## **Electronic Supporting Information (ESI) for:**

# The effect of particle size, morphology and support on the formation of palladium hydride in commercial catalysts

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### **Experimental Section**

## Materials

Porous and non-porous high purity carbon were used as support materials in this study: a powder type high surface area activated carbon (AC), (nitrogen surface area > 1000 m<sup>2</sup>/g, steam activated, total pore volume > 1.3 ml  $g^{-1}$ , hydrogen content 3900 ppm H), and carbon black (CB) with enhanced sp<sup>2</sup> character as indicated by the low hydrogen content (295 ppm H). The hydrogen content of the carbon supports was determined by hot extraction using a LECO TCH600 instrument. The freshly impregnated 20% Pd/CB catalyst was additionally treated by carbo-thermal reduction at 300 ° and 400 °C in an argon atmosphere. In the literature, this treatment is described as a suitable means to produce fine particle distributions of colloidal entities at the surface of a non-porous carbon black support.<sup>1</sup> It also allows us to numerically probe the influence of temperature on controlled particle growth, the changes of average particle size and morphology, the impact on hydrogen absorption capacity and site occupation. In addition, a Pd(20%)/CB with a very low hydrogen content (60 ppm H) that has been previously described<sup>2</sup> and a shell-type Pd(1.04%)/Au(0.43) alloy catalyst supported on silica-pellets were also studied. The sample masses used in an individual IINS measurement were in the range 14 - 50 g, Table S1, so provided a representative, average sample of the catalysts, all of which were manufactured by Evonik Resource Efficiency GmbH.<sup>3</sup>

A 60.5 g sample of high purity palladium black (99,11%; BET surface  $\geq 25 \text{ m}^2 \text{ g}^{-1}$ ; CAS No. 7440-05-3; Umicore Precious Metals Chemistry) was also investigated. Further details on this material are given elsewhere.<sup>2</sup>

Sample No./catalyst	IINS sample weight / g					
Activated Carbon support background	18.57					
Carbon Black support background 14.34						
1 1.04%Pd,0.43%Au/SiO <sub>2</sub> (PdAu)	49.57					
2 20% Pd on Activated Carbon (Pd/AC)	27.08					
3 20% Pd on Carbon Black (295 ppm H) (Pd/CB)	32.27					
4 as 3 calcined 300°/Ar (Pd/CB300)	25.51					
5 as 3 calcined 400°/Ar (Pd/CB400)	28.77					
6 20% Pd on Carbon Black (60 ppm H) (Pd/CB2)	25.79					

 Table S1 Catalyst samples and amount probed in a single neutron experiment.

### **Transmission Electron Microscopy (TEM)**

A Hitachi H7500 and a Jeol 2010F field emission transmission electron microscope were operated at 100 and 200 keV acceleration voltage, respectively. For confirming the chemical identity of precious metal primary particles and aggregates and regarding alloying in the Pd/Au-catalyst, energy dispersive X-ray spot-analyses at the nanoscale (EDX) of the supported particles and the support particles were performed using a Noran SiLi detector with a 30 mm<sup>2</sup> crystal and a Noran System Six device. A catalyst sample was dispersed and transferred onto Holey Carbon Foil supported by a 200 mesh copper grid. For statistical evaluation of the primary particle sizes of the supported primary particles the I-TEM software of Soft Imaging Systems (SIS), Münster, Germany, was utilized. The average primary particle

sizes of the supported Pd-based catalyst particles were determined by statistical evaluation of 2000 particles in TEM images per catalyst sample (Table 2) and Fig. S1. The quality, stability and calibration of the TEM system were maintained by the use of the Magical No. 641 standard (Norrox Scientific Ltd., Beaver Pond, Ontario, Canada).

## Scanning Electron Microscopy (SEM)

A Jeol 7600F field emission instrument with EDX detector (150 mm<sup>2</sup>, Oxford Aztec Advanced System) was used.

## X-ray Photoelectron Spectroscopy (XPS)

A Thermo Fisher 250Xi instrument was operated using mono-chromatised Al K $\alpha$  radiation, 20 eV pass energy A catalyst sample was introduced into a differentially pumped prechamber as a loose powder. Integral XPS spectra of an area of 1 mm<sup>2</sup> size were recorded.

## Inelastic Incoherent Neutron Scattering (IINS)

Each catalyst was sealed into a thin-walled (0.5 mm) stainless steel (1.4571) can which was closed by a top-flange with a stainless steel pipe and a welded bellows valve (Nupro) via a OFHC-copper (oxygen-free high conductivity) gasket. A sealed can containing macroscopic amounts of catalyst (Table 1) was evacuated using a turbo-molecular pump which was backed by a dual stage rotary pump with a zeolite trap to avoid back-diffusion of oil and other potential molecular contaminants. In order to remove surface-hydroxides, traces of adsorbed water and sub-stoichiometric surface-oxides, each catalyst was subjected to slow and careful cycles of hydrogenation (99.999% hydrogen, Linde) and dehydrogenation at room temperature to avoid fast local heating due to a spontaneous excessive release of the heat of the dissociative absorption of hydrogen in the palladium in fast-step dosing. No heating during degassing of a hydrogenated catalyst by pumping down a sample can was performed, in order to avoid particle growth induced by heat under the presence of residual pressure of hydrogen and further reactions. The hydrogen uptake of the supported palladium was monitored by capacitive pressure transducers (Baratron). After 5 cycles at room temperature and 24 h of evacuation with a turbomolecular pump each sample was topped to 700 mbar hydrogen sorption equilibrium pressure and measured with IINS.

IINS spectra were recorded on TOSCA,<sup>4,5</sup> a high resolution indirect geometry spectrometer. Spectra of the surface occupation in on-top site were recorded with the MAPS<sup>4,6</sup> and MERLIN,<sup>7</sup> direct geometry chopper (all at the ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton UK). Neutron spectra on the hydrogenated palladium black reference sample were taken at IN1-Lagrange, a high resolution beryllium filter spectrometer using the Cu(220) monochromator<sup>8,9</sup> (ILL, Institute Max von Laue/Paul Langevin, Grenoble, France). The different characteristics of the instruments are discussed in detail elsewhere.<sup>10</sup> For the present work, the relevant properties are that TOSCA and IN1-Lagrange provide excellent spectra in the 0 – 1600 cm<sup>-1</sup> region, while MAPS and MERLIN provide access to the 1600 – 4000 cm<sup>-1</sup> region. MAPS provides good resolution and modest sensitivity while MERLIN provides modest resolution and excellent sensitivity. All of the TOSCA spectra shown are normalised to 1 g Pd (or equivalently, 4 g carbon), allowing relative intensities to be compared. For the Pd/C catalysts, the hydrogen was pumped off in several steps and the sequential decomposition of the hydride phase measured by means of IINS. Difference spectra were generated by subtraction of either the sample after prolonged evacuation at 200 °C or the appropriate reference carbon. Finally, residual hydrogen was removed by pumping at 200 °C for recording background runs. For the Pd/Au/SiO<sub>2</sub> catalyst only time to record the spectrum under hydrogen and the 200 °C degassing run was available.

#### **Neutron Diffraction**

The catalyst was prepared as described in the previous section. It was then transferred to a flow-through TiZr cell in an argon-filled glovebox. The total scattering neutron diffraction pattern was then measured at room temperature using the SANDALS<sup>11</sup> diffractometer at the ISIS Pulsed Neutron and Muon Facility<sup>4</sup> (Chilton, UK). The sample was then dosed *in situ* with hydrogen. The sample was then measured again. Data reduction was carried out with the Gudrun package.<sup>12</sup>

### **Computational Studies**

Periodic density functional theory calculations (periodic-DFT) calculations were carried out using a plane wave basis-set and pseudopotentials as implemented in the CASTEP code.<sup>13,14</sup> The generalised gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional was used in conjunction with optimised norm-conserving pseudopotentials with a plane-wave cut-off energy of 1050 eV.  $15 \times 15 \times 15$  (120 k-points) and  $16 \times 16 \times 1$  (30 k-points) Monkhorst-Pack k-point grids were used for the bulk and the surface species respectively. Phonon modes were calculated using density-functional perturbation-theory.<sup>15</sup> As a prerequisite to any lattice dynamics calculation a full geometry optimization of the internal atomic co-ordinates was performed, the residual forces were |0.0025| eV Å<sup>-1</sup>. The output of the phonon calculation includes the atomic displacements of the atoms in the mode, which was used to generate the INS spectra with ACLIMAX.<sup>16</sup> The transition energies have *not* been scaled.

#### **Results and discussion**



**Fig. S1** TEM images. Top: left, Pd/AC (mostly isolated primary particles on/in the porous high surface area AC support), right, Pd/CB (mostly linear aggregate chains and branched aggregates, some agglomerates at the surfaces); middle: Pd/CB300 °C, Pd/CB400 °C (mostly isolated primary particles of enlarged size (Table 1) and only few aggregates/agglomerates left), scale bar 100 nm; bottom: Pd/Au alloy catalyst on SiO<sub>2</sub> pellet support (mostly isolated primary particles of larger size).



**Fig. S2** TEM: Size distribution determined by evaluation of *ca*. 2000 isolated as well as aggregated primary particles per sample. Top to bottom, left: Pd/CB, Pd/CB300 °C, Pd/CB400 °C, right: Pd/AC, PdAu/SiO<sub>2</sub>



**Fig. S3** Left: SEM/EDX element mappings of sectioned and polished  $SiO_2$  pellet particles illustrating the close local correlation of Pd (top) and Au (bottom) at the outer perimeter of the shell-type catalyst at the macroscale. Right: TEM of abraded particles from the outer surface for nano-spot EDX analyses which confirm that mostly Pd/Au alloy particles are present.



**Fig. S4** IINS spectra of sample 3 (Pd/CB): (a): normalised spectra as recorded, top-tobottom: under 700 mbar  $H_2$ , evacuated to 14.5 mbar  $H_2$ , evacuated to 0.1 mbar  $H_2$ , evacuated at 200 °C overnight and the carbon black support. (b) Difference spectra after subtraction of the sample evacuated at 200 °C overnight, top-to-bottom: under 700 mbar  $H_2$ , evacuated to 14.5 mbar  $H_2$ , evacuated to 0.1 mbar  $H_2$ .



**Fig. S5** IINS spectra of sample 5 (Pd/CB400): (a): normalised spectra as recorded, top-tobottom: under 700 mbar  $H_2$ , evacuated to 10 mbar  $H_2$ , evacuated to 5 mbar  $H_2$ , evacuated at 200 °C overnight and the carbon black support. (b) Difference spectra after subtraction of the sample evacuated at 200 °C overnight, top-to-bottom: under 700 mbar  $H_2$ , evacuated to 10 mbar  $H_2$ , evacuated to 5 mbar  $H_2$ .

Sample	700		1st			2nd			3rd	
	mbar		evac			evac			evac	
	$H_2$									
	Area	Limits	Area	Limits	P /	Area	Limits	P /	Area	Limits
		/ cm <sup>-1</sup>		/ cm <sup>-1</sup>	mbar		/ cm <sup>-1</sup>	mbar		/ cm <sup>-1</sup>
1		From								
Pd/Au	180.00	curvefit								
		400-		400-			400-			400-
2	41.33	800	23.41	700	9	20.68	700	3	11.4	700
		350-		350-			350-		12.2	350-
2	59.87	800	32.97	800	9	29.66	800	3	8.05	800
		350-		350-			600-			
3	78.87	800	55.14	800	14.5	6.84	1200	0.1		
		350-		350-			350-			
4	99.00	800	74.66	800	13.3	18.68	1065	3		
		400-		400-			400-			415-
5	67.27	800	13.54	600	10	4.93	600	5	9.98	670
		350-		350-			350-			
5	77.97	800	23.15	800	10	9.06	800	5		

**Table S2:** Sample treatments and integrated hydrogen areas (arbitrary units, normalised to 1 g Pd).



**Fig. S6** 20%Pd/CB catalyst under 700 mbar  $H_2$  equilibrium pressure recorded with the direct geometry spectrometer MAPS; (a) background of the clean catalyst, (b) measured under 700 mbar hydrogen equilibrium pressure and (c) ×5 ordinate expansion of (b) in the 1400 – 2400 cm<sup>-1</sup> region.

#### Estimation of the relative proportion of the on-top site to that of bulk $\beta$ -PdH

Since both, the  $\beta$ -PdH signal and that of the on-top site at 2150 cm<sup>-1</sup> are available from one single spectrum, (Fig. 7, main text), a rough estimate of the ratio of hydrogen stored inside the nanoparticle as  $\beta$ -PdH and located on the on-top sites of the supported palladium particles becomes possible. A total neutron scattering study of this catalyst showed that at room temperature the sample was actually  $\beta$ -PdH<sub>0.7</sub>, as often found for nanoparticulate palladium.<sup>17</sup> Integration of the IINS area of the  $0 \rightarrow 1$  transition of  $\beta$ -PdH<sub>0.7</sub> centred at 485 cm<sup>-1</sup> and the area of the on-top Pd-H-stretch region gave 22248 and 351 (arb. units), respectively. The  $\beta$ -PdH<sub>0.7</sub> area also includes the bending modes of the on-top species. Their contribution can be estimated as:

(area of on-top)  $\times$  2 (since two bending modes)  $\times$  4 (ratio of amplitude of motion of stretch to bend, assuming the harmonic approximation) = 2808

Hence ratio of surface: bulk-hydrogen = 2808 : 22248 = 1 : 8 (note that this includes an unknown contribution from hydrogen in high coordination sites at the surface, so is an underestimate of the relative populations).

The relative populations can also be estimated from the particle size. Assuming, as a first approximation, the primary particle size of the palladium is a cube of PdH with a length of 2.28 nm on each edge, has a diagonal length of 3.78 nm, which is in the right size regime (Table 1). Each edge has 6 Pd atoms (and 6 H atoms), hence 36 Pd per side, hence 6 x 36 = 216 surface Pd atoms. The cube contains a total of 863 Pd atoms + 863 H atoms, (note that 216 of these are at the surface in high coordination sites). If we assume the actual stoichiometry is *ca*. PdH<sub>0.7</sub><sup>10</sup> at the 700 mbar hydrogen loading pressure, it means there are 604 H atoms present. Assuming each surface Pd atom is capped by an on-top H, this gives a surface-to-bulk ratio of 216 : 604 *i.e.* 1 : 2.8. If we exclude the H atoms at the surface in high coordination sites, then the ratio is 216 : (604 – 216 x 0.7) = 216 : 453 *i.e.*1 : 2.1.



**Fig. S7** Palladium black with residual hydrogen loading of  $\beta$ -PdH after two dehydrogenation steps. The main peak at 485 cm<sup>-1</sup> and the smaller one at 640 cm<sup>-1</sup> are assigned to  $\beta$ -PdH,<sup>17e</sup> the overtone is centred at 1050 cm<sup>-1</sup>. The weak peak at 574 cm<sup>-1</sup> (arrowed) is assigned to  $\alpha$ -PdH.<sup>18</sup> Spectra recorded using IN1-Lagrange<sup>9</sup> at the ILL<sup>8</sup> (the spectrum of the original black before hydrogenation is shown elsewhere.<sup>19</sup>



**Fig. S8** Dispersion curves of surface and sub-surface hydrogen on Pd(111) calculated from the model shown in Fig. 9 of the main text. Note that the modes are real across the entire Brillouin zone.

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