## Supplementary Information

## The direct synthesis of hydrogen peroxide using a combination of a hydrophobic solvent and water.

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**Table S.1.** Table S.1. Nominal and actual total metal loading of supported AuPd catalysts as determined by ICP-MS.

Actual Au loading / %	Actual Pd loading / %
2.10	2.15
2.46	2.37
2.34	2.50
2.22	2.50
	Actual Au loading / % 2.10 2.46 2.34 2.22

All catalysts calcined (3 h, 400 °C, 20 °Cmin<sup>-1</sup>, static air).



**Figure S.1.** X-ray diffractograms of AuPd catalysts supported on A)C(G60), B), SiO2 C) TiO2 and D) CeO2 prepared by wet co-impregnation (3 h, 400 °C, static air, ramp rate = 20 °C min<sup>-1</sup>). Au reflections (dashed lines) Pd reflections (solid lines).

**Table S.2**. Summary surface atomic concentrations of Au and Pd present in supported AuPd catalysts, as derived from XPS using Au (4f) and Pd (3d) features.

Pd: Au*
46.7
12.2
24.9
0.9

All catalysts calcined (3 h, 400 °C, 20 °Cmin<sup>-1</sup>, static air).

\* Expected value for homogeneous alloy based on Au: Pd = 1: 1 by weight = 1.9.



**Figure S.2.** XPS spectra of Au (4f) and Pd (3d) regions of as prepared A) 2.5%Au-2.5%Pd/ B) 2.5%Au-2.5%Pd/ C) 2.5%Au-2.5%Pd/ and D) 2.5%Au-2.5%Pd/ catalysts.

**Table S.3.** Catalytic activity towards  $H_2O_2$  synthesis and degradation using a water/methanol solvent system at sub-ambient temperature.

Catalyst	Productivity / mol <sub>H2O2</sub> kg <sub>cat</sub> - <sup>1</sup> h <sup>-1[a]</sup>	Degradation / % <sup>[b]</sup>	Reference
2.5%Au-2.5%Pd/TiO <sub>2</sub>	64	12	1,2
2.5%Au-2.5%Pd/SiO <sub>2</sub>	74	23	3,4
2.5%Au-2.5%Pd/ CeO <sub>2</sub>	68	9	5,6
2.5%Au-2.5%Pd/C (G60)	110	5	7, 8

**[a]** H<sub>2</sub>O<sub>2</sub> direct synthesis reaction conditions: Catalyst (0.01 g), H<sub>2</sub>O (2.9 g), MeOH (5.6 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 0.5 h, 2° C, 1200 rpm.

**[b]** H<sub>2</sub>O<sub>2</sub> degradation reaction conditions: Catalyst (0.01 g), H<sub>2</sub>O<sub>2</sub> (50 wt.% 0.68 g) H<sub>2</sub>O (2.22 g), MeOH (5.6 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 0.5 h, 2°C, 1200 rpm.

**Note:** For extensive comparison of catalytic performance as well as the ability of the catalytic support to alter nanoparticle composition and morphology we direct the reader to references 2 and 8.

**Table S.4.** Catalytic activity towards  $H_2O_2$  synthesis and degradation using a water/decan-1-ol solvent system at ambient temperature.

Catalyst	Productivity / mol <sub>H2O2</sub> kg <sub>cat</sub> -1h <sup>-</sup> 1[a]	Degradation / % <sup>[b]</sup>
2.5%Au-2.5%Pd/TiO <sub>2</sub>	24	94
2.5%Au-2.5%Pd/SiO <sub>2</sub>	19	99
2.5%Au-2.5%Pd/ CeO <sub>2</sub>	13	89
2.5%Au-2.5%Pd/C (G60)	8	37

**[a]** H<sub>2</sub>O<sub>2</sub> direct synthesis reaction conditions: Catalyst (0.01 g), H<sub>2</sub>O (2.9 g), MeOH (5.6 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 0.5 h, 2° C, 1200 rpm.

**[b]** H<sub>2</sub>O<sub>2</sub> degradation reaction conditions: Catalyst (0.01 g), H<sub>2</sub>O<sub>2</sub> (50 wt.% 0.68 g) H<sub>2</sub>O (2.22 g), MeOH (5.6 g), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 0.5 h, 2°C, 1200 rpm.

Solvent (8.5 g)	Observed pressure drop /psi*	
Methanol	60	
Hexan-1-ol	78	
Octan-1-ol	87	
Decan-1-ol	100	

 Table S.5. Observed pressure drop after the addition of reagent gases to different alcohol solvents.

\* Initial pressure 580 psi - 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi).



**Figure S.3**. NMR spectra showing the stability of the decan-1-ol during  $H_2O_2$  synthesis (A) and a blank reaction (B) against a reference Decan-1-ol spectra (C)

## References.

- 1. J. K. Edwards, B. Solsona, P. Landon, A. Carley, A. Herzing, C. Kiely and G. Hutchings, *J. Catal.*, 2005, **236**, 69-79.
- 2. J. K. Edwards, A. Thomas, B. E. Solsona, P. Landon, A. F. Carley and G. J. Hutchings, *Catal. Today*, 2007, **122**, 397-402.
- 3. R. J. Lewis, K. Ueura, Y. Fukuta, S. J. Freakley, L. Kang, R. Wang, Q. He, J. K. Edwards, D. J. Morgan, Y. Yamamoto and G. J. Hutchings, *ChemCatChem*, 2019, **11**, 1673-1680.
- 4. J. K. Edwards, S. F. Parker, J. C. Pritchard, M. Piccinini, S. J. Freakley, Q. He, A. F. Carley, C. J. Kiely and G. J. Hutchings, *Catal. Sci. Technol.*, 2013, 3, 812-818
- 5. E. N. Ntainjua, M. Piccinini, J. C. Pritchard, J. K. Edwards, A. F. Carley, C. J. Kiely and G. J. Hutchings, *Catal. Today*, 2011, **178**, 47-50.
- 6. J. K. Edwards, J. Pritchard, L. Lu, M. Piccinini, G. Shaw, A. F. Carley, D. J. Morgan, C. J. Kiely and G. J. Hutchings, Angew. Chem Int. Ed., 2014, 53, 2381-2384
- 7. J. K. Edwards, B. Solsona, E. N. N, A. F. Carley, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *Science*, 2009, **323**, 1037-1041.
- 8. E. N. Ntainjua, J. K. Edwards, A. F. Carley, J. A. Lopez-Sanchez, J. A. Moulijn, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *Green Chem.*, 2008, **10**, 1162.