

Supporting information

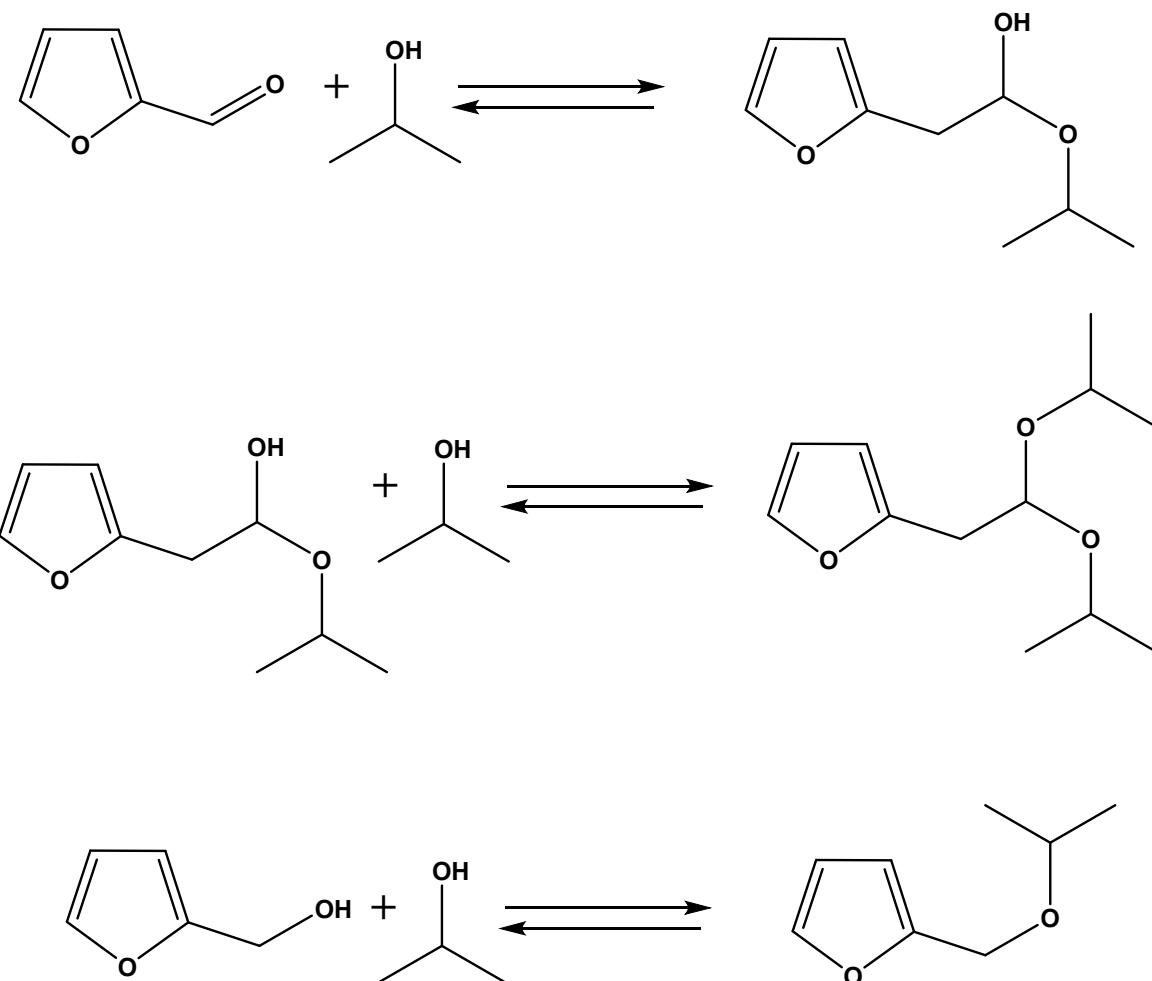
Controlling the Nanoparticles Size and Shape of Pt/TiO₂ catalyst for Enhanced Hydrogenation of Furfural to Furfuryl Alcohol

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Scheme S1 Schematic representation of the formation of hemiacetal and subsequent acetylation product from the reaction between furfural and isopropanol (solvent). Acetylation of furfuryl alcohol using isopropanol (last reaction).

Table S1: Liquid phase hydrogenation of FF to 2-FFA over 4.2%Pt/TiO₂ catalyst – Effect of heat treatment

Catalyst	Heat treatment	Conv. (%)	Products Selectivity (%)		
			2-FFA	2-MF	Solvent Product
4.2%Pt/TiO ₂	Calcination	90	42	31	27
	Reduction	25	90	-	10
	Calcination + Reduction ^[a]	99	59	9	1

Reaction conditions: H₂ : 3 bar; Temp : 30 °C; FF: 4.45 mmol; Isopropanol (solvent) : 15 mL; Time : 6h; FF/Pt molar ratio : 207. [a] Rest of the products is a mixture of 4 unknown products.

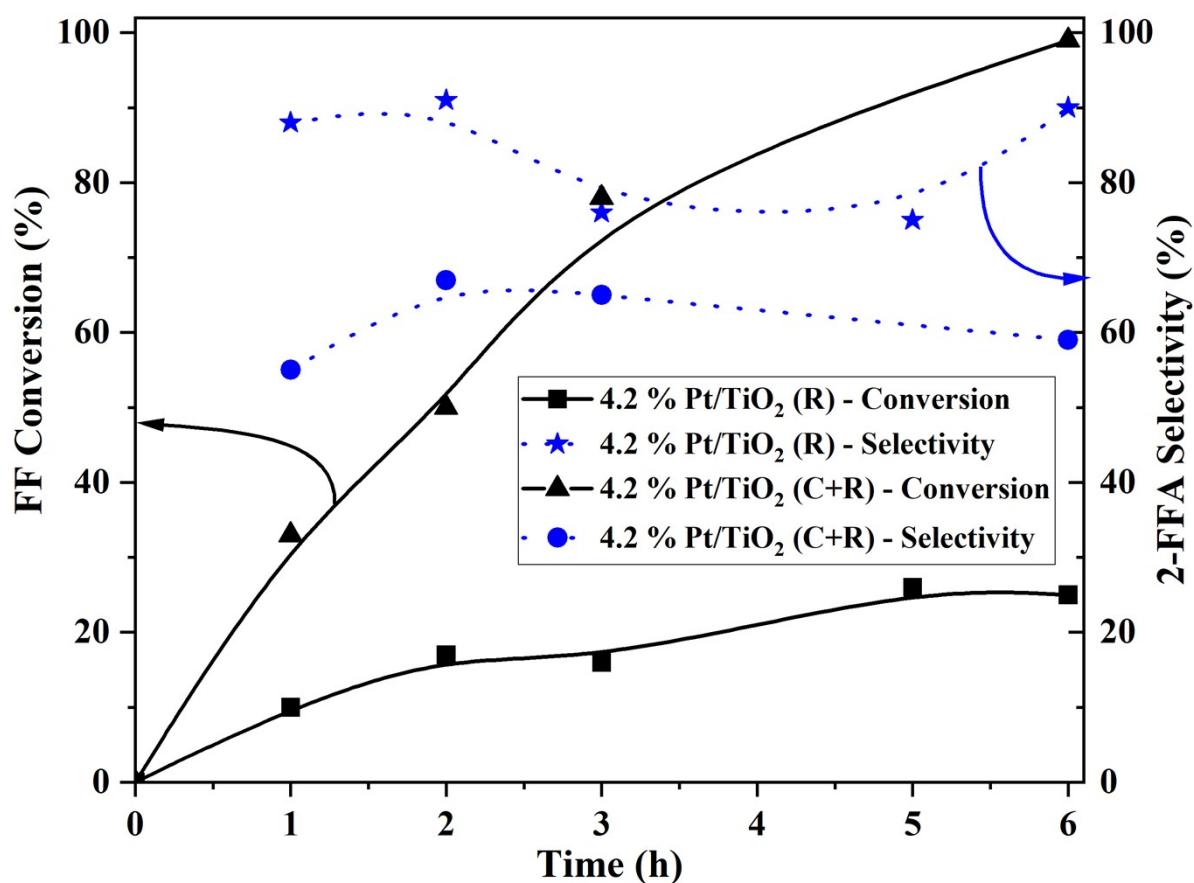


Figure S1: Catalytic performance of 4.2% Pt/TiO_2 as a function of time for the hydrogenation of FF to 2-FFA. Effect of catalyst reduction vs calcination + reduction. Reaction conditions: H_2 : 3 bar; Temp : 30 °C; FF: 4.45 mmol; Isopropanol (solvent) : 15 mL; FF/Pt molar ratio : 207.

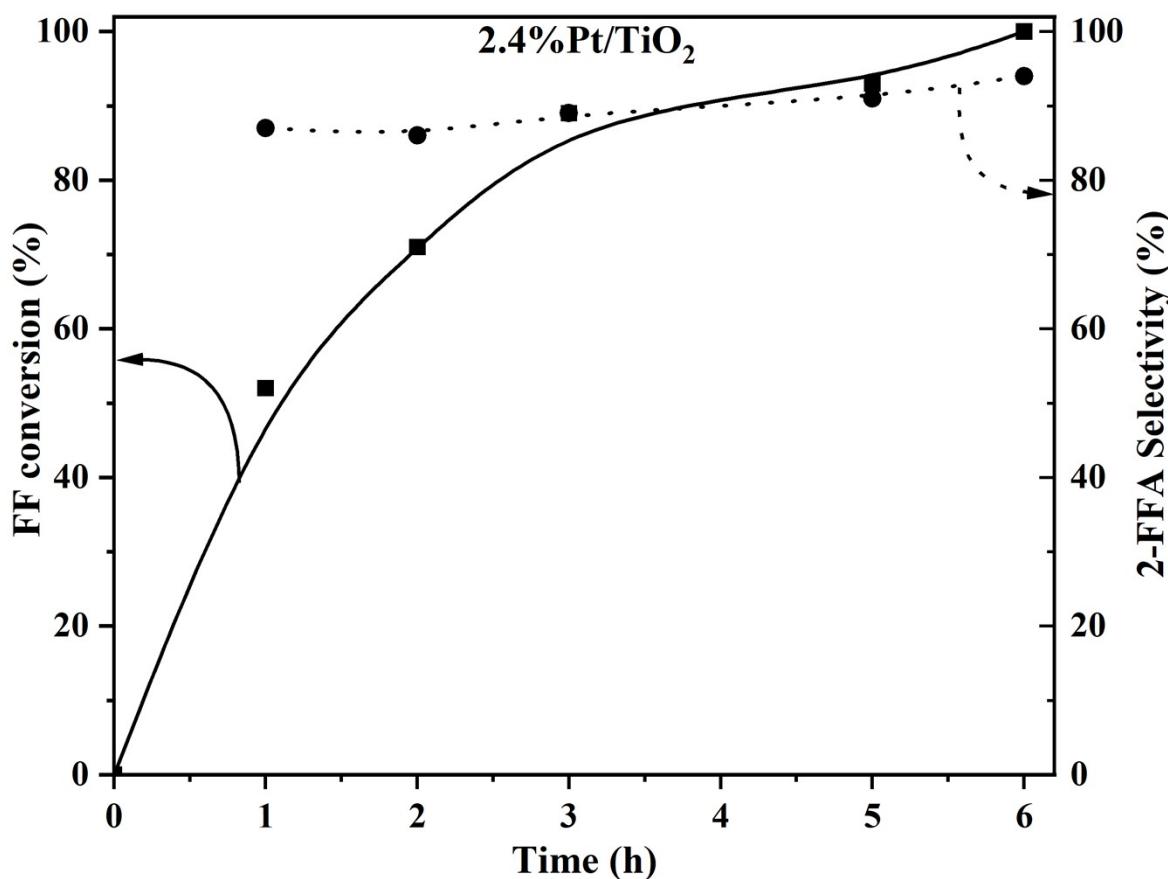


Figure S2: Catalytic performance of 2.4%Pt/TiO₂ (calcination + reduction) as a function of time for the hydrogenation of FF to 2-FFA. Reaction conditions: H₂ : 3 bar; Temp : 30 °C; FF: 4.45 mmol; Isopropanol (solvent) : 15 mL; FF/Pt molar ratio : 207.

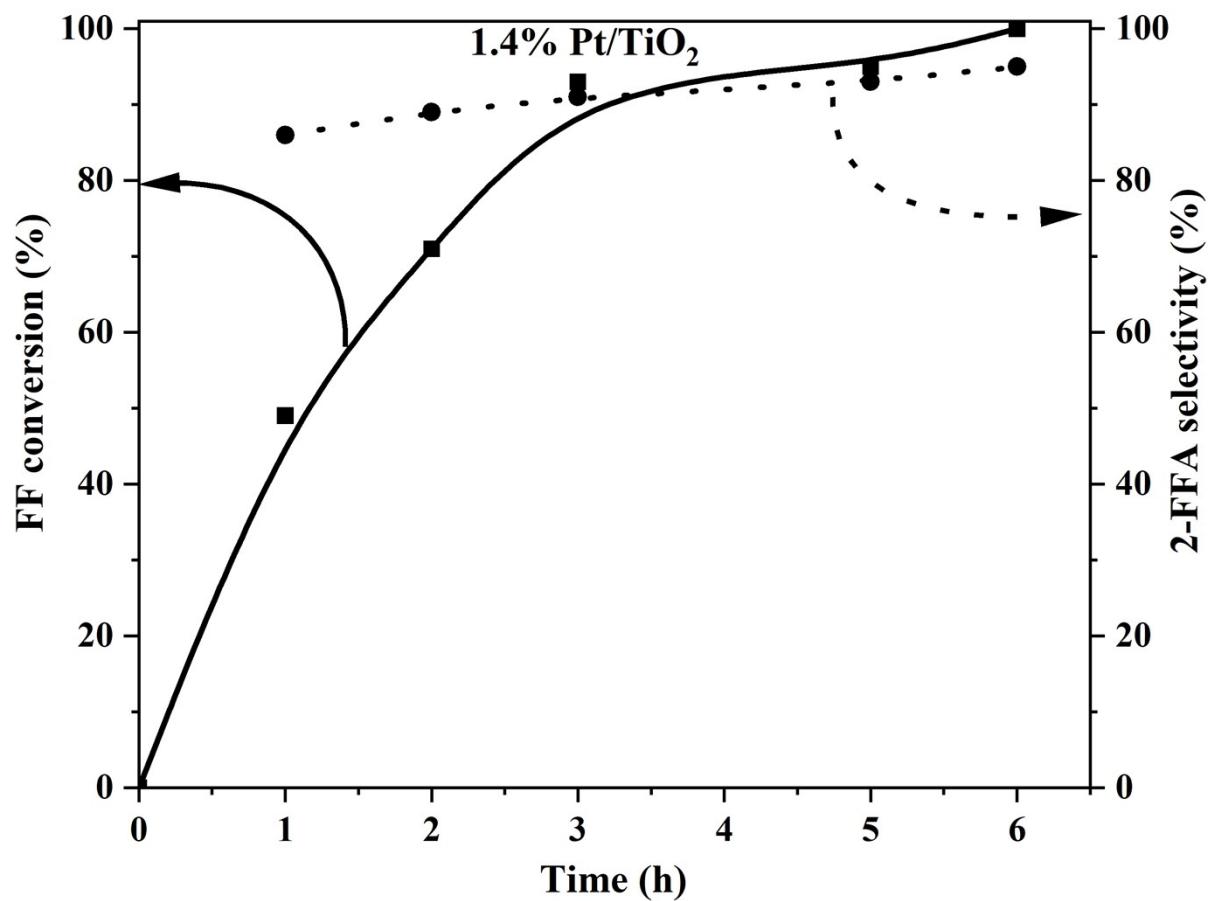


Figure S3: Catalytic performance of 1.4%Pt/TiO₂ (calcination + reduction) as a function of time for the hydrogenation of FF to 2-FFA. Reaction conditions: H₂ : 3 bar; Temp : 30 °C; FF: 4.45 mmol; Isopropanol (solvent) : 15 mL; FF/Pt molar ratio : 207.

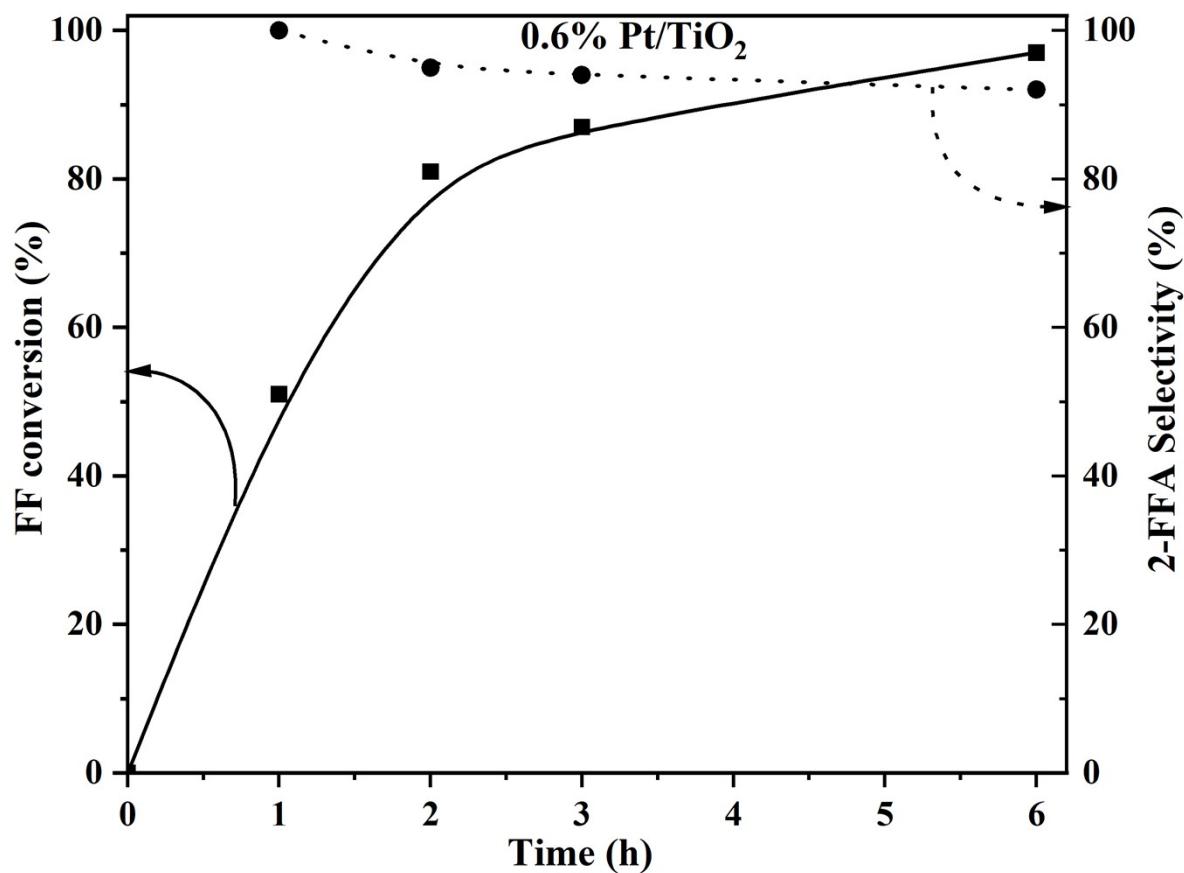


Figure S4: Catalytic performance of 0.6% Pt/TiO_2 (calcination + reduction) as a function of time for the hydrogenation of FF to 2-FFA. Reaction conditions: H_2 : 3 bar; Temp : 30 °C; FF: 4.45 mmol; Isopropanol (solvent) : 15 mL; FF/Pt molar ratio : 207.

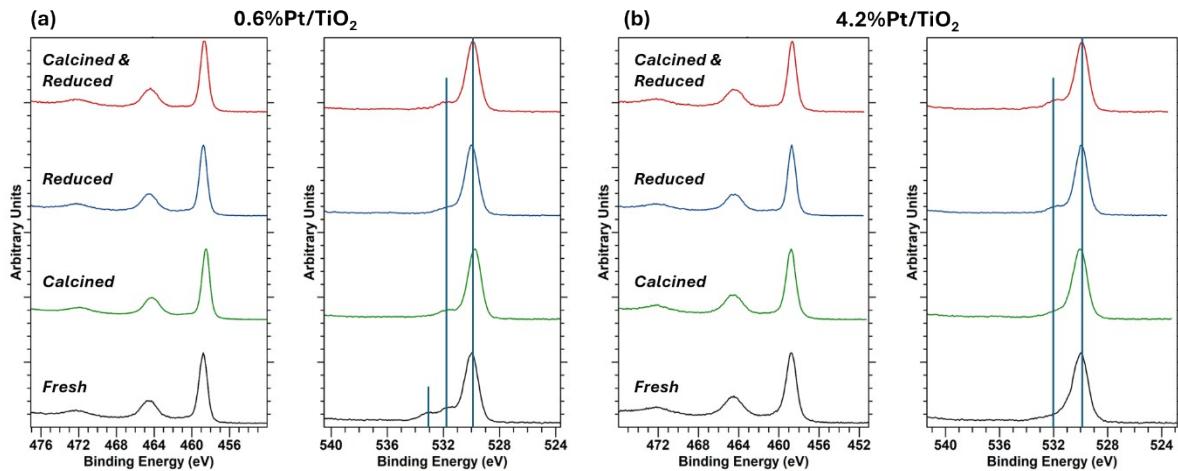
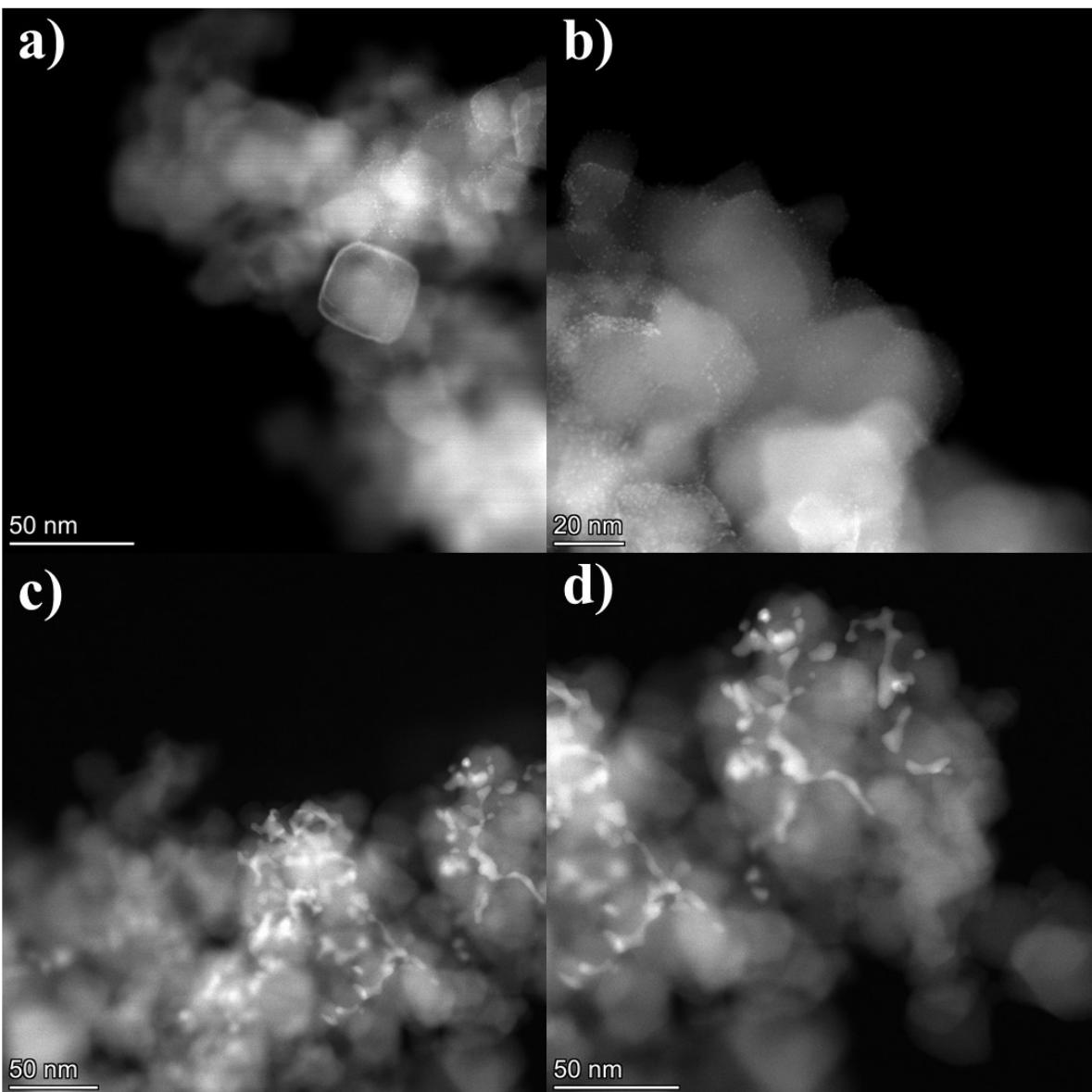


Figure S5: Ti(2p) and O(1s) core-levels spectra for 0.6%Pt/TiO₂ series of catalysts (a) and the 4.2%Pt/TiO₂ series of catalysts (b)

Table S2: XPS data for the two Pt/TiO₂ catalysts after different heat treatments.

Catalyst	Heat Treatment	B.E. / eV	Pt species	Pt Concentration (%)	Total Pt concentration
4.2%Pt/TiO ₂	Dried	72.7	Pt ²⁺ (OH)	0.92	1.74
		74.7	PtCl _x	0.82	
	Calcined	72.7	Pt ²⁺	1.28	1.96
		74.8	PtCl _x	0.68	
	Reduced	70.5	Pt ⁰	0.14	0.14
0.6%Pt/TiO ₂	Dried only	72.5	Pt ²⁺	0.28	0.28
	Reduced only	70.7	Pt ⁰	0.15	0.15
	Calcined + reduced	70.6	Pt ⁰	0.24	0.24



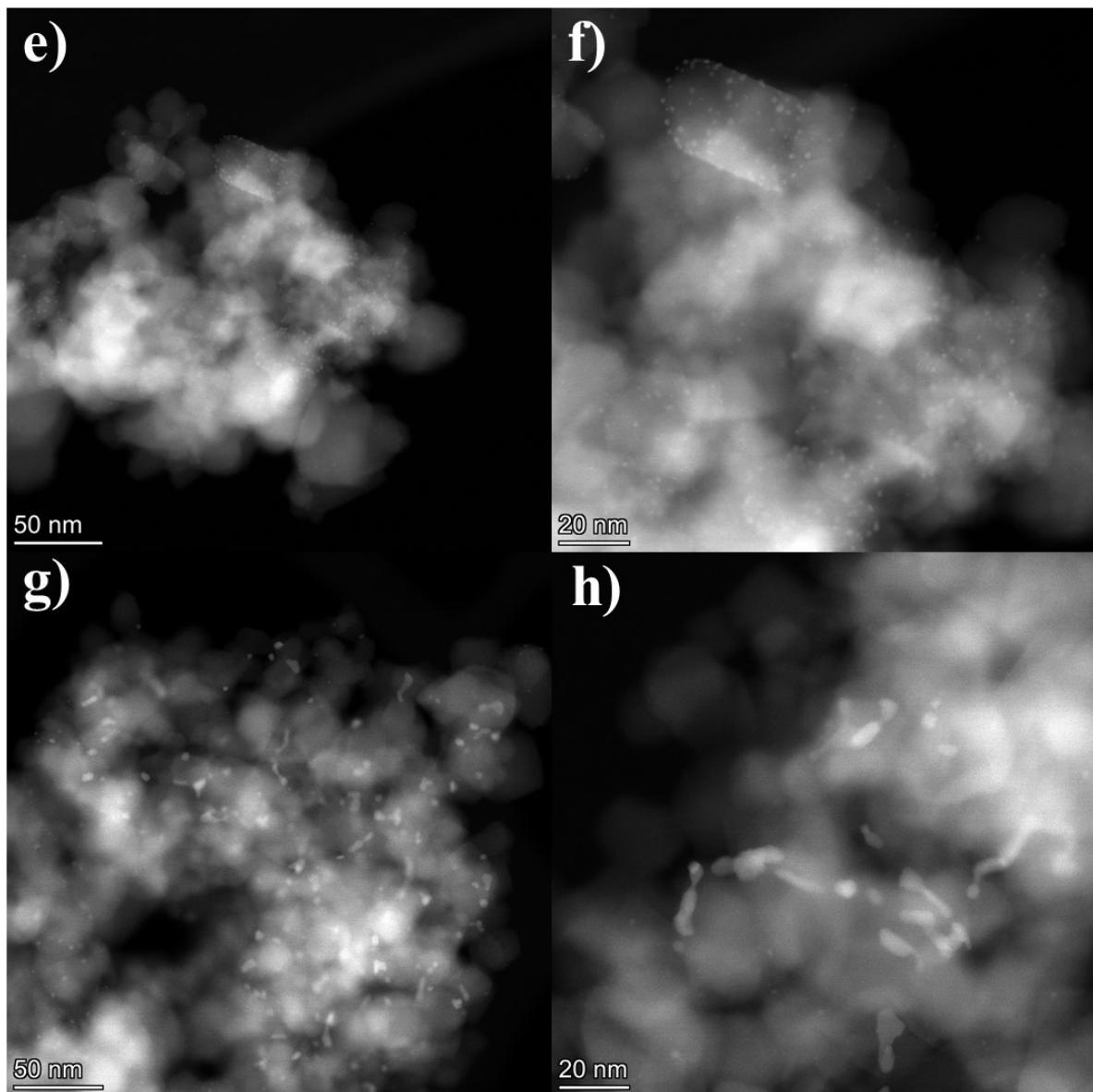


Figure S6: Scanning Transmission Electron microscopic images of 4.2%Pt/TiO₂ (C+R) (a & b); 4.2%Pt/TiO₂ (R) (c & d); 0.6%Pt/TiO₂ (C+R) (e & f); 0.6%Pt/TiO₂ (R) (g & h). The lower magnification images highlight the presence of large irregular Pt particles on the reduced only catalysts.

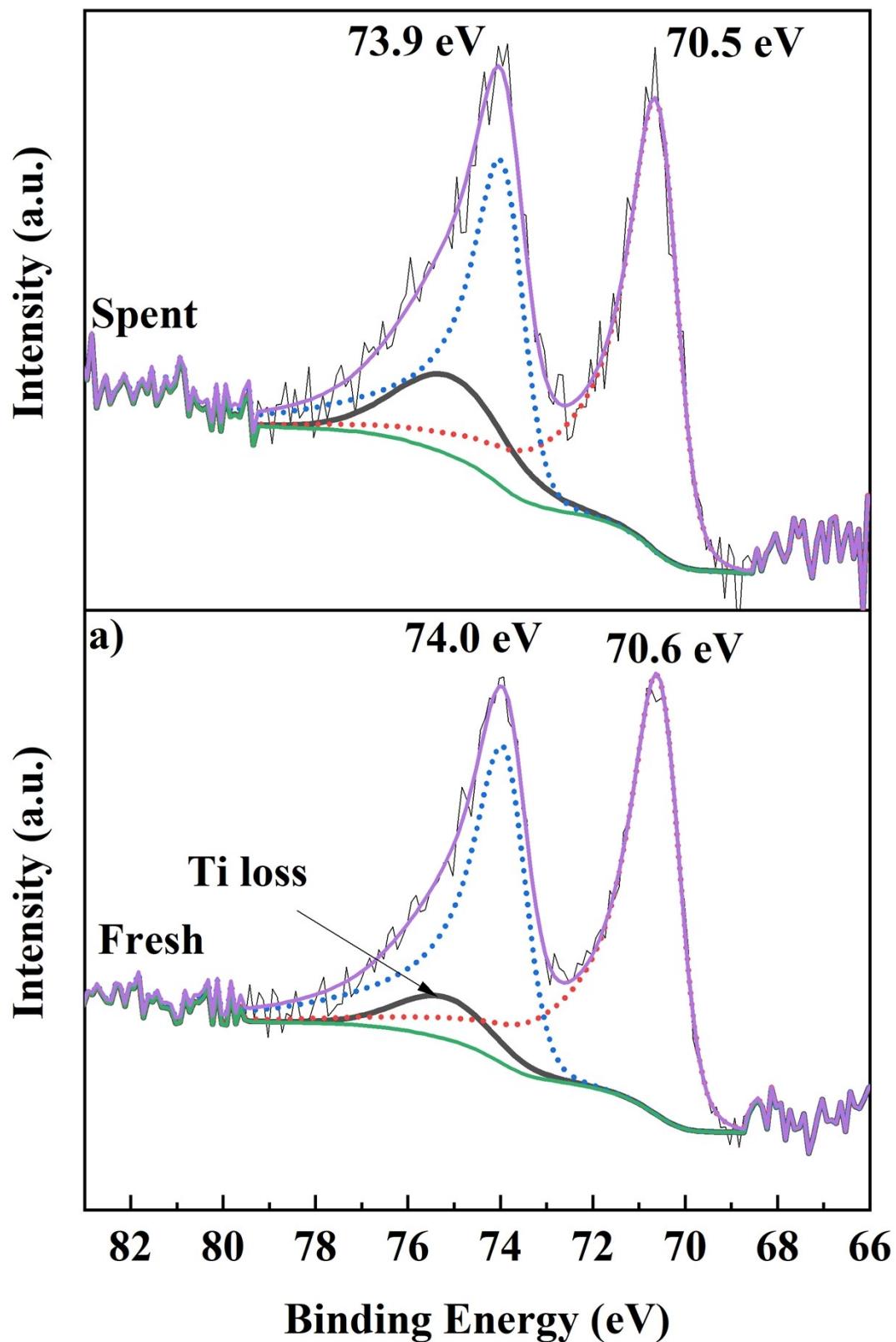


Figure S7 XPS results of the fresh and spent samples of 0.6% Pt/TiO₂ calc +red

Table S3: Quantitative analyses of the metal composition using Inductively Coupled Plasma coupled with Mass Spectra (ICP-MS)

Sample	Pt (mg/g)
0.6%Pt/TiO ₂ - Fresh sample	8.77
0.6%Pt/TiO ₂ - Spent sample after 3 runs	8.92

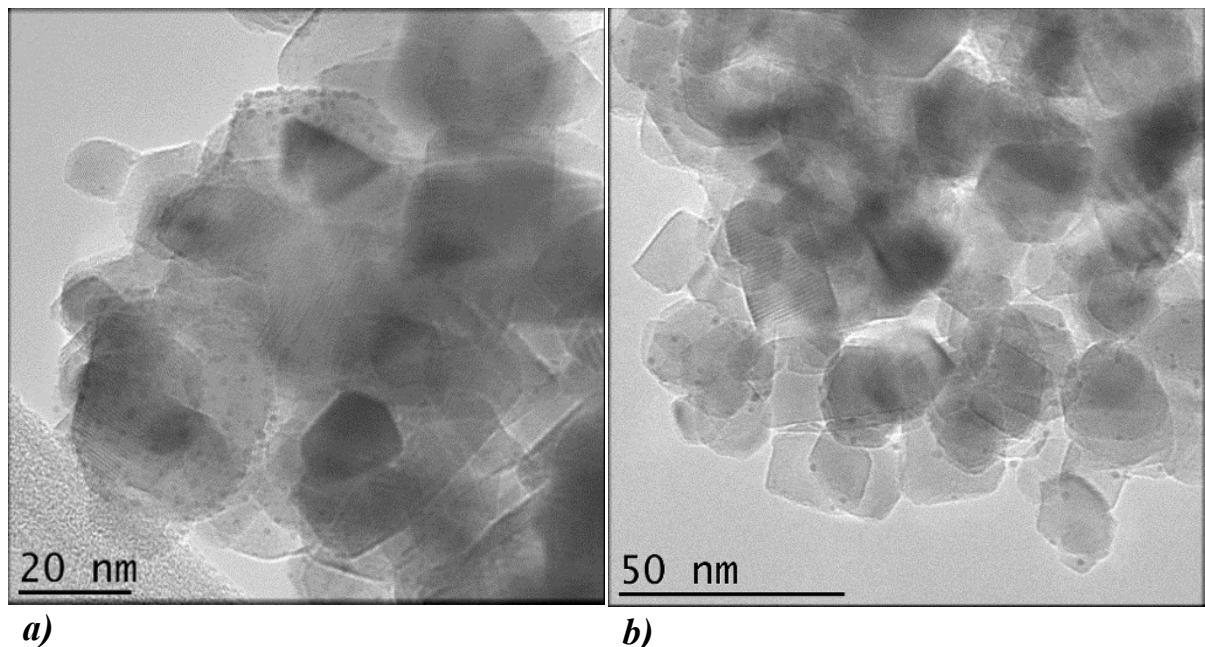


Figure S8: TEM images of fresh (a) and spent (b) samples of 0.6 wt. % Pt/TiO₂ catalyst. .

Table S4: Comparison of different supported Pt nanoparticulate catalysts for the hydrogenation of FF to 2-FF including the current work.

Catalyst	Preparation method	Catalyst & FF	Temp./Press./Solvent/Time	Conv. (%)	Selec. (%)	Ref
3% Pt/HT	Wetness impregnation	FF (0.75 mmols), catalyst (50 mg)	30 °C, /15 bar/ water/ 2 h	99	99	¹
3% Pt/SiC–C	Ultrasound promoted impregnation	FF (0.3 ml), catalyst (20 mg),	25 °C/ 10 bar/ water/ 5h	99	99	²
2.3% Pt/MgO,	Colloidal deposition	FF (0.02 mmols) , catalyst (20 mg)	50 °C/1.03 bar /methanol/ 7 h	80	99	³
1.4% Pt/CeO ₂	Colloidal deposition	FF (0.02 mmols) , catalyst (20 mg)	50 °C/ 1.03 bar /methanol/ 7 h	79	97	³
1.9% Pt/ γ -Al ₂ O ₃	Colloidal deposition	FF (0.02 mmols) , catalyst (20 mg)	50 °C/ 1.03 bar /methanol/ 7 h	77	98	³
5% Pt/TiO ₂ nanorod (NR)	Impregnation–chemical reduction	FF (26 mmol), catalyst (100 mg)	170 °C/20 bar/ water/ 2 h.	90	2	⁴
0.7% Pt/TiO ₂	One-step flame spray pyrolysis (FSP)	FF (0.05 ml), catalyst (50 mg)	50 °C/ 20 bar/ methanol/ 2 h.	83	95	⁵
0.5% Pt/TiO ₂	Strong electrostatic adsorption method (SEA)	FF (0.6 mmol), catalyst (50 mg)	50 °C/ 20 bar/ methanol/ 2 h.	89	80	⁶
1% Pt/SnNb ₂ O ₆	Photoreduction method	FF (0.1 mmol), catalyst (8 mg)	25 °C/ 1 bar/ methanol/ 2 h.	99.9	99.9	⁷
1% Pt/Al ₂ O ₃	Incipient wetness impregnation	FF (0.3 mmol),	150 °C/ 5 bar/ isopropanol/ 5 h.	95	98	⁸

		catalyst (58 mg)				
Pt/CeO ₂ /UIO	Deposition method	FF (0.2 mmol), catalyst (Pt: 0.5 mol %)	80 °C/ 10 bar/ isopropanol/ 30 h.	100	99	⁹
0.6% Pt/TiO ₂	Wetness impregnation	FF (0.3 ml), catalyst (100 mg),	30 °C/ 3 bar /isopropanol/ 6 h	97	95	Current work

Supplementary References

1. G. Gao, J. Remón, Z. Jiang, L. Yao and C. Hu, *Appl. Catal. B: Environ.*, 2022, **309**, 121260.
2. G. Wang, R. Yao, H. Xin, Y. Guan, P. Wu and X. Li, *RSC Advances*, 2018, **8**, 37243-37253.
3. M. J. Taylor, L. J. Durndell, M. A. Isaacs, C. M. A. Parlett, K. Wilson, A. F. Lee and G. Kyriakou, *Appl. Catal. B: Environ.*, 2016, **180**, 580-585.
4. M. Y. Byun, Y. E. Kim, J. H. Baek, J. J. and M. S. Lee, *RSC Adv.*, 2022, **12**, 860-868.
5. W. Tolek, K. Khruechao, B. Pongthawornsakun, O. Mekasuwandumrong, F. J. C. S. Aires, P. Weerachawanarak and J. Panpranot. *Cat. Commun.*, 2021, **149**, 106246.
6. S. Kuhaudomlap, O. Mekasuwandumrong, P. Praserthdam, S.-I. Fujita, M. Arai and J. Panpranot, *Catalysts* 2018, **8**, 87.
7. Y. Shi, H. Wang, Z. Wang, C. Liu, M. Shen, T. Wu and L. Wu, *J. Energy Chem.*, 2022, **66**, 566-575.
8. M. Agote-Arán, S. Alijani, C. Coffano, A. Villa and D. Ferri, *Catal. Lett.*, 2021, **152**, 980-990.
9. Y. Long, S. Song, J. Li, L. Wu, Q. Wang, Y. Liu, R. Jin and H. Zhang, *ACS Catal.*, 2018, **8**, 8506-8512.

