Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

The Selective Hydrogenation of Furfural over Supported Palladium Nanoparticle Catalysts Prepared by Sol-Immobilisation: Effect of Catalyst support and Reaction Conditions

Reem Albilali*[1], Mark Douthwaite,[2] Qian He[2] and Stuart H. Taylor*[2]

Department of Chemistry, College of Science, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia.

[2] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, CF10 3AT Cardiff, United Kingdom.*

*Corresponding authors e-mail: taylorsh@cardiff.ac.uk, ralblali@iau.edu.sa

Supplementary Information

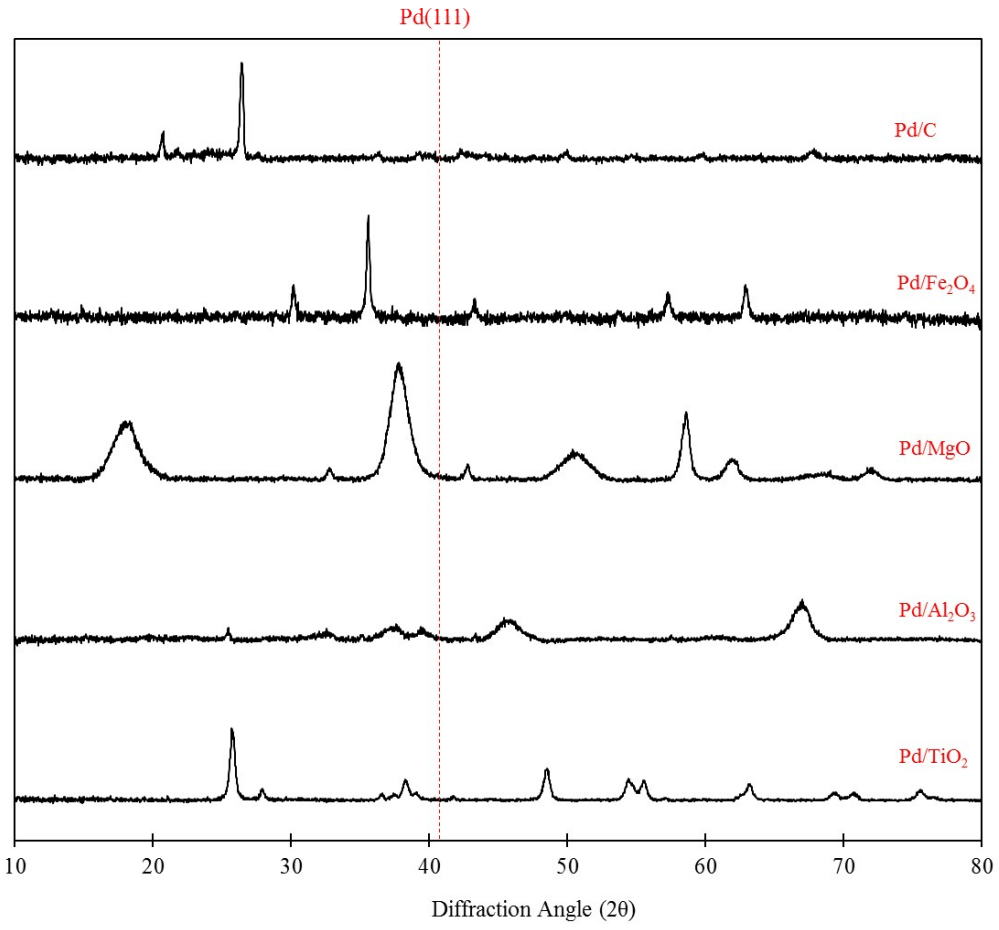

Figure S1. X-ray diffraction patterns corresponding to each of the supported Pd catalysts

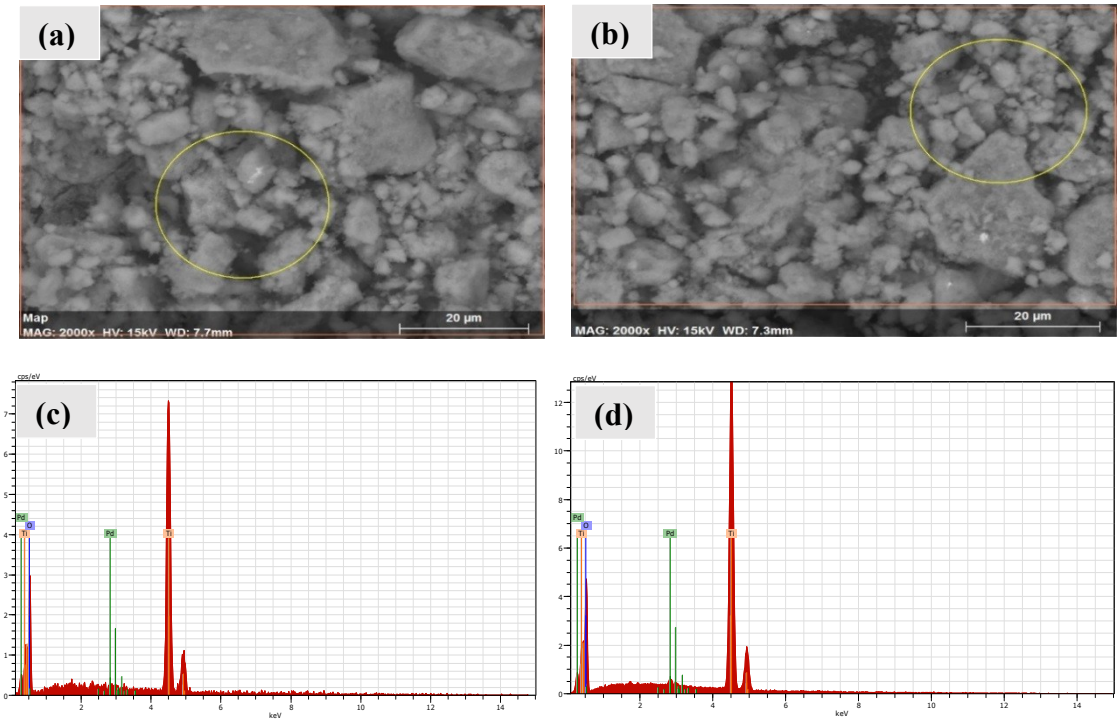

Figure S2. SEM images of (a) 0.57 % Pd/TiO_2 and (b) 1.19 % Pd/TiO_2 and the corresponding EDX spectra of (c) 0.57 % Pd/TiO_2 and (d)) 1.19 % Pd/TiO_2.

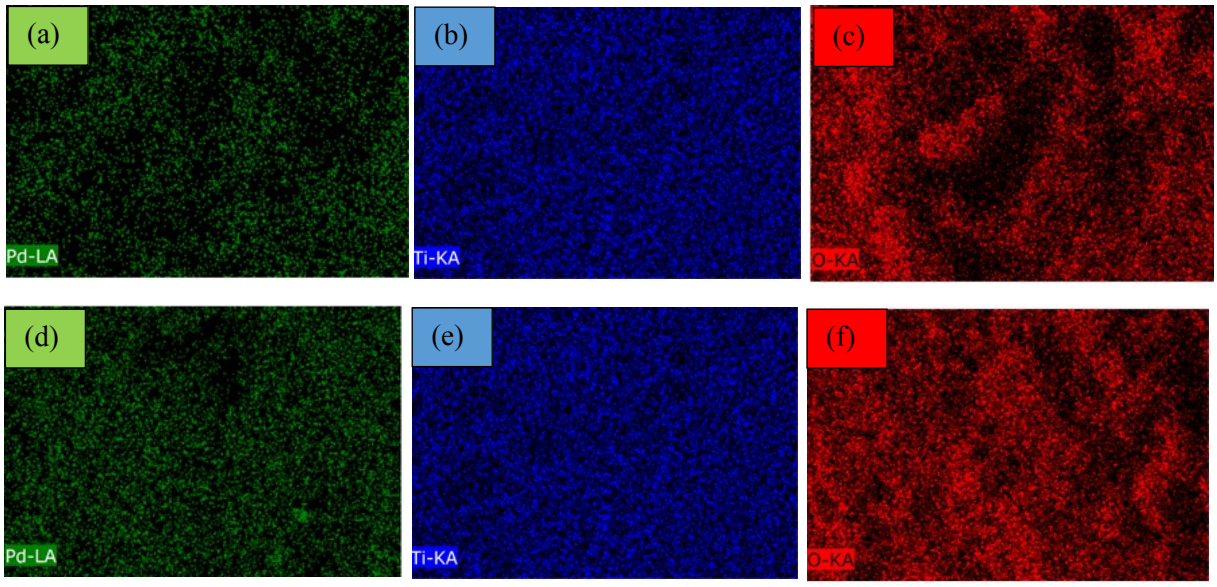

Figure S3. Elemental mapping images for Pd/TiO_2 catalysts with different metal loading (a): Palladium mapping for 0.57 % Pd/TiO_2 ,(b) Titanium mapping for 0.57 % Pd/TiO_2 (c) Oxygen

mapping for 0.57 % Pd/TiO_2, (d), Palladium mapping for 1.19 % Pd/TiO_2 and (e) Titanium mapping for 1.19 % Pd/TiO_2 (f) Oxygen mapping for 1.19 % Pd/TiO_2.

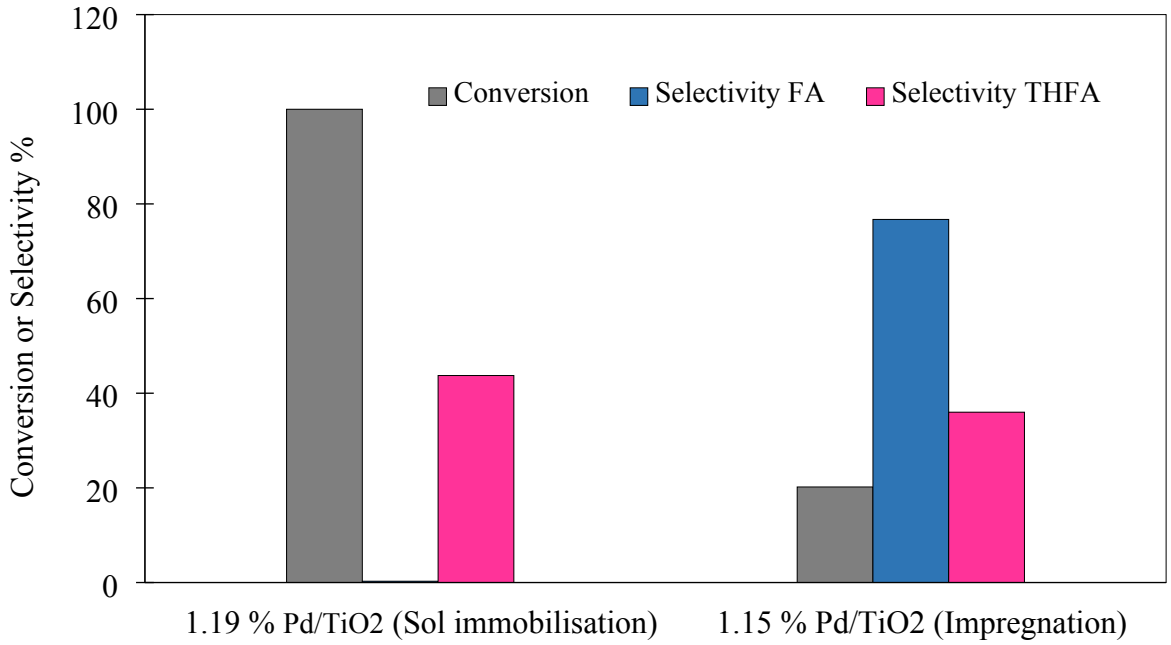

Figure S4. A graphical comparison between the performances of Pd/TiO_2 catalysts prepared by sol-immobilisation and conventional impregnation techniques for the liquid phase hydrogenation of furfural. Reaction Conditions: 0.3 M FF (15 ml), substrate/metal molar ratio = 500, 3 bar H_2, 30 °C, reaction time = 120 minutes.

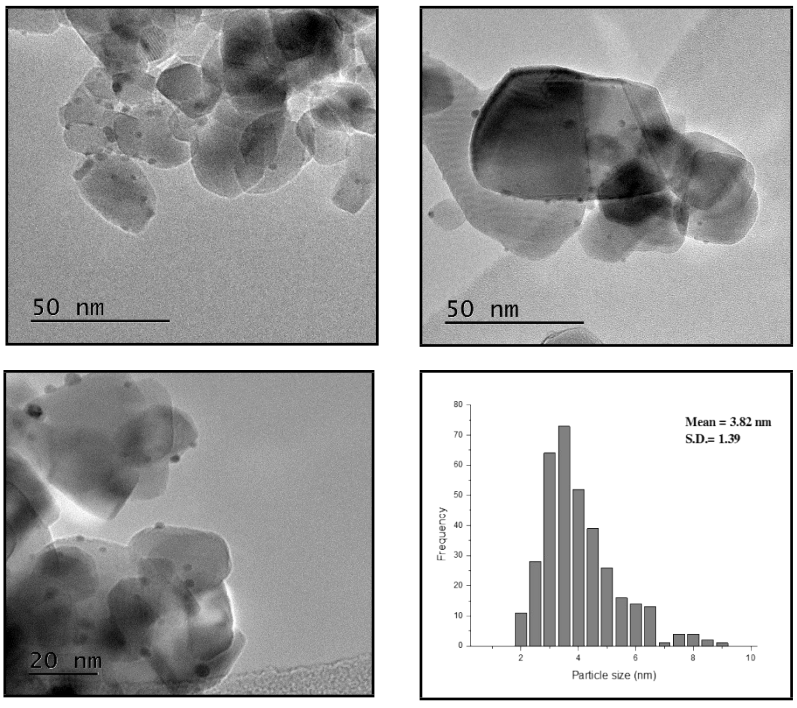

Figure S5. TEM images and corresponding particle size distribution for 1.19 % Pd/TiO_2 after fifth use.

Table S1. Effect of palladium loading on the hydrogenation of FF over Pd/TiO_2 catalysts. Reaction Conditions: 0.3 M FF (15 ml), substrate/metal molar ratio = 500, 3 bar H_2, 30 °C.

Pd loading	Reaction time	Conversion	Selectivity [%]						Initial rate
%	[Min]	[%]	FA	THFA	2-MF	GVL	THFF	Unknown	mol g^{-1} h^{-1}
0.57	30	28.2	38.4	11.1	0.0	2.0	40.7	7.8	2. 32
	60	49.1	27.2	18.2	0.0	3.3	50.0	1.3	
	120	76.9	15.4	25.7	0.0	4.7	52.3	1.8	
1.19	30	36.4	41.9	20.2	0.0	14.3	23.6	0.0	2.75
	60	73.2	18.8	26.3	0.0	14.1	18.3	22.5	
	120	100.0	0.3	43.7	0.0	15.0	30.0	11.0	

Table S2. Effect of presence of H_2 on the hydrogenation of furfural. Reaction conditions: 0.3 M FF (15 ml), substrate/metal molar ratio = 500, 3 bar H_2 and 30°C.

Catalyst	Reaction time	Conversion	Selectivity [%]						Initial rate
	[Min]	[%]	FA	THFA	2-MF	GVL	THFF	Unknown	mol.$g^{-1}h^{-1}$
1.19%Pd/TiO_2	30	36.4	41.9	20.2	0	14.3	23.6	0	2.75
	60	73.2	18.8	26.3	0	14.1	18.3	22.5	
	120	100	0.3	43.7	0	15	30	11	
1.19%Pd/TiO_2*	30	0	—	—	—	—	—	—	—
	60	0	—	—	—	—	—	—	—
	120	0	—	—	—	—	—	—	—
TiO_2 (P25)*	30	0	—	—	—	—	—	—	—
	60	0	—	—	—	—	—	—	—
	120	0	—	—	—	—	—	—	—

*Reaction conducted under 3 bar N_2 instead of H_2.

Table S3. Quantified XPS results for the various Pd catalysts.

Catalyst	Pd Loading (wt. %)	Assignment	Conc (At %)	Pd^0/Pd^{2+}
Pd/TiO_2	1.19	Pd 3d	1.26	9.8
		O 1S	69.54	
		Ti 2P	29.2	
Pd/C	0.49	Pd 3d	3.06	5.61
		C 1s	96.94	
Pd/MgO	1.34	Pd 3d	1.72	*
		Mg 2s	3.31	
		O 1s	94.96	
Pd/Al_2O_3	1.51	Pd 3d	1.2	3.121
		O 1S	59.15	
		Al 2p	39.65	
Pd/Fe_3O_4	1.57	Pd 3d	2.48	11.41
		O 1S	65.38	
		Fe 2p	32.14	

*The sample shows only Pd(0), Pd(II) may be present but it is difficult to determine due to Mg auger

Table S4. The Pd metal leaching in each reaction was determined using ICP. The Pd leached from the catalyst is calculated with respect to the concentration of Pd detected in solution and the corresponding Pd metal loadings associated with each catalyst. A blank sample of the 2-Propanol reaction solvent was also assessed in order to provide a figure for the Pd background concentration.

Catalysts	Pd detected (ppm)	Pd leached from Catalyst (%)
1 % Pd/Al_2O_3	0.014	0.014
1% Pd/MgO	0.009	0.010
1% Pd/C	0.008	0.025

1% Pd/TiO_2	0.021	0.027
1% Pd/Fe_3O_4	0.008	0.008
Solvent Blank	5.8365E-05	-

Table S5. Catalytic data for the reusability test of the 1.19 % Pd/TiO_2 in liquid phase hydrogenation of furfural. Reaction conditions: 0.3 M FF (15 ml), substrate/metal molar ratio = 500, 3 bar H_2, 30 °C

Cycle number	Reaction time	Conversion	Selectivity [%]					
	[Min]	[%]	FA	THFA	2-MF	GVL	THFF	Unknown
First cycle	30.00	36.36	41.87	20.21	0.00	14.31	23.57	0.04
	120.00	100.00	0.28	43.74	0.00	15.04	29.99	10.95
Second cycle	30.00	36.40	42.29	19.36	0.00	3.74	25.53	9.09
	120.00	88.79	16.34	40.36	0.00	5.60	14.67	23.02
Third cycle	30.00	26.65	54.94	19.35	0.00	0.00	25.71	0.00
	120.00	66.24	30.30	29.12	0.00	2.24	32.32	6.01
forth cycle	30.00	10.66	79.55	15.61	0.00	0.00	0.00	4.85
	120.00	48.17	35.91	22.52	0.00	5.01	33.60	2.95
Fifth cycle	30.00	11.74	65.00	15.00	0.00	0.00	20.00	0.00
	120.00	31.14	55.00	16.20	0.00	0.00	28.80	0.00

Table S6. Quantified XPS data for the bimetallic 0.97 wt.% Pd-Pt/TiO_2 catalyst.

Catalyst	**Pd Loading (wt. %)**	**Assignment**	**Conc (At %)**	**Pd/Pt**
Pd-Pt/TiO_2	0.97	Pd 3d	0.47	4.27
		Pt 4d	0.11	
		O 1S	70.00	
		Ti 2P	29.41	