

Supplementary Materials

Microemulsion Derived Titania Nanospheres: An Improved Pt Supported Catalyst for Glycerol Aqueous Phase Reforming

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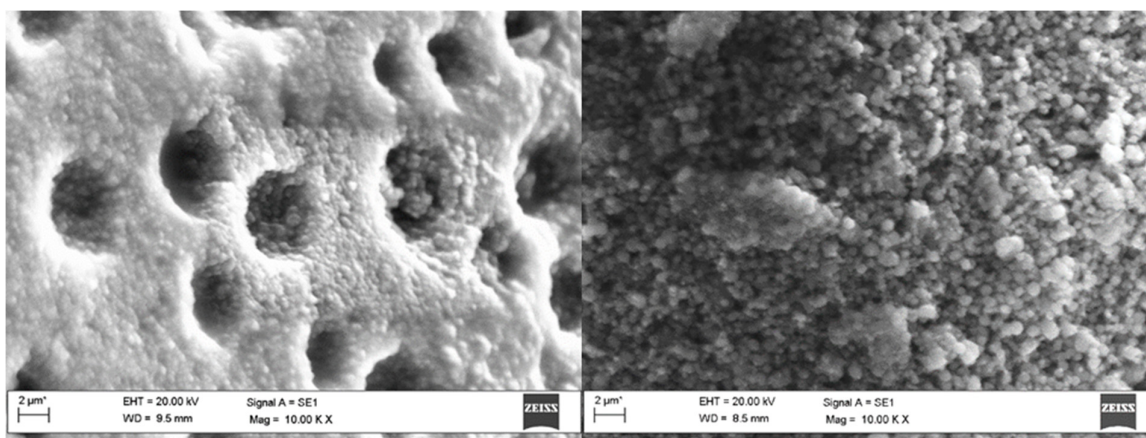


Figure S1. Scanning electron microscopy (SEM) images of the sponge-like solid deposited on the bottom of the flask soon after the synthesis.

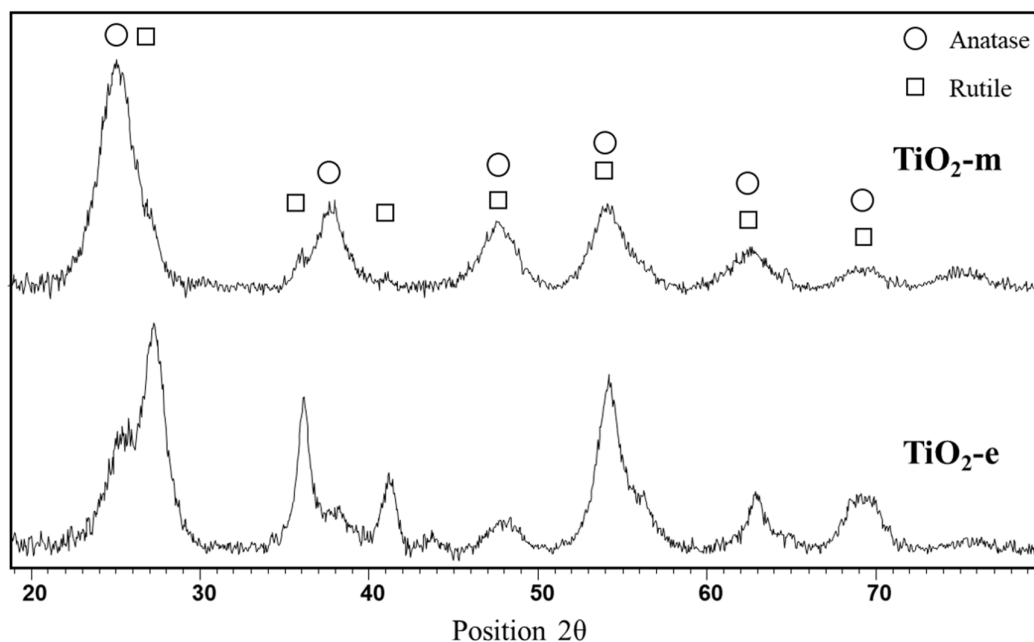


Figure S2. X-ray diffraction (XRD) analysis of TiO_2 samples synthesized with ($\text{TiO}_2\text{-m}$) and without ($\text{TiO}_2\text{-e}$) the presence of a surfactant and co-surfactant.

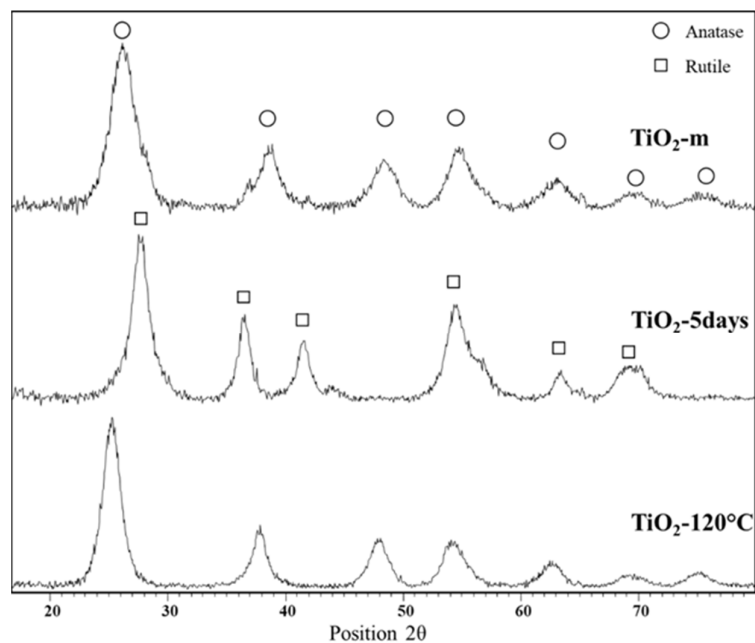


Figure S3. XRD analyses of TiO₂ samples synthesized with different synthetic methods (see Table 1).

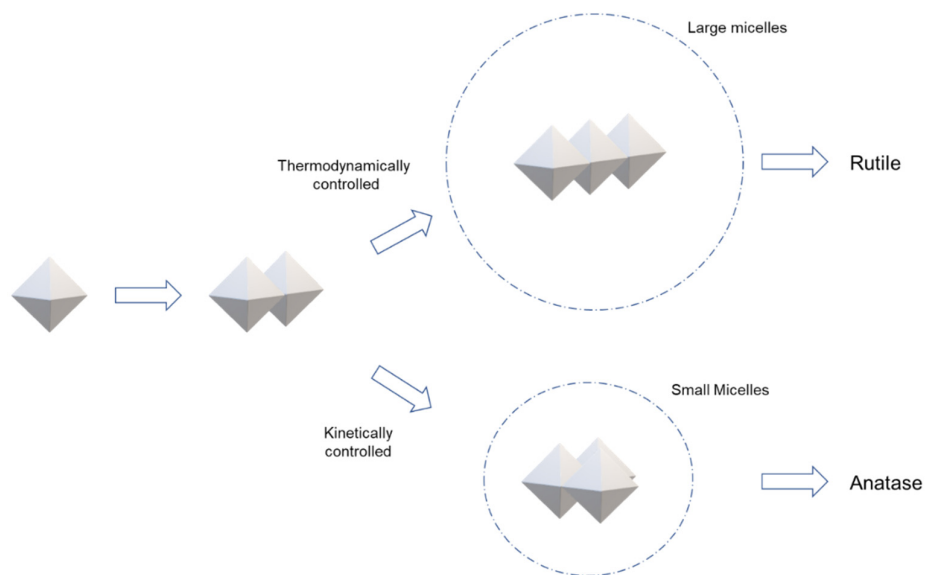


Figure S4. Schematic representation of the kinetically controlled and thermodynamically controlled crystal growth leading to anatase or rutile; each octahedra represent a TiO₆²⁻ anion.

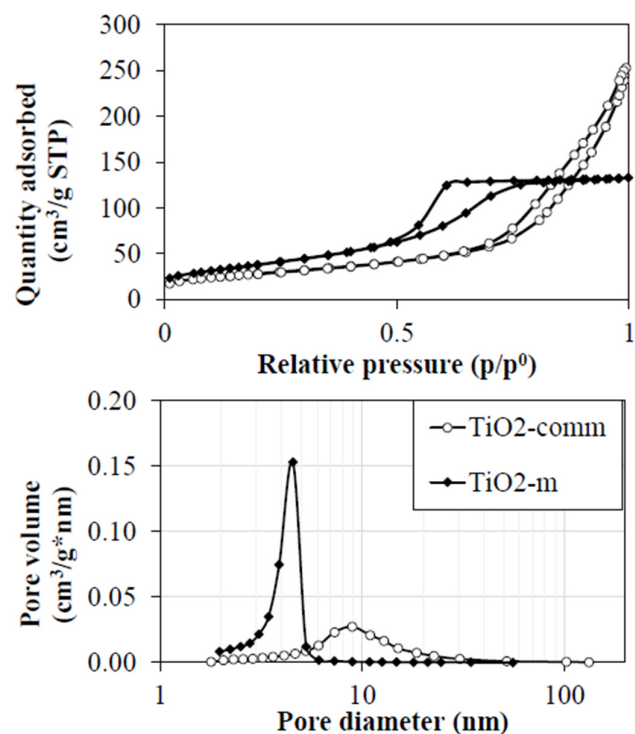


Figure S5. Adsorption/desorption isotherms and pore distribution of the TiO₂ samples.

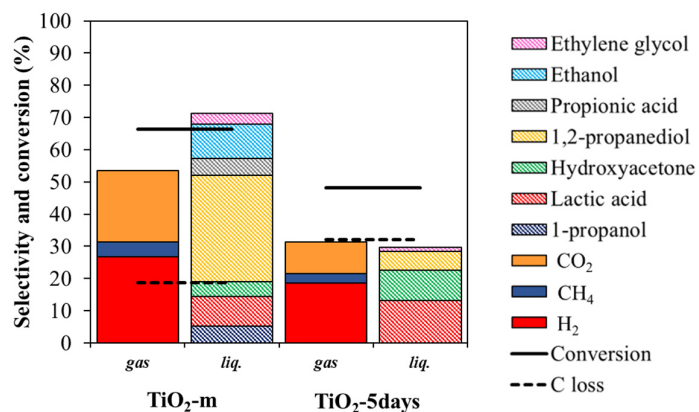


Figure S6. Comparison of glycerol aqueous phase reforming (APR) reactivity within Pt 3 wt% on TiO₂-m400 and Pt 3 wt% on TiO₂-5days400. Reaction performed at 225 °C for 3 h; glycerol loading 6 wt%.

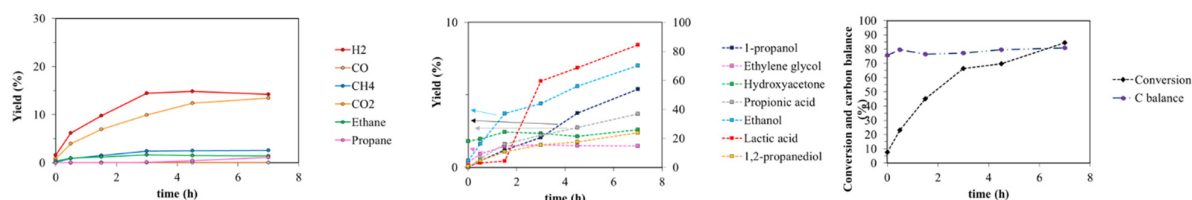


Figure S7. Liquid phase (centre), gas phase (left) products yields and conversion and carbon loss (right). Reactions performed at 225 °C over 3 wt% Pt/TiO₂-m400 catalyst; 6 wt% glycerol loading in water.

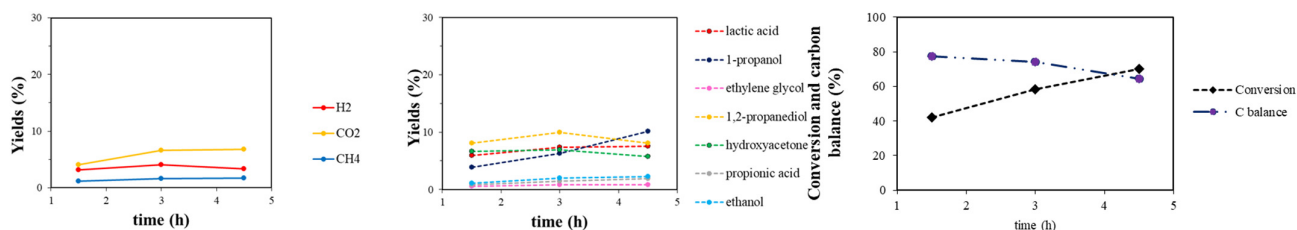


Figure S8. Liquid phase (centre), gas phase (left) products yields and conversion and carbon loss (right). Reactions performed at 250 °C over 1 wt% Pt/TiO₂-m400 catalyst; 17 wt% glycerol loading in water.

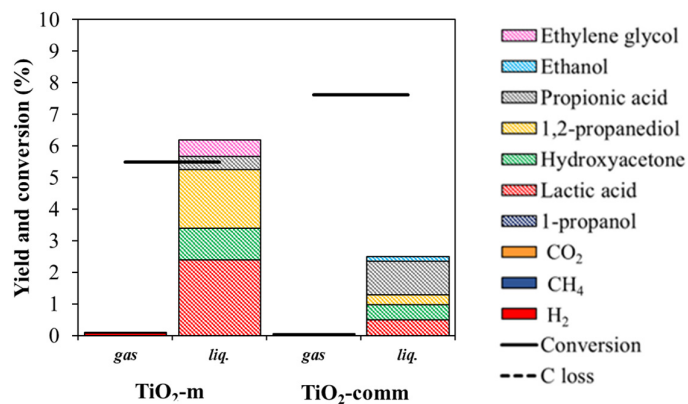


Figure S9. Comparison within TiO₂-m and commercial supports without Pt impregnation. Reaction performed at 250 °C for 3 h; glycerol loading 17 wt%.

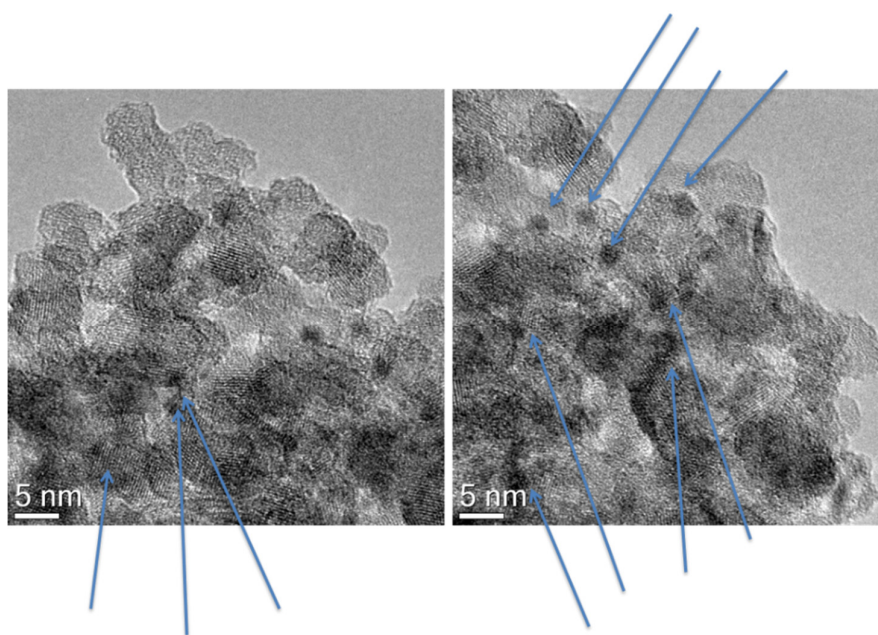


Figure S10. TEM analysis of Pt 3% wt on TiO₂-m400 after the aqueous phase reforming reaction performed at 225 °C for 3 h; 6 wt% glycerol loading in water. Arrows indicate Pt nanoparticles.

Table S1. Results of reactivity tests with intermediates in terms of conversion and product selectivity. Reactions performed at 225 °C for 3 h over 3 wt% Pt/TiO₂-m400 in water; 3 wt% loading of reagent in water, 0.45 g of catalyst. Inner circle reports conversion (%), outer circle reports selectivities (%).

Reagent	P (H ₂) bar	Conv	CO ₂	CH ₄	LA	PrOH	1,2-PDO	HA	PA	EtOH
LA	3	19	11	4	-	2	9	0	61	12
HA	3	96	11	4	1	4	33	-	2	9
EG	3	46	23	2	0	0	0	0	0	22
Pyruvaldehyde	-	100	5	1	72	0	9	8	8	4
Pyruvaldehyde	3	100	5	1	56	0	23	5	6	0

Table S2. Glycerol conversion, hydrogen selectivity and liquid product selectivity for some Pt based catalysts reported in literature. * Results reported as hydrogen yield.

Catalyst	T (°C)	Time (h)	Process	Conv. (%)	Sel. H ₂	Sel. 1,2-PDO	Sel. LA	Sel. HA	Sel. EG	Sel. PrOH	Sel. PA	Sel. EtOH	Ref.
Pt/TiO ₂	225	/	Fixed Bed	27	56*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[1]
Pt/TiO ₂	210	6	Batch	46	17*	49	n.a.	n.a.	12	2	n.a.	10	[2]
Pt/Al ₂ O ₃	250	/	Fixed bed	43	85	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[3]
Pt/MgO	225	/	Fixed bed	n.a.	28	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[1]
Ru/Al ₂ O ₃ + Pt/Al ₂ O ₃	220	6	Batch	50	n.a.	47	2	n.a.	6	n.a.	n.a.	1	[4]
Pt-Ir-ReO _x /SiO ₂	190	17	Batch	30	n.a.	19	n.a.	n.a.	1	4	2	2	[5]
Pt/Al ₂ O ₃	210	6	Batch	10	31*	21	n.a.	n.a.	32	n.a.	n.a.	6	[2]

References

- Guo, Y.; Azmat, M.U.; Liu, X.; Wang, Y.; Lu, G. Effect of Support's Basic Properties on Hydrogen Production in Aqueous-Phase Reforming of Glycerol and Correlation between WGS and APR. *Appl. Energy* **2012**, *92*, 218–223, doi:10.1016/j.apenergy.2011.10.020.
- Delgado, S.N.; Yap, D.; Vivier, L.; Especel, C. Influence of the Nature of the Support on the Catalytic Properties of Pt-Based Catalysts for Hydrogenolysis of Glycerol. *J. Mol. Catal. Chem.* **2013**, *367*, 89–98, doi:10.1016/j.molcata.2012.11.001.
- Lehnert, K.; Claus, P. Influence of Pt Particle Size and Support Type on the Aqueous-Phase Reforming of Glycerol. *Catal. Commun.* **2008**, *9*, 2543–2546, doi:10.1016/j.catcom.2008.07.002.
- Roy, D.; Subramaniam, B.; Chaudhari, R.V. Aqueous Phase Hydrogenolysis of Glycerol to 1,2-Propanediol without External Hydrogen Addition. *Catal. Today* **2010**, *156*, 31–37, doi:10.1016/j.cattod.2010.01.007.
- Liu, S.; Tamura, M.; Shen, Z.; Zhang, Y.; Nakagawa, Y.; Tomishige, K. Hydrogenolysis of Glycerol with In-Situ Produced H₂ by Aqueous-Phase Reforming of Glycerol Using Pt-Modified Ir-ReO_x/SiO₂ Catalyst. *Catal. Today* **2018**, *303*, 106–116, doi:10.1016/j.cattod.2017.07.025.