

## SUPPORTING INFORMATION

### **Efficient aqueous hydrogenation of biomass platform molecules using supported metal nanoparticles on Starbons®**

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#### **Experimental**

##### *Materials preparation*

The preparation of SMNPs on Starbons was carried out using a facile impregnation/reduction methodology<sup>1</sup>. Starbons® were suspended in a ethanol/(acetone) solution of the metal precursor (Ru and Rh chlorides, palladium acetate and tetramine platinum (II) nitrate) containing the theoretical metal loading (5 wt% metal) and stirred under mild heating (45-55°C) overnight. The final solid containing MNPs was then vacuum filtered, washed thoroughly with fresh acetone and activated in a vacuum oven at 45-60°C overnight.

##### *Materials characterisation*

The electron microscopy images were recorded in a JEOL 2200FS double aberration corrected (AC-TEM/STEM and HAADF-STEM), with integral in-column energy filter, operating at 200kV and at the highest atomic scale resolution (0.1 nm or below) with crystallographic and chemical analysis.

For AC-TEM/STEM studies, samples were prepared by ultrasonically dispersing as-synthesised catalyst powders in alcohol and placing the solution on holey carbon coated copper microgrids. Low dose electron beam imaging methods were employed throughout.

XPS measurements were performed in a ultra high vacuum (UHV) multipurpose surface analysis system (Specs<sup>TM</sup> model, Germany) operating at pressures  $<10^{-10}$  mbar using a conventional X-Ray source (XR-50, Specs, Mg-K $\alpha$ , 1253.6 eV) in a “stop-and-go” mode to reduce potential damage due to sample irradiation. The survey and detailed metal high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser.

Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum ( $<10^{-6}$  Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

The metal content in the materials was determined using Inductively Coupled Plasma (ICP) in a Philips PU 70000 sequential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution). Samples were digested in HNO<sub>3</sub> and subsequently analysed by ICP/AES at the University of Newcastle.

### *Catalytic experiments*

A typical hydrogenation experiment was performed as follows: 10 mmol substrate, 30 mmol EtOH (2.7 mL), 50 mmol water (0.9 mL) and 0.1 g of the catalyst (e.g. 5%Ru-Starbon<sup>®</sup>) were added to the reaction vessel of a Parr hydrogenator (model 5RH35HN60T). The reactor was then filled and purged with H<sub>2</sub> several times prior to its filling with H<sub>2</sub> at 10 bar pressure. The reaction temperature was then set to 100°C and the reaction started after the vessel reached the target temperature. The evolution of the reaction was monitored by periodically sampling aliquots of reaction mixture that

were subsequently analysed by GC/GC-MS using an Agilent 6890N GC model equipped with a 7683B series autosampler and fitted with a DB-5 capillary column and a FID detector.

### ***Characterisation***

#### *Metal content*

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#### *AC-(S)TEM and HAADF-STEM*

The electron microscopy images (Figures 1 to 3) were recorded in a JEOL 2200FS double aberration corrected instrument (AC-TEM/STEM), operating at 200kV<sup>2</sup>. The dual aberration-correctors allow AC-TEM and AC-STEM imaging from the same regions of the nanocatalyst sample, providing powerful insights into the catalyst nanostructure. Aberration corrected high-angle annular dark-field TEM (AC-HAADF-TEM) were also recorded to directly image the isolated metal centres. Due to its sensitivity to atomic number, HAADF can image heavy atoms that appear as bright spots in the experiments (Figures 1 to 3, 1a, 2b and d, 3b and d)<sup>3</sup>.

With aberration correction, a continuous range of interpretable spatial frequencies can be transferred by the optics without the contrast inversions the data are therefore much more directly interpretable. More directly interpretable (sub) Angstrom level imaging, complemented by compositional data, uniquely provides new direct insights

into the structure of nanoparticles, critical to understanding the nanostructures and reactivity properties of nanocatalysts.

In high angle annular dark field STEM (HAADF-STEM) imaging we exploit the fact that electrons scattered at high angles ( $> 30\text{mrad}$ ) obey Rutherford scattering law, with the scattering cross section proportional to  $Z^2$  where  $Z$  is the atomic number. A HAADF detector is used for imaging. Imaging of the highly scattered electrons using HAADF STEM detector allows the detection of catalyst nanoparticles with higher  $Z$ , on lighter supports such as starbons.

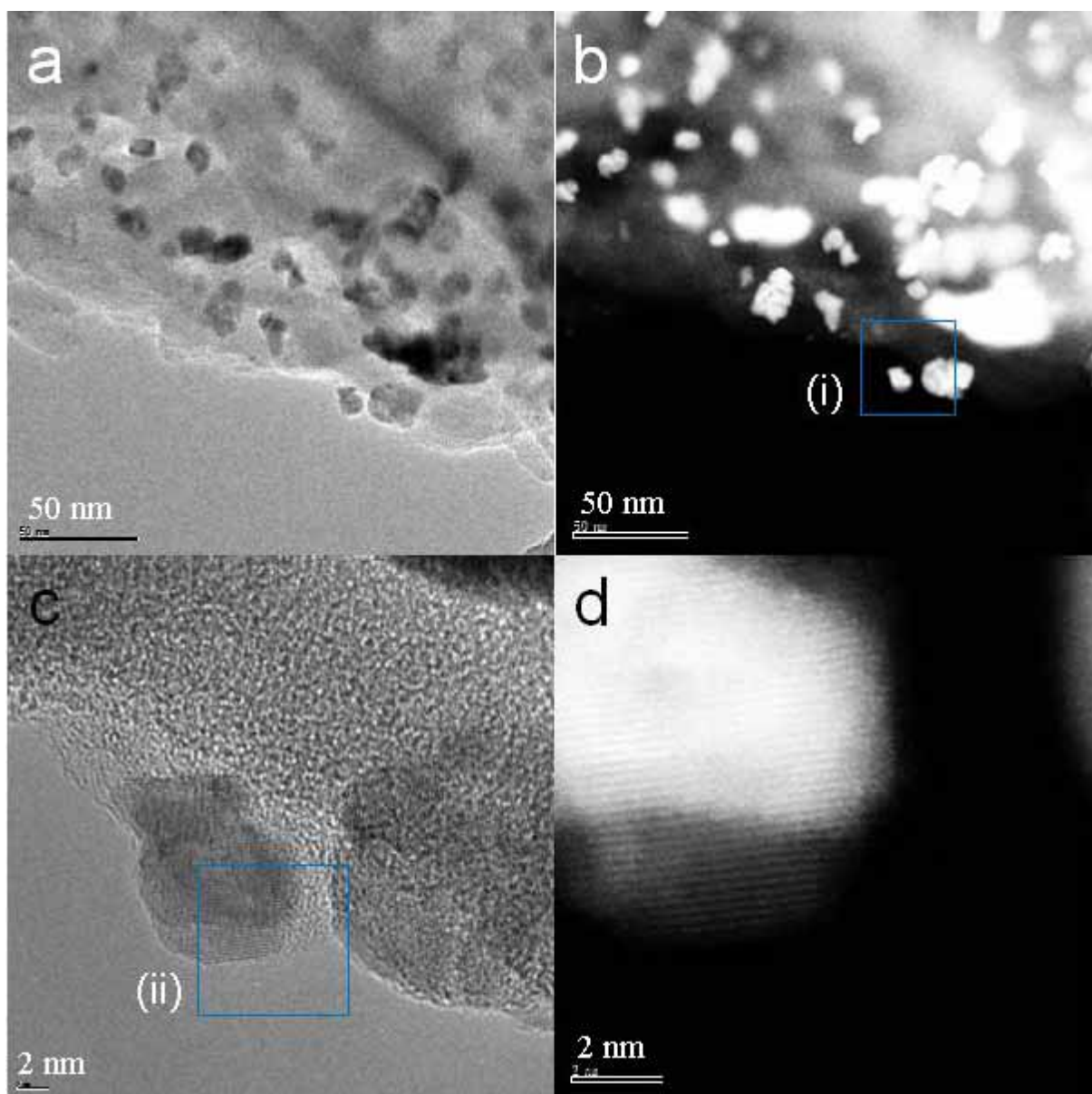


Figure 1S. (a) AC-TEM and (b) HAADF-STEM images from the same area of the 5%Rh-Starbon® powder catalyst sample. (c) High-Resolution AC-TEM and (d) High-Resolution AC-HAADF-STEM images corresponding to areas marked by squares (i) and (ii), respectively.

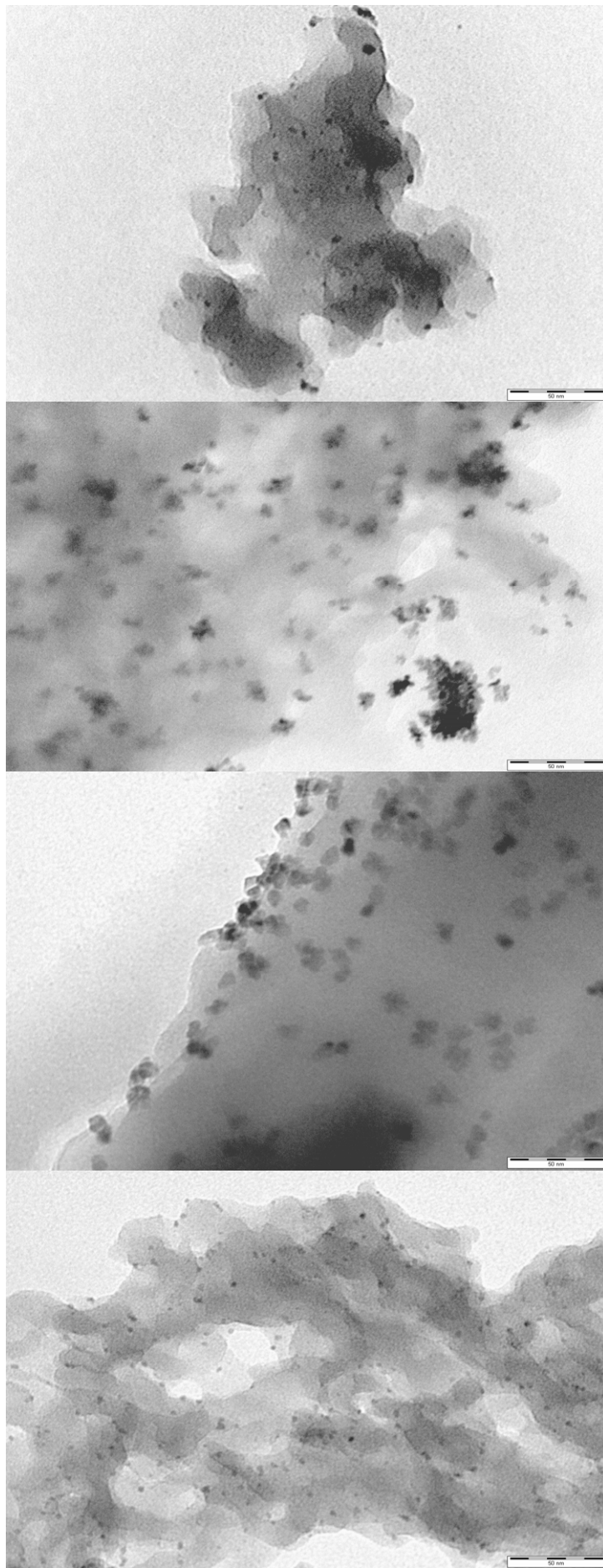


Figure 2S. TEM images (from top to bottom) of 5%Pd/Starbon (top), 5%Pt/Starbon (second from top), 5%Rh/Starbon (third from top) and 5%Ru/Starbon (bottom).

Table 1S. Metal loading measured for the SMNPs-Starbon® materials by elemental analysis and XPS.

Catalyst	Elemental analysis (ICP, wt % metal)	XPS (% atomic)
5%Pd-Starbon®	4.87	5.76
5%Pt-Starbon®	4.75	3.08
5%Rh-Starbon®	4.32	3.99
5%Ru-Starbon®	4.11	4.44

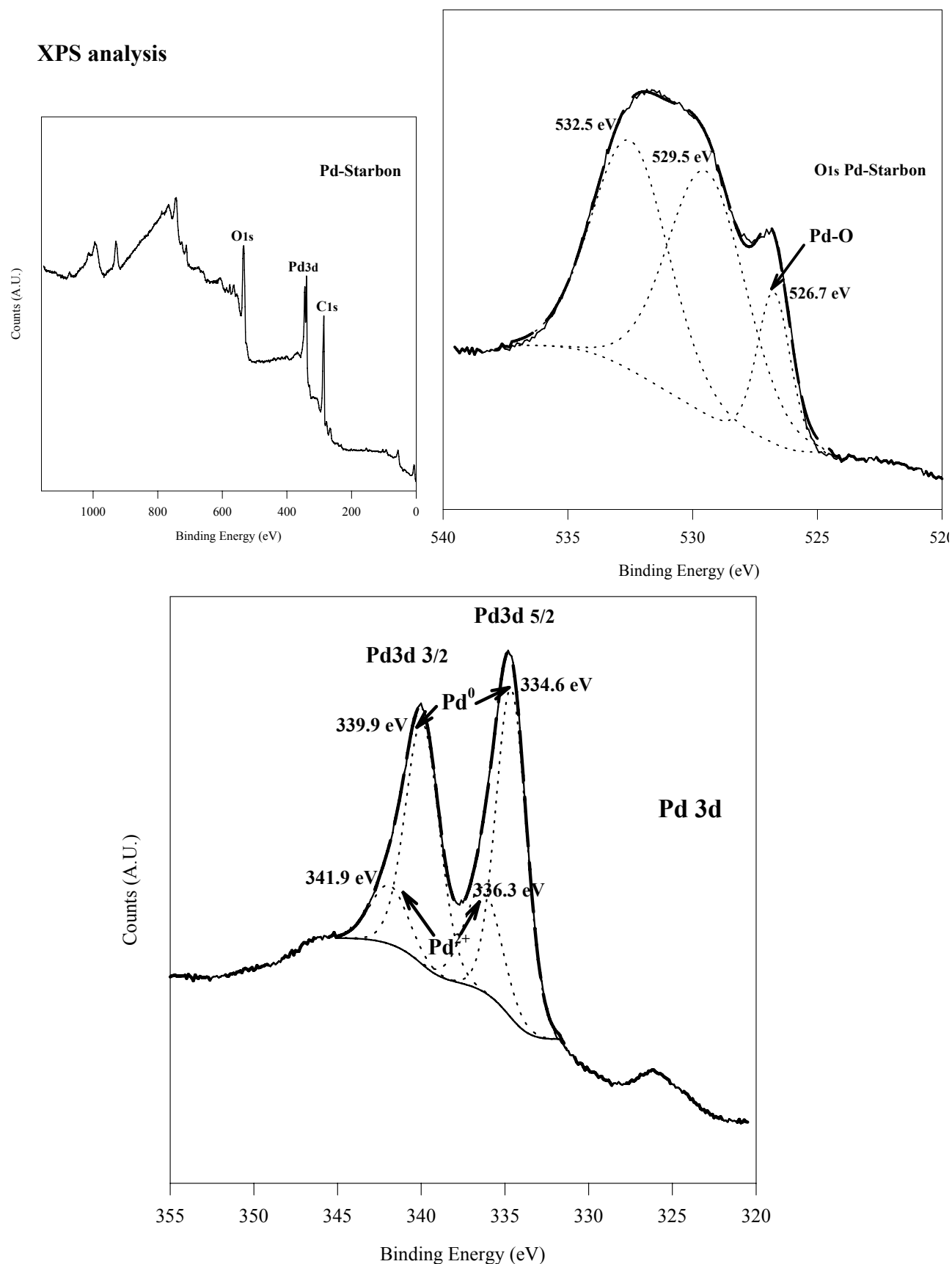


Figure 2S. XPS spectra of survey (top-left), O1s (top-right) and Pd3d region of 5%-Pd-Starbon® material.



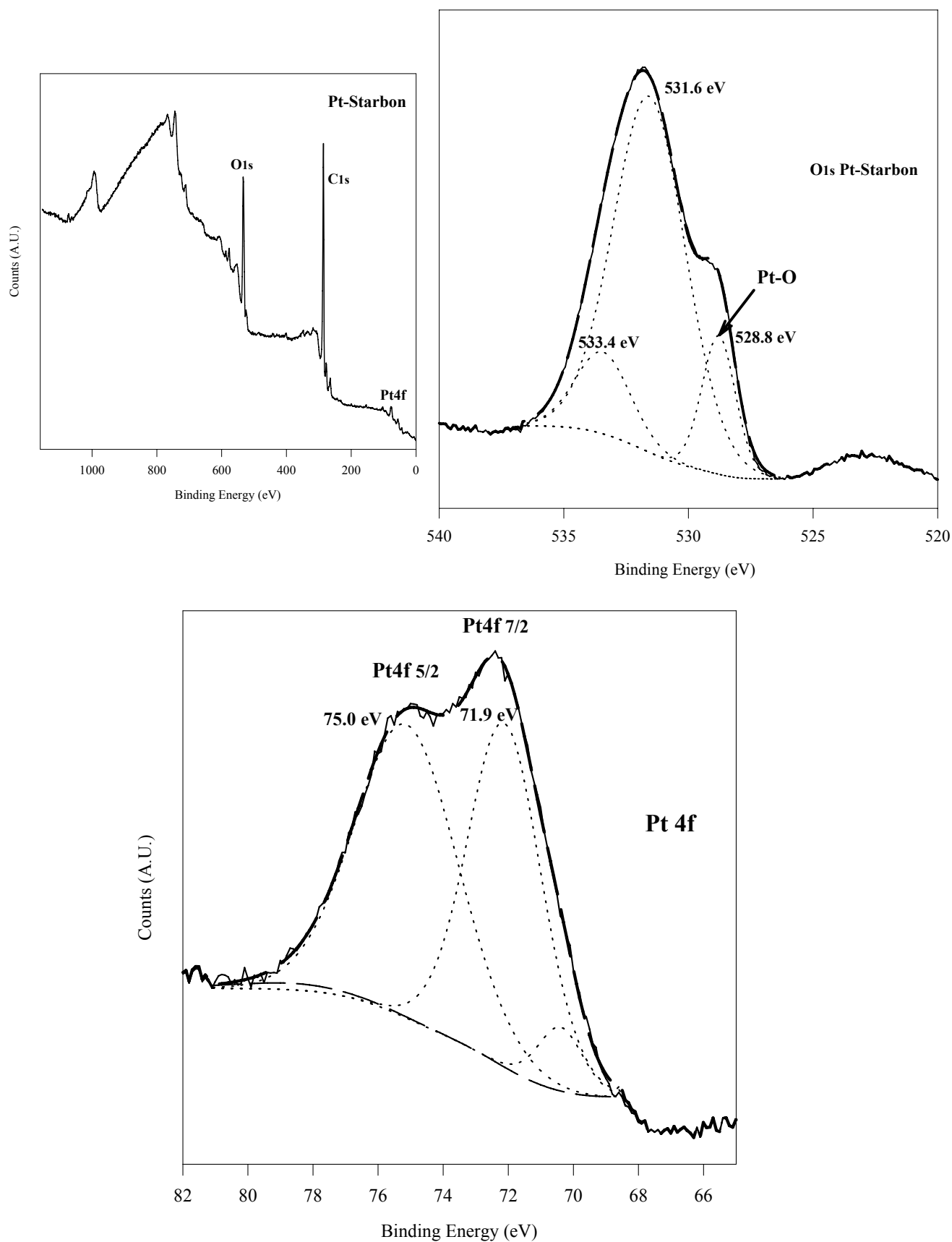


Figure 3S. XPS spectra of survey (top-left), O1s (top-right) and Pt4f region of 5%-Pt-Starbon® material.

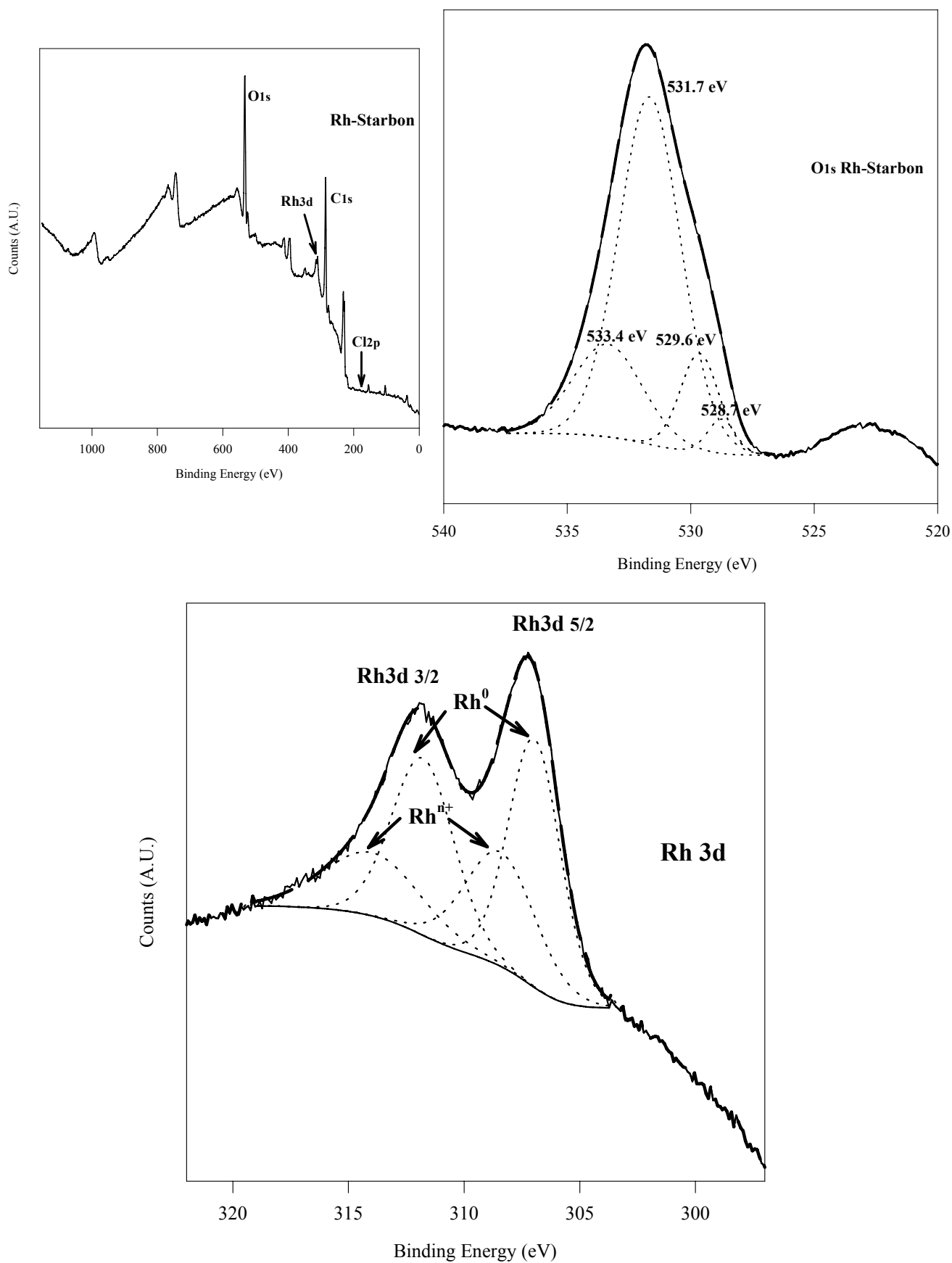


Figure 4S. XPS spectra of survey (top-left), O1s (top-right) and Rh3d region of 5%-Rh-Starbon® material.

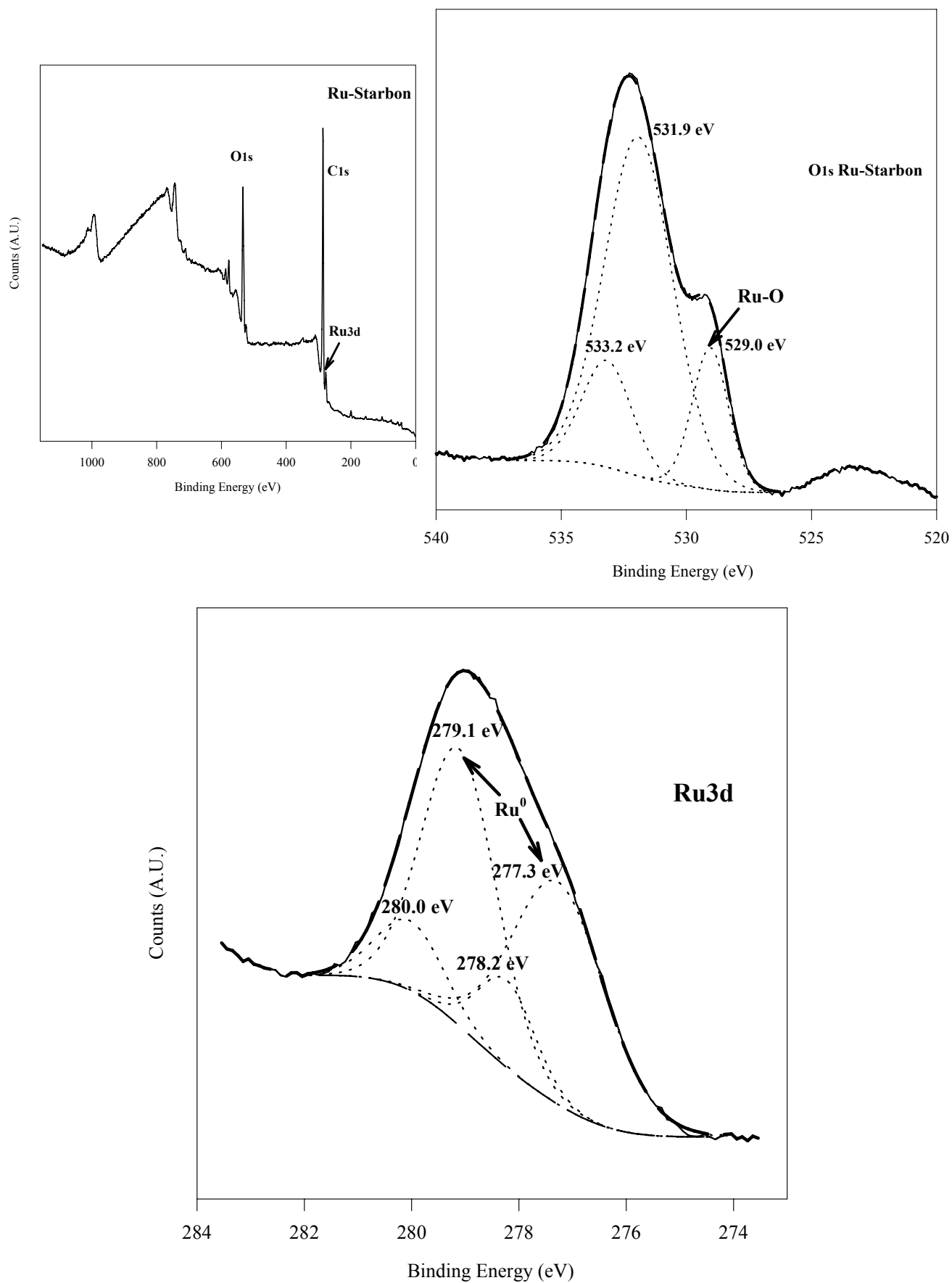


Figure 5S. XPS spectra of survey (top-left), O1s (top-right) and Ru3d region of 5%-Ru-Starbon® material.

Table 2S. Reuses of the 5%Pt-Starbon® material in the aqueous hydrogenation of succinic acid to 1,4-butanediol.<sup>a</sup>

Run	Conversion (mol%)	S <sub>1,4-butanediol</sub> <sup>b</sup> (mol%)	TON	TOF (h <sup>-1</sup> )
1	78	85	320	13
2	75	88	308	13
3	73	90	300	12
4	75	89	308	13
5	72	89	296	12
After 5 cycles	72	89	1532 <sup>c</sup>	63 <sup>c</sup>

<sup>a</sup>Reaction conditions: 10 mmol succinic acid, 30 mmol EtOH (2.7 mL), 50 mmol water (0.9 mL), 0.1 g of the catalyst, 100°C, 10 bar pressure, 24 h reaction; <sup>b</sup>The difference to 100 corresponds to the formation of  $\gamma$ -butyrolactone; <sup>c</sup>Cumulative TON and TOF values after 5 reuses.

## References

- 1 R. Luque, R.J. White, V. Budarin, J.H. Clark, *PCT Int. Appl.* 2009, WO 2009044146 A120090409.
- 2 P.L. Gai, E.D. Boyes, *Microsc. Res. Tech.* 2009, 72, 153-164.
- 3 S.J. Pennycook, L.A. Boatner, *Nature* 1988, 336, 565-567.