, black), h ν =700 eV (2.8 nm, red), h ν =950 eV (3.6 nm, blue), h ν =1386 eV (4.7 nm, green).

Table 1 Sampling depth profile of the as prepared PdHT-EDTA catalyst obtained from synchrotron XPS analysis using variable X-ray energies.

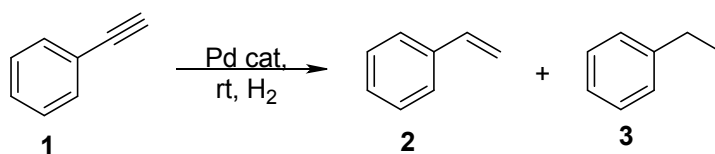
X-ray energy (eV)	Sample depth (nm)	Pd/C ^a	PdC (%) / Pd ⁰ (%) / PdO _x (%)
500	1.9	12.4 / 87.6	60.3 / 33.1 / 6.6
700	2.8	23 / 77	57.5 / 31.6 / 10.8
950	3.6	32.5 / 67.5	59.7 / 40.3 / 0
1386	4.7	38.8 / 61.2	43.2 / 56.8 / 0

a) Pd/C: Palladium/Carbon surface composition (mol %) obtained from the area of the Pd 3d and C 1s core levels, corrected by their respective cross section value and the intensity of the incident X-ray radiation.

3.3. Catalytic performance of the PdHT sample

In order to study the catalytic effect of a PdC phase present in the upper layers of the PdHT catalyst, we carried out various hydrogenation reactions with different substrates. Given results are referred to the PdHT-EDTA sample, while similar behaviour has been observed with the PdHT–Glucose sample (see Table S2). The results are compared with those obtained with a commercial 5 wt % Pd/C sample where no dissolved carbon species (i.e. PdC phase) are detected in the Synchrotron XPS spectra acquired at low X-ray excitation energy (700 eV) (Figure S5) and with literature data.

3.3.1. Selective hydrogenation of phenylacetylene



Scheme 1. Hydrogenation of Phenylacetylene

Table 2 Results of hydrogenation of phenylacetylene.^a

Entry	Catalyst	Time (min)	Conv. 1 (%)	Yield 2 (%)	Yield 3 (%)	Selec. 2 (%)	TOF (h ⁻¹) / (s ⁻¹) ^c
1 ^b	Pd/C	15	23.4	22.7	0.7	97	1800 / 0.5
		45	75	55	20	73	
		60	99	51	49	52	
2	PdHT-EDTA	15	80	80	0	100	24120 / 6.7
		20	100	90	10	90	

[a] 1 mmol phenylacetylene (**1**), room temperature, balloon H₂, 5 mg cat, 10 mL EtOH.

[b] 5% Pd/C from Sigma-Aldrich.

[c] TOF are calculated as initial reaction rate of disappearance of **1** divided by Pd (μmol/g) obtained by chemisorption of CO.

The hydrogenation of phenylacetylene (Scheme 1) was performed at room temperature in H₂ at atmospheric pressure. The results given in Table 2 and Figures S6 and S7 show much enhanced activity and selectivity to the alkene with the PdHT-EDTA sample that was hydrothermally prepared and contains PdC species. Moreover, when it is compared to the literature ^[29-33] (Table S3), the PdHT-EDTA catalyst maintains high selectivity (~90%) at 100% conversion, with reaction rates (2·10⁻⁴ mol·g⁻¹·s⁻¹) one order superior to most of the catalysts reported in the literature (~10⁻⁵ mol·g⁻¹·s⁻¹). Only a recent study reported by Peng et al ^[30] using an ionic liquid (IL) micro

phase and highly dispersed Pd nanoparticles inside a porous MOF shows similar activity than the PdHT-EDTA catalyst. However, the use of IL has main drawbacks such as difficulties in recycling and purification, hindering industrial applicability.

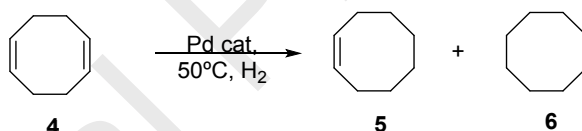
Achieving high selectivity and activity is still a challenge, being important for energy efficient processes. Many strategies have been developed in order to improve catalyst performance based on novel and complex synthetic strategies: ^[29, 30] formation of single metal alloys, ^[31] selective deposition of metal or metal oxides on the surface of the Pd particles, ^[32] and formation of intermetallic compounds with isolation of Pd active sites in the crystalline structure. ^[33] Our results show high activity and selectivity in the hydrogenation of phenylacetylene ascribed to the presence of palladium carbide species, where the presence of carbon atoms modifies the electronic state of surface Pd atoms, resulting in more electropositive Pd species ($\text{Pd}^{\delta+}$), as shown by XPS. This influences the adsorption of reactant and/or intermediates ^[34] and, accordingly, the activity and selectivity. Indeed, studying the adsorption-desorption of phenylacetylene and styrene on the PdHT-EDTA and Pd/C samples (Figure S8) a much higher adsorption of both reactants is observed on the Pd/C sample. In addition, as previously reported, ^[11] the presence of carbon species inhibits hydrogen (H) bulk diffusion enhancing accordingly the selectivity to phenylethylene.

Hydrogenation of phenylacetylene is a standard reaction where the role of dissolved carbon has been widely accepted. Most of the studies refer to Pd particle sizes <6 nm (see table S3) where the effect of the particle size in the activity and selectivity to styrene has resulted in controversial conclusions. ^[3,35] In a recent work Murzin et al. ^[36] reported a positive effect on the selectivity to styrene at increasing the Pd particle size in a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, which could influence the catalytic performance of the PdHT-EDTA compared to the Pd/C sample. Thus, in order to disentangle the effect of the carbide phase from the particle size, other reactions for which activity and selectivity is disfavoured at increased particle size are selected. This is the case of

the selective hydrogenation of 1,5-cyclooctadiene to 1,5-cyclooctene (Scheme 2) ^[37-39] and the reductive amination of furfural (Scheme 3) ^[40,41].

3.3.2. Selective hydrogenation of cyclooctadiene

The selective hydrogenation of 1,5-cyclooctadiene into cyclooctene is a reaction of interest since cyclooctene is an important industrial intermediate for manufacturing special polymers used as modifiers in rubbers and thermoplastics. ^[42] When using Pd catalysts, the selectivity to monoalkene considerably decreases when conversion of the dialkene increases. However, with the PdHT-EDTA catalyst, that contains surface carbon species, it has been found (see results in Table 3 and Figures S9, S10 and S11) not only a higher intrinsic catalytic activity of Pd (i.e. TOF) than Pd/C and Pd black for the hydrogenation of 1,5-cyclooctadiene, but a much better selectivity for the formation of the mono-olefins.



Scheme 2. Hydrogenation of 1,5-cyclooctadiene

Table 3 Hydrogenation of 1,5-cyclooctadiene with different Pd catalysts.^a

Entry	Catalyst	Time (min)	Conv. 4 (%)	Yield 5 (%)	Yield 6 (%)	Selec. 5 (%)	TOF (h ⁻¹) / (s ⁻¹) ^c
1	PdHT-EDTA	20	80	80	-	100	12960 / 3.6
		45	100	100	-	100	
2 ^b	Pd/C	6	80	78	2	98	6120 / 1.7
		10	100	76	24	76	

3	Pd black	120	85	77	8	90	485 / 0.13
		180	100	78	22	78	

[a] 2 mmol 1,5-cylooctadiene (**1**), 4mL n-octane, 14 mg cat, 10 bar H₂.

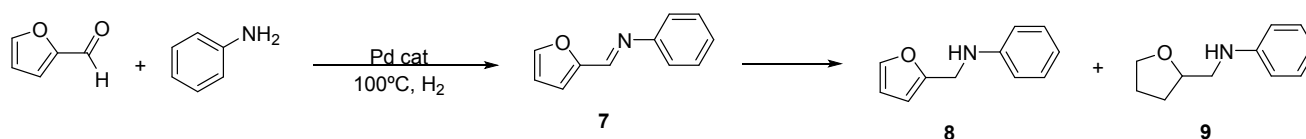
[b] 5% Pd/C from Sigma-Aldrich.

[c] TOF are calculated as initial reaction rate of disappearance of **4** divided by Pd (μmol/g) obtained by chemisorption of CO.

Remarkably, 100% selectivity to cyclooctene at 100% conversion is achieved on the PdHT-EDTA sample. These values are higher to those of the literature ^[37,43,44] (Table S4) when comparing Pd based catalysts, showing also a higher intrinsic activity of the Pd surface site. Some reports have shown high selectivity, using gold based catalyst ^[45] in the hydrogenation of dienes, while their activity is lower than Pd based catalysts.

3.3.3. Reductive amination of furfural with aniline

In the case of the reductive amination of furfural with aniline, the aniline acts as a nucleophile that attacks the carbonyl group of the HMF forming imine **7**, which is subsequently hydrogenated to the corresponding secondary amine. Notice that the production of secondary furfurylamines by reductive amination of furanic aldehydes with amines and hydrogen as reducing agent in presence of metal catalysts is not usually a selective process due to the competitive hydrogenation of the furanic ring. ^[46-48] In this reaction, the formation of the intermediate imine (**7**) (Scheme 3) is a very fast process, being the imine hydrogenation the controlling step of the process.



Scheme 3. Reductive amination of furfural with aniline

Table 4 Reductive amination of furfural with aniline.^a

Entry	Catalyst	Time (min)	Conv. 7 (%)	Yield 8 (%)	Yield 9 (%)	Selec. 8 (%)	TOF (h ⁻¹) / (s ⁻¹) ^c
1	PdHT-EDTA	10	53	53	0	100	5061 / 1.4
		30	100	99	1	99	
2 ^b	Pd/C	30	26	26	0	100	533 / 0.14
		45	57	57	0	100	
		180	100	87	13	87	

[a] 2 mmol furfural, 2 mmol aniline , 20 mg cat, 2 mL TFT, 100 °C, 4 bar H₂.

[b] 5% Pd/C from Sigma-Aldrich

[c] TOF are calculated as initial reaction rate of disappearance of **7** divided by Pd (μmol/g) obtained by chemisorption of CO.

As it can be observed in Table 4 the TOF for the hydrogenation of the imine **7** using PdHT-EDTA catalyst is ten times higher than for Pd/C while the selectivity to furfurylamine **8** using the PdHT-EDTA catalyst is ~100% (Figures S12 and S13). These values are superior to those of the literature [25,40,48] (Table S5). In a recent work [40] we reported 100% selectivity at 100% conversion on a 1 wt % Pd/C catalyst prepared by wet impregnation of Pd(acac)₂ on carbon (Norit ROW 0.8mm). In that case, deposition of carbon species onto Pd(111) facets have been determined experimentally, being responsible of the 100 % selectivity. However the intrinsic activity of that Pd catalyst is markedly lower (TOF of 0.4 s⁻¹) than the PdHT-EDTA catalyst (TOF of 1.4 s⁻¹) while 100 % selectivity is maintained.

The positive effect of the PdC surface layer in the PdHT-EDTA catalyst has been further demonstrated using the *ex situ* H₂ reduced PdHT-EDTA (Figure S11 and S14). H₂ reduction results

in the destabilization of the Pd carbide and its transformation into a Pd-Hydride phase ^[49,50] keeping the particle size unaltered (see Fig. S2b). Indeed, we confirmed by synchrotron XPS studies (see detailed description of the procedure and results in the supplementary part and Figure S15) that the PdHT-EDTA is transformed in a less selective catalyst when the PdC phase disappears. In the case of 1,5-cyclooctadiene the selectivity to cyclooctene was decreased from 100% to 80% at 100% conversion after *ex situ* reduction at 150 °C (Figure S10). Similarly, in the case of the reductive amination of furfural, after the *ex situ* reduction of the PdHT-EDTA catalyst, the selectivity to the secondary amine **8** decreased from 100% to 90% at 100% conversion (Figure S14). It is interesting to point out that in both examples, the selectivity achieved with the *ex situ* reduced PdHT-EDTA was similar to those obtained with the commercial catalyst.

Interestingly, while PdC species in the PdHT-EDTA catalyst are unstable in the presence of H₂ during *ex situ* sample reduction, the catalyst remains quite stable when working in liquid phase under H₂ atmosphere. Indeed, the PdHT-EDTA catalyst is fully reusable maintaining both activity and selectivity, at least after three catalytic cycles (see Figure 3). In opposite, an 87% activity drop is observed with the commercial Pd/C sample already after the second reuse (see Figure 4). The high stability of the PdHT-EDTA sample is remarkable since deactivation is an important drawback in the selective hydrogenation of alkynes and dienes, leading to a short life of the catalyst. ^[50]

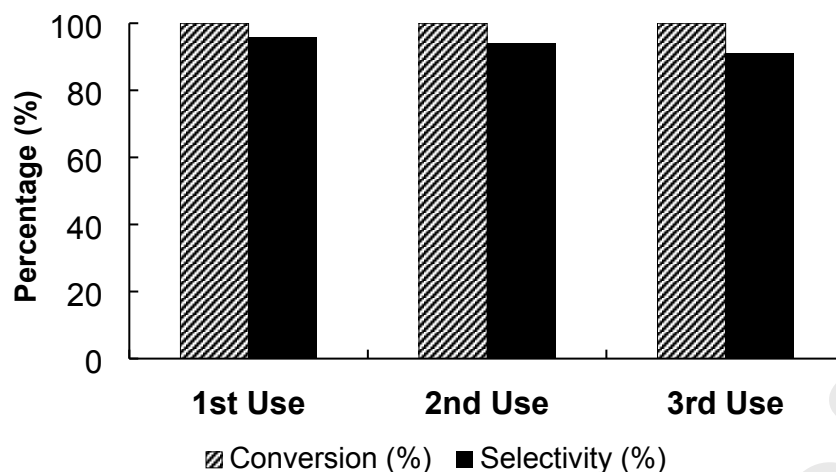


Figure 3. Results of 1,5-cyclooctadiene reduction using PdHT-EDTA catalyst. Reaction conditions: 1,5-cyclooctadiene (2.08 mmol), n-octanol (4 mL), 14 mg PdHT, 50 °C, 5 bar H₂, 1 h reaction time.

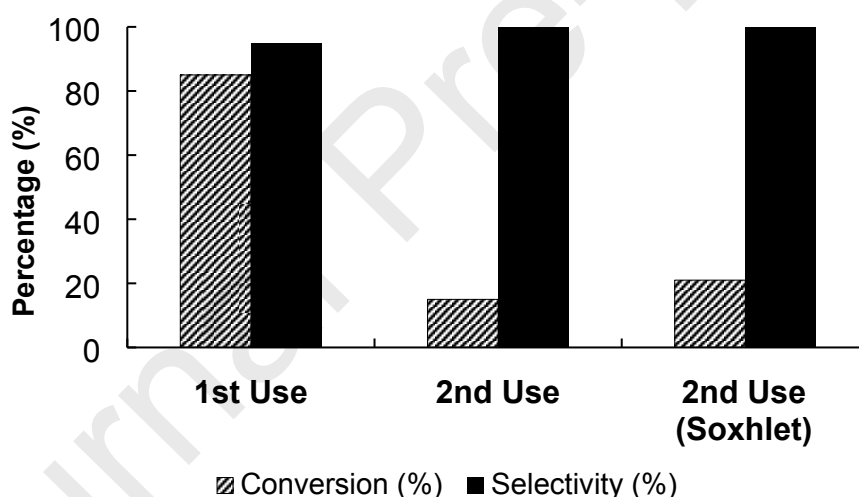


Figure 4. Results of 1,5-cyclooctadiene reduction using 5% Pd/C catalyst. Reaction conditions: 1,5-cyclooctadiene (2.08 mmol), n-octanol (4 mL), 14 mg 5% Pd/C, 50 °C, 5 bar H₂, 1 h reaction time.

In this type of reactions, deactivation is usually caused by the deposition of oligomers and polymeric material on the catalyst surface as a result of the condensation of unsaturated compounds. In fact, thermogravimetric analysis (TG) shows strong adsorption of organic species

(~15%) on the used Pd/C catalysts. Thus, a stronger adsorption can be inferred on the commercial Pd/C sample, exhibiting Pd⁰ surface sites. This is in line with the higher adsorption of reactants and intermediate species observed previously in the temperature programmed desorption experiments of Fig. S8 on Pd/C sample.

4. Conclusions

We present a highly selective and active hydrogenation Pd catalyst composed by a palladium carbide phase stabilized on the upper surface layers of a Pd carbon catalyst. The catalyst synthesis method comprises a hydrothermal process at 200 °C, starting from a palladium precursor (i.e. Pd(NO₃)₂), an organic compound (i.e. Na₂EDTA or glucose) and a water-methanol solution. The easy and mild conditions of this synthetic procedure contrast with those reported in the literature, where scalability and efficiency are main drawbacks. XPS depth profile analysis using synchrotron radiation at variable X-ray excitation energy shows an enrichment of PdC on the upper layers of the catalyst, independently of the organic precursor used in the hydrothermal synthesis. In detail, at a sample thickness of 1.9 nm 56-60 % Pd carbide is observed, and around 66-43 at % a depth of 4.7 nm. The presence of surface Pd carbide modifies the electronic properties of the Pd resulting in Pd^{δ+} species. This has a strong positive effect on activity and selectivity for a variety of demanding selective hydrogenation reactions as, for instance, the hydrogenation of phenylacetylene, hydrogenation of 1,5-cyclooctadiene and the reductive amination of furfural with aniline. In all cases, selectivities close to 100% at almost full conversion are achieved with higher intrinsic activity per surface Pd atom to that reported in the literature. The positive effect of the PdC species on the catalytic performance of the PdHT catalyst has been demonstrated by *ex situ* reduction of the sample, that results in the destabilization of the PdC phase with formation of Pd-hydride and Pd⁰, and the corresponding

decrease in selectivity. PdHT catalysts, in contrary to Pd/C, are quite stable under reaction conditions, and no loss of activity or selectivity has been found after several catalyst reuses.

Appendix A. Supplementary material

Figure S1. Images TEM of PdHT-EDTA at different zoom

Figure S2a. XRD of PdHT-EDTA sample

Figure S2b. XRD of the *ex situ* reduced PdHT-EDTA sample

Figure S3. Raman spectra of the as prepared PdHT-EDTA sample

Figure S4. Pd 3d XPS spectra of the as prepared PdHT-Glucose sample acquired under UHV at variable X-ray excitation energy (h ν) corresponding to different sample depth

Figure S5. Pd 3d XPS spectra of the commercial 5% Pd/C sample (Sigma Aldrich) acquired at 700 eV X-ray excitation energy

Figure S6. Kinetic curve of reduction reaction of phenylacetylene with PdHT-EDTA

Figure S7. Kinetic curve of reduction reaction of phenylacetylene with commercial 5% Pd/C

Figure S8. Temperature desorption of phenylacetylene and styrene adsorbed on PdHT-EDTA and commercial 5% Pd/C samples

Figure S9. Kinetic curve of reduction reaction of 1,5-cyclooctadiene with PdHT-EDTA

Figure S10. Kinetic curve of reduction reaction of 1,5-cyclooctadiene with commercial 5% Pd/C

Figure S11. Kinetic curve of reduction reaction of 1,5-cyclooctadiene with *ex situ* reduced PdHT-EDTA

Figure S12. Kinetic curve of reductive amination of furfural with aniline with PdHT-EDTA

Figure S13. Kinetic curve of reductive amination of furfural with aniline with commercial 5% Pd/C

Figure S14. Kinetic curve of amination reduction reaction of furfural and aniline with *ex situ* reduced PdHT-EDTA

Figure S15. Pd 3d XPS spectra of the as prepared PdHT-EDTA sample acquired at 500 eV X-ray excitation energy and in the presence of 1 mbar H₂ at 175 °C and 250 °C

Table S1. Sampling depth profile of the as prepared PdHT-Glucose catalyst obtained from synchrotron XPS analysis using variable X-ray energies

Table S2. Catalytic activity of PdHT-Glucose sample in the a) reductive amination of furfural with aniline, b) selective hydrogenation of cyclooctadiene

Table S3. Hydrogenation of phenylacetylene (PhA) to styrene using Pd based catalysts

Table S4. Hydrogenation of cyclooctadiene (COD) to cyclooctene (COE) on Pd based heterogeneous catalysts

Table S5. Reductive amination of furfural with aniline on Pd based catalysts

Acknowledgments

Funding: The research leading to these results has received funding from the Spanish Ministry of Science, Innovation and Universities through “Severo Ochoa” Excellence Programme (SEV-2016-0683) and the PGC2018-097277-B-100 project. The authors also thank the Microscopy Service of UPV for kind help on measurements. A. García-Ortiz thanks “Severo Ochoa” Programme (SEV-2016-0683) for a predoctoral fellowship. J. Cored thanks the Spanish Government (MINECO) for a “Severo Ochoa” grant (BES-2015-075748). D. R. thanks European Research Council project SYNCATMATCH (671093). The NAP-XPS experiments were performed at the NAPP branch of the CIRCE beamline at the ALBA Synchrotron with the collaboration of

ALBA staff. **Author contributions:** A.C. conceived the project and contributed in the production of the manuscript. S.I, M.J.C and P.C. directed the study and wrote the manuscript. P.C. did the Raman and participated together with D.R., V.P.D and J.C. in the XPS measurements at ALBA Synchrotron. A.G.O. did the synthesis of the samples, the TEM analysis and the catalytic study. All authors participated in the discussion of the results. **Competing interest:** The authors declare no competing financial interest. **Data and materials availability:** all data are presented in the paper and/or supplementary materials.

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References

- [1] A. Borodzinski, G.C. Bond, "Selective hydrogenation of ethyne in ethane-rich streams on palladium catalysts, Part 2: Steady-state kinetics and effects of palladium particle size, carbon monoxide, and promoters", *Catal. Rev.*, **2008**, *50*, 379-469.
- [2] G. Vile, D. Albani, N. Almora-Barrios, N. Lopez, J. Perez-Ramírez, "Advances in the design of nanostructure catalysts for selective hydrogenation", *Chem. Cat. Chem.*, **2016**, *8*(1), 21-33.
- [3] Á. Molnár, A. Sárkány, M. Varga, "Hydrogenation of carbon-carbon multiple bonds: chemo-, regio-and stereo-selectivity", *J. Mol. Catal. A: Chem.*, **2001**, *173*(1), 185-221.

- [4] W. Jones, P.P. Wells, E.K. Gibson, A. Chutia, I.P. Silverwood, C.R.A. Catlow, M. Bowker, "Carbidisation of Pd nanoparticles by ethene decomposition with methane production", *ChemCatChem.*, **2019**, *11*, 4334-4339.
- [5] A.L. Bugaev, A.A. Guda, I.A. Pankin, E. Groppo, R. Pellegrini, A. Longo, A.V. Soldatov, C. Lamberti, "The role of palladium carbides in the catalytic hydrogenation of ethylene over supported palladium nanoparticles", *Catal. Today.*, **2019**, *336*, 40-44.
- [6] A.L. Bugaev, A.A. Guda, A. Lazzarini, K.A. Lomachenko, E. Groppo, R. Pellegrini, A. Piovano, H. Emerich, A.V. Soldatov, L.A. Bugaev, V.P. Dmitriev, J.A. van Bokhoven, C. Lamberti. "In Situ Formation of Hydrides and Carbides in Palladium Catalyst: When XANES Is Better than EXAFS and XRD", *Catal. Today* **2017**, *283*, 119-126.
- [7] D. Teschner, J. Borsodi, A. Wootsch, Z. Révay, M. Hävecker, A. Knop-Gericke, S.D. Jackson, R. Schlögl, "The roles of subsurface carbon and hydrogen in palladium-catalyzed alkyne hydrogenation", *Sci.*, **2008**, *320(5872)*, 86.
- [8] A. Michaelides, P. Hu, "Physical origin of the high reactivity of subsurface hydrogen in catalytic hydrogenation", *J. Chem. Phys.*, **1999**, *111*, 1343-1345.
- [9] N.A. Khan, S. Shaikhutdinov, H.J. Freund, "Acetylene and ethylene hydrogenation on alumina supported Pd-Ag model catalysts" *Catal. Lett.*, **2006**, *108(3)*, 159-164.
- [10] D. Teschner, Z. Révay, J. Borsodi, M. Hävecker, A. Knop-Gericke, R. Schlögl, D. Milroy, S.D. Jackson, D. Torres, P. Sautet, "Understanding Palladium hydrogenation catalysts: When the nature of the reactive molecule controls the nature of the catalyst active phase", *Angew. Chem.*, **2008**, *120(48)*, 9414-9418
- [11] D. Teschner, J. Borsodi, Z. Kis, L. Szentmiklósi, Z. Révay, A. Knop-Gericke, R. Schlögl, D. Torres, P. Sautet, "Role of hydrogen species in Palladium-catalyzed alkyne hydrogenation" *J. Phys. Chem. C*, **2010**, *114(5)*, 2293-2299.

- [12] D. Torres, F. Cinquini, P. Sautet, "Pressure and temperature effects on the formation of a Pd/C surface carbide: Insights into the role of Pd/C as a selective catalytic state for the partial hydrogenation of acetylene", *J. Chem. Phys. C*, **2013**, 117(21), 11059-11095.
- [13] N. Singh, M.T. Nguyen, D.C. Cantu, B.L. Mehdi, N.D. Browning, J.L. Fulton, J. Zheng, M. Balasubramanian, O.Y. Gutiérrez, V.A. Glezakou, R. Rousseau, N. Govind, D.M. Camaioni, C.T. Campbell, J. A. Lercher, "Carbon-Supported Pt during Aqueous Phenol Hydrogenation with and without Applied Electrical Potential: X-Ray Absorption and Theoretical Studies of Structure and Adsorbates". *J. Catal.* **2018**, 368, 8-19.
- [14] F. Huang, Z. Jia, J. Diao, H. Yuan, D. Su, H. Liu, "Palladium nanoclusters immobilized on defective nanodiamond-graphene core-shell supports for semihydrogenation of phenylacetylene", *J. Energy. Chem.*, **2019**, 33, 31-36.
- [15] K. Okitsu, Y. Mizukoshi, H. Bandow, T.A. Yamamoto, Y. Nagata, Y. Maeda, "Synthesis of palladium nanoparticles with interstitial carbon by sonochemical reduction of tetrachloropalladate (II) in aqueous solution", *J. Phys. Chem. B*, **1997**, 101(28), 5470-5472.
- [16] R. Guo, Q. Chen, X. Li, Y. Li, C. Wang, W. Bi, C. Zhao, Y. Guo, M. Jin, "PdC_x nanocrystals with tunable compositions for alkyne semihydrogenation", *J. Mater. Chem. A*, **2019**, 7, 4714-4720.
- [17] A. Beltzung, M.A. Newton, M. Nachtegaal, H. Wu, G. Storti, M. Morbidelli, "Research update: Distribution and stabilization of Pd catalysts in porous carbon-based supports by aggregation of pre-doped colloid particles" *APL Mater.*, **2018**, 6, 100704-1-15.
- [18] M. Sevilla, A.B. Fuertes, R. Mokoya, "High density hydrogen storage in superactivated carbons from hydrothermally carbonized renewable organic materials", *Energy Environ. Sci.*, **2011**, 4, 1400-1410.
- [19] L. Liu, F. Gao, P. Concepción, A. Corma, "A new strategy to transform mono and bimetallic non-noble metal nanoparticles into a highly active and chemoselective hydrogenation catalysts", *J.Catal.*, **2017**, 350, 218-225.

- [20] P. Makowski, R.D. Cakan, M. Antonietti, F. Goettmann, M.M. Titirici, "Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on hydrophilic carbon", *Chem. Commun.*, **2008**, 999, 999-1001.
- [21] L. Liu, A.V. Puga, J. Cored, P. Concepción, V. Pérez-Dieste, H. García, A. Corma, "Sunlight-assisted hydrogenation of CO₂ into ethanol and C₂⁺ hydrocarbons by sodium-promoted Co@C nanocomposites", *Appl. Catal. B.* **2018**, 235, 186-196.
- [22] L. Liu, P. Concepción, A. Corma, "Non-noble metal catalysts for hydrogenation: A facile method for preparing Co nanoparticles covered with thin layered carbon", *J. Catal.*, **2016**, 340, 1-9.
- [23] J. Cored, A. García-Ortiz, S. Iborra, M.J. Climent, L. Liu, C-H. Chuang, T-S. Chan, C. Escudero, P. Concepción, A. Corma "Hydrothermal synthesis of ruthenium nanoparticles with a metallic core and a ruthenium carbide shell for low temperature activation of CO₂ to methane", *J. Am. Chem. Soc.*, **2019**, 141(49), 19304-19311.
- [24] C.J. Powell, A.J., *NIST Electron Inelastic Mean Free Path Database, version 1.1*. National Institute of Standards and Technology: Gaithersburg, MD, 2002.
- [25] H. Sharma, M. Bhardwaj, M. Kour, S. Paul, "Highly efficient magnetic Pd(0) nanoparticles stabilized by amine functionalized starch for organic transformations under mild conditions", *Mol. Catal.*, **2017**, 435, 58-68.
- [26] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, "Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information", *Carbon*, **2005**, 43(8), 1731-1742.
- [27] A. Baylet, P. Marécot, D. Duprez, P. Castellazzi, G. Groppi, P. Forzatti, "In situ Raman and in situ XRD analysis of PdO reduction and Pd⁰ oxidation supported on γ -Al₂O₃ catalyst under different atmospheres", *Phys. Chem. Chem. Phys.*, **2011**, 13, 4607-4613.

- [28] C.D. Wagner, A.V. Naumkin, A. Kraut-Vass, J.W. Allison, C.J. Powell, J.R.Jr. Rumble, NIST Standart Reference Database 20, Version 3.4 can be found under <http://srdata.nist.gov/xps/>, **2003**.
- [29] H. Tian, F. Huang, Y. Zhu, S. Liu, Y. Han, M. Jaroniec, Q. Yang, H. Liu, G. Q. M. Lu, J. Liu, "The development of yolk-shell-structured Pd&ZnO@Carbon submicroreactors with high selectivity and stability", *Adv. Funct. Mater.*, **2018**, 28, 1801737.
- [30] L. Peng, J. Zhang, S. Yang, B. Han, X. Sang, C. Liu, G. Yang, "The ionic liquid microphase enhaces the catalytic activity of Pd nanoparticles supported by a metal-organic framework", *Green Chem.*, **2015**, 17, 4178-4182.
- [31] M.B. Boucher, B. Zugic, G. Cladaras, J. Kammert, M.D. Marcinkowski, T.J. Lawton, E.C.H. Sykes, M. Flytzani-Stephanopoulos, "Single atom alloy surface analogs in Pd_{0.18}Cu₁₅ nanoparticles for selective hydrogenation reactions", *Phys. Chem. Chem. Phys.*, **2013**, 15, 12187-12196.
- [32] W. Zhang, W. Wu, Y. Long, J. Qin, F. Wang, J. Ma, "Promoting role of iron elements modification on palladium/nitrogen doped carbon for the semihydrogenation of phenylacetylene", *Chem. Cat. Chem.*, **2019**, 11, 1510-1517.
- [33] M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Y. Grin, R. Schlögl, "Pd-Ga intermetallic compounds as highly selective semihydrogenation catalysts", *J. Am. Chem. Soc.* **2010**, 132, 14745-14747.
- [34] J. Panpranot, K. Phandinthong, T. Sirikajorn, M. Arai, P. Praserttham, "Impact of palladium silicide formation on the catalytic properties of Pd/SiO₂ catalysts in liquid-phase semihydrogenation of phenylacetylene", *J. Mol. Catal. A: Chem.*, **2007**, 261, 29-35.
- [35] J. Hu, Z. Zhou, R. Zhang, L. Li, Z. Cheng, "Selective hydrogenation of phenylacetylene over a nano-Pd/ α -Al₂O₃ catalyst", *J. Mol. Catal. A.*, **2014**, 381, 61-69.
- [36] P.V. Markov, I.S. Mashkovsky, G.O. Bragina, J. Wärna, E.Y. Gerasimov, V.I. Bukhtiyarov, A.Y. Stakheev, D.Y. Murzin; "Particle size effect in liquid-phase hydrogenation of

- phenylacetylene over Pd catalysts: Experimental data and theoretical analysis", Chem. Eng. J., **2019**, 358, 520-530.
- [37] D. Tang, X. Sun, D. Zhao, J. Zhu, W. Zhang, X. Xu, Z. Zhao, "Nitrogen-doped carbon xerogels supporting palladium nanoparticles for selective hydrogenation reactions: the role of pyridine nitrogen species", Chem. Cat. Chem., **2018**, 10, 1291-1299.
- [38] T.S. Huang, Y.H. Wang, J.Y. Jiang, Z.L. Jin, "PEG-stabilized palladium nanoparticles: An efficient and recyclable catalyst for the selective hydrogenation of 1,5-cyclooctadiene in thermoregulated PEG biphasic system", Chinese Chemical Letters, **2008**, 19, 102-104.
- [39] T. Yuan, H. Gong, K. Kailasam, Y. Zhao, A. Thomas, J. Zhu, "Controlling hydrogenation selectivity with Pd catalysts on carbon nitrides functionalized silica", J. Catal., **2015**, 326, 38-42
- [40] A. Garcia-Ortiz, J.D. Vidal, M.J. Climent, P. Concepcion, A. Corma, S. Iborra, "Chemicals from Biomass: Selective synthesis of N-substituted furfuryl amines by the one-pot direct reductive amination of furanic aldehydes", ACS. Sust. Chem. Eng., **2019**, 7, 6243- 6250.
- [41] J.D. Vidal, M.J. Climent, P. Concepción, A. Corma, S. Iborra, M.J. Sabater, "Chemicals from Biomass: Chemoselective reductive amination of ethyl levulinate with amines", ACS Catalysis, **2015**, 5(10), 5812-5821.
- [42] T. Schiffer, G. Oenbrink, *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-Interscience: New York, **2009**, 11, 37-40.
- [43] P. Concepcion, S. García, J.C. Hernández-Garrido, J.J. Calvino, A. Corma, "A promoting effect of dilution of Pd sites due to gold surface segregation under reaction conditions on supported Pd-Au catalysts for the selective hydrogenation of 1,5-cyclooctadiene", Catal. Today., **2015**, 259, 213-221.
- [44] A.T. Mubarak, A.M. Alhanash, M. Benaissa, H.H. Hegazy, M.S. Hamdy, "In-situ activation of Pd-TUD-1 during the selective reduction of 1,5-cyclooctadiene", Micropor. Mesopor. Mat., **2019**, 278, 225-231.

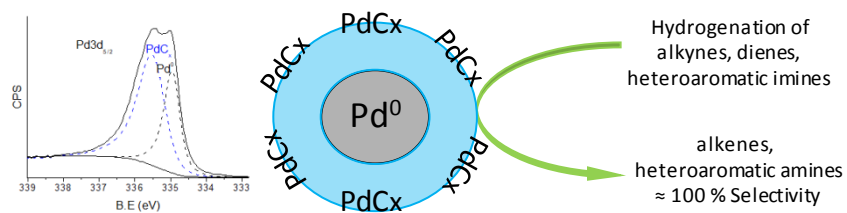
- [45] X. Zhang, F.X. Llabrés, A. Corma, "Gold (III)-metal organic framework bridges the gap between homogeneous and heterogeneous gold catalysts", *J. Catal.*, **2009**, 265 (2), 155-160.
- [46] M. Chatterjee, T. Ishizaka, H. Kawanami, "Reductive amination of furfural to furfurylamine using aqueous ammonia solution and molecular hydrogen: an environmentally friendly approach", *Green Chem.*, **2016**, 18, 487-496.
- [47] T. Komanoya, T. Kinemura, Y. Kita, K. Kamata, M. Hara, "Electronic effect of ruthenium nanoparticles on efficient reductive amination of carbonyl compounds", *J. Am. Chem. Soc.*, **2017**, 139 (33), 11493-11499.
- [48] D.B. Bagal, R.A. Watile, M.V. Khedkar, K.P. Dhake, B.M. Bhanage, "PS-Pd-NHC: an efficient and heterogeneous recyclable catalyst for direct reductive amination of carbonyl compounds with primary/secondary amines in aqueous medium", *Catal. Sci. Technol.*, **2012**, 2, 354-358.
- [49] A.L. Bugaev, O.A. Usoltsev, A. Lazzarini, K.A. Lomachenko, A.A. Guda, R. Pellegrini, M. Carosso, J.G. Vitillo, E. Groppo, J.A. van Bokhoven, A.V. Soldatov, C. Lamberti, "Time-resolved operando studies of carbon supported Pd nanoparticles under hydrogenation reactions by X-ray diffraction and adsorption", *Faraday Discuss.*, **2018**, 208(0), 187-205.
- [50] V.D. Stytsenko, D.P. Mel'nikov, "Selective hydrogenation of dienic and acetylenic compounds on metal-containing catalysts", *Russ. J. Phys. Chem. A*, **2016**, 90(5), 932-942.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

GRAPHICAL ABSTRACT



Palladium carbide species (PdC_x) are formed on the upper layers of a Palladium carbon catalyst using a hydrothermal synthesis method. Its presence modifies the electronic state of surface Pd atoms resulting in a highly active and selective catalyst for hydrogenation of alkynes, dienes and heteroaromatic imines.

Highlights

- Synthesis of palladium carbide species by an easy hydrothermal method
- Sampling depth profile XPS analysis of palladium carbide species in the catalyst
- Modification of the electronic properties of surface palladium atoms resulting in more positive
- High catalyst stability after several re-use