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Supplementary Materials

TiO_2-Supported Pd as an Efficient and Stable Catalyst for the Mild Hydrotreatment of Tar-Type Compounds

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Preliminary catalytic screening:

Table S1. Catalytic activity (Conversion and selectivity to the different groups of products) of carbon-supported Pd, Pt and Ru commercial catalysts (comparison at 50–60% conversion).[a]

Catalyst	Conv. (mol%)	TON [b]	Product selectivity (mol%) [c]							
			MonoAr	Tetralin	Decalin	Ace	HAce-1	HPhe-1	HPhe-2	HAce-2 /HPhe-3
5wt%Pd/C	**71**	21	2	32	0	4	42	18	2	0
5wt%Pt/C	55	30	2	29	0	34	13	21	1	0
5wt%Ru/C	52	15	2	32	0	35	14	16	1	0

[a] Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, 0.2 g of catalyst, at 250 ºC and 30 bar of H_2 during 7 h. [b] TON = mols of products / mols of metal. [c] Liquid phase composition; Selectivity = mol of product (t) × 100 / total mol of identified products (t).

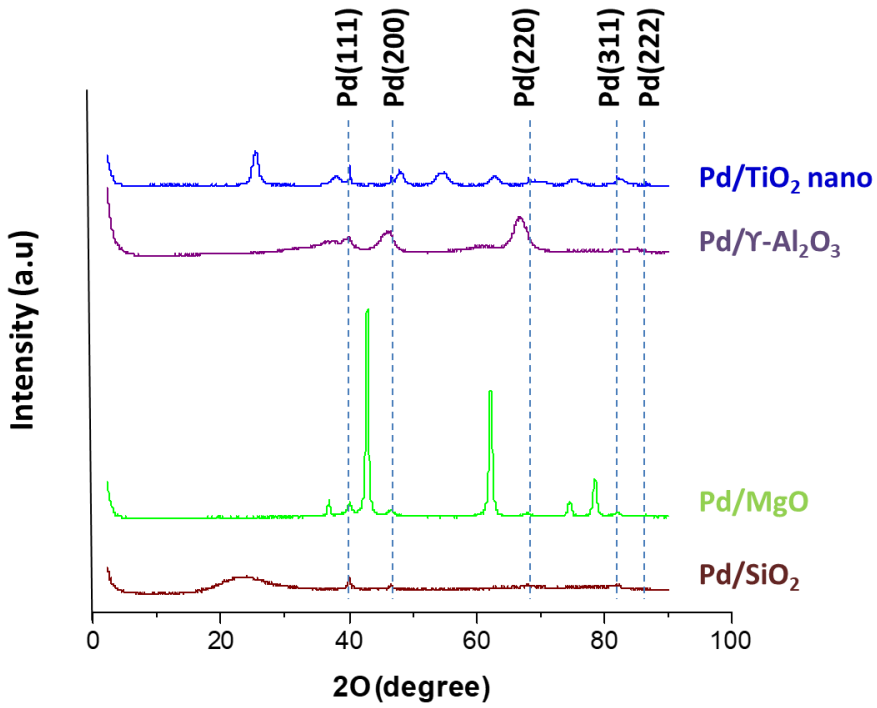

Figure S1. XRD patterns for different metal oxides-supported Pd catalysts.

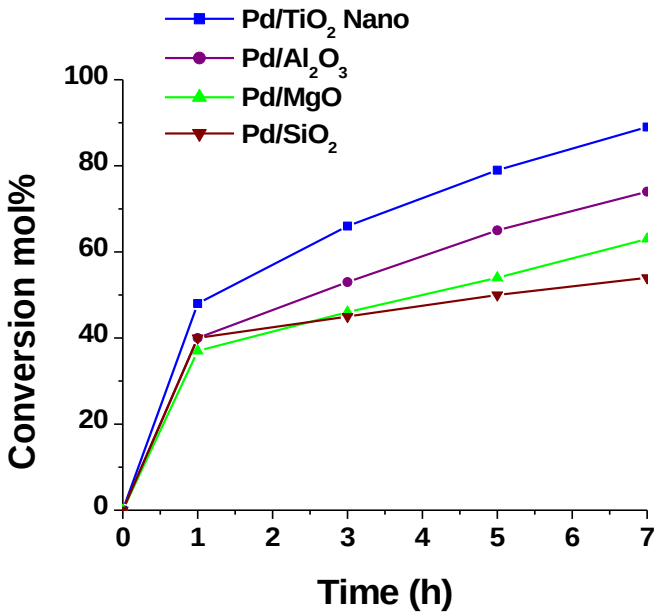

Figure S2. Conversion vs time for different metal oxides-supported Pd catalysts. Reaction conditions: 0.5 g of tar-type compounds, 4 g of n-hexadecane at 250 °C and 30 bar of H_2 during 7 h.

Effect of Pd content in Pd/TiO_2 (Nano) catalysts:

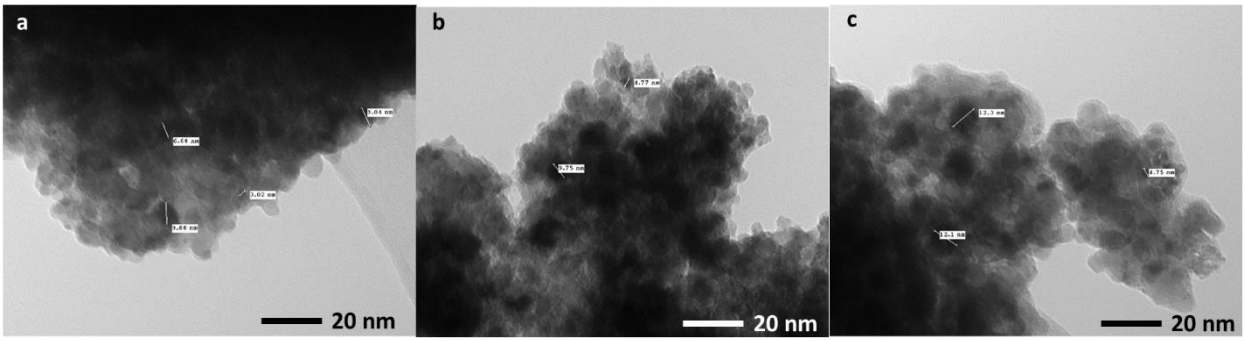

Figure S3. TEM images of (**a**) 0.8wt%Pd/TiO_2 (4–7 nm),(**b**) 1.3wt%Pd/TiO_2 (5–9 nm), and (**c**) 2.2wt% Pd/TiO_2 (6–12 nm).

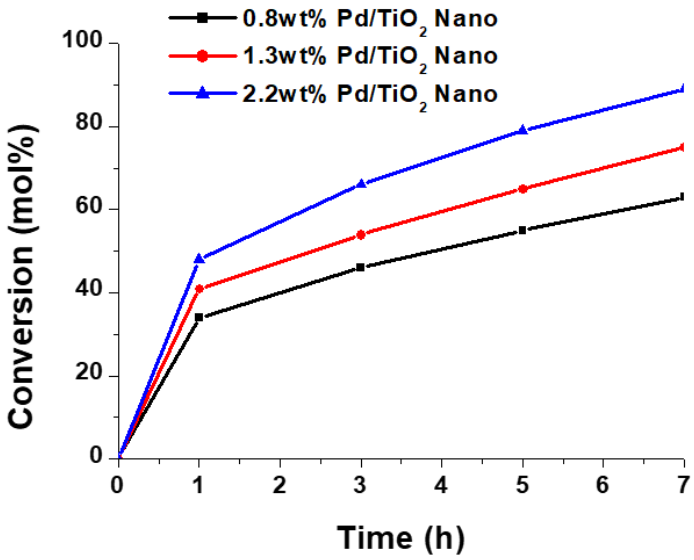

Figure S4. Conversion vs time for Pd/TiO_2 Nano catalysts with different Pd loadings. Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, 0.2 g of catalyst, at 250 °C and 30 bar of H_2 during 7 h.

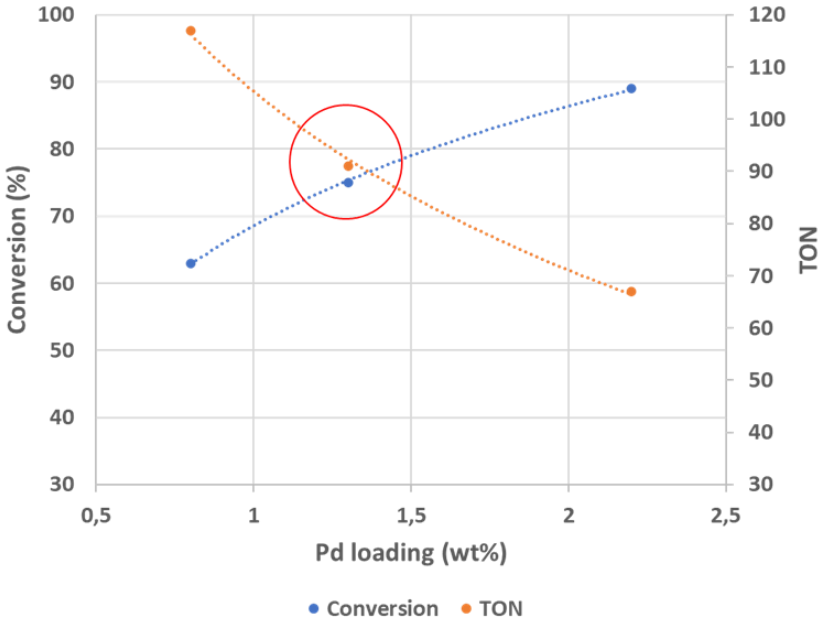

Figure S5. Conversion and TON (mols prod. / mols of Pd in solid) vs Pd loading for Pd/TiO_2 nano catalysts. Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, 0.2 g of catalyst, at 250 °C and 30 bar of H_2 during 7 h.

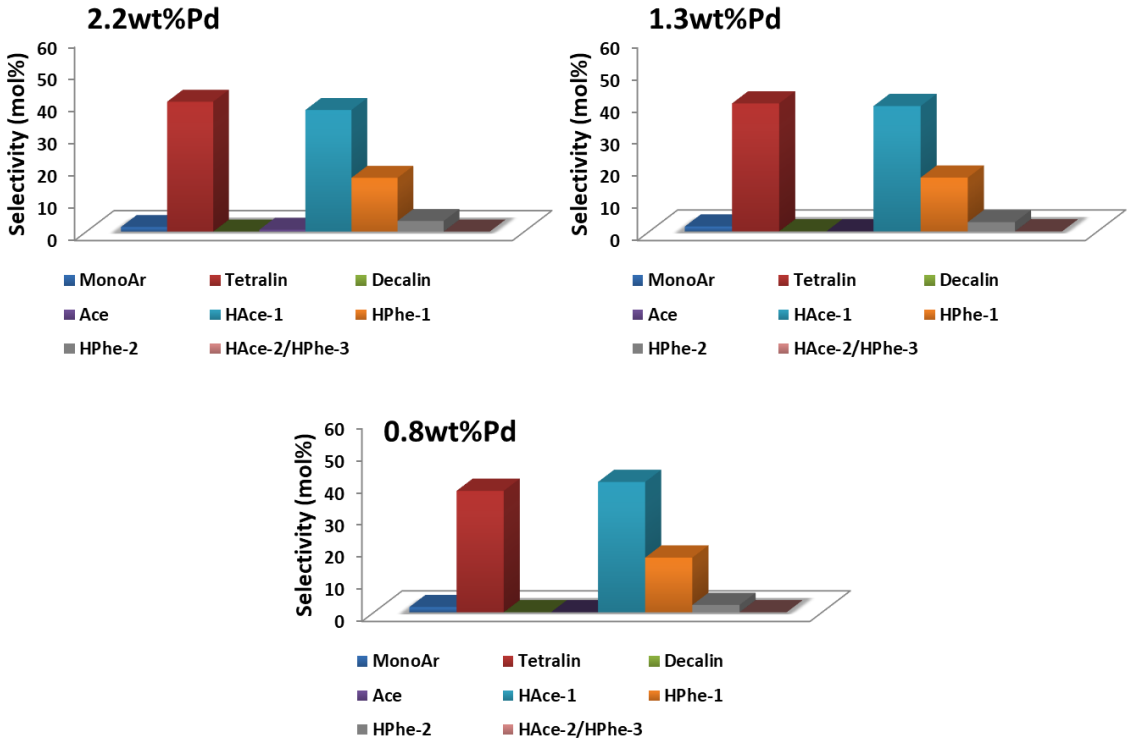

Figure S6. Selectivity to the different groups of products for Pd/TiO_2 Nano catalysts compared in the range 63-65% of conversion. Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, 0.2 g of catalyst, at 250 °C and 30 bar of H_2 during 7 h.

Table S2. Pd/TiO_2 Nano catalysts prepared by using different Pd precursors and their catalytic results in tars mild hydrotreatment.[a]

Pd Precursor	Pd (wt%)[b]	Conversion (mol%)	TON[c]
$Pd(NH_3)_4.Cl_2.H_2O$	1.3	75	91
$Pd(NO_3)_2.2H_2O$	1.3	79	90
$Pd(NO_3)_2.4NH_3$	0.8	68	127
$Pd(NH_3)_4.Cl_2.H_2O$	0.8	63	117

[a] Reactions conditions: 0.5 g of tars -type compounds, 4 g of n-hexadecane, at 250 °C, 30 bar of H_2, 0.2 g catalyst during 7 h. [b] Measured by ICP; [c] TON = mols of products / mols of metal in solid.

Effect of TiO_2 crystalline phase used as support

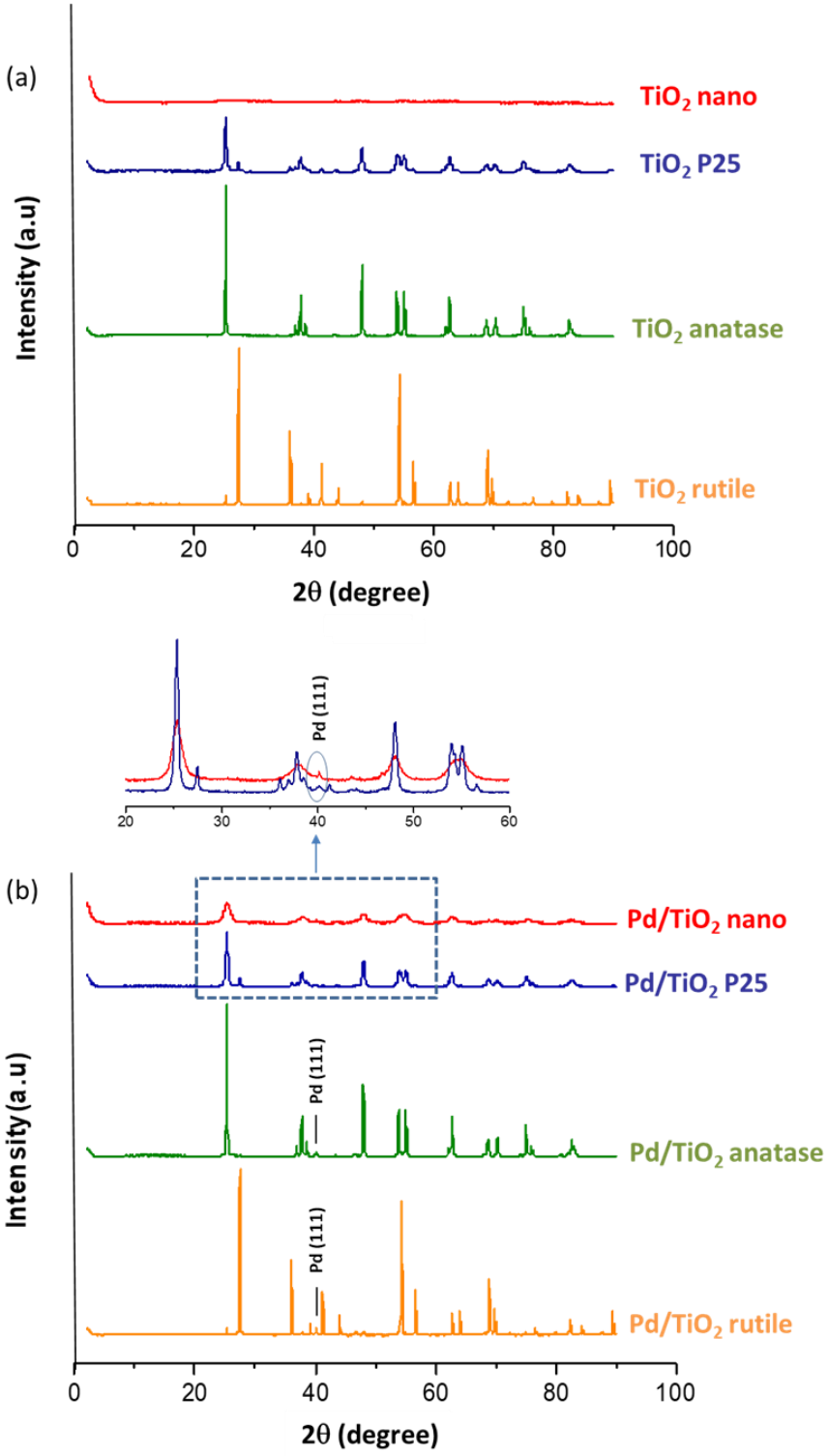

Figure S7. XRD patterns of different (a) pure TiO_2 supports and (b) TiO_2-supported Pd catalysts (Inset showing a zoom of 20-60 2Q region for Pd/TiO_2 nano and Pd/TiO_2 P25).

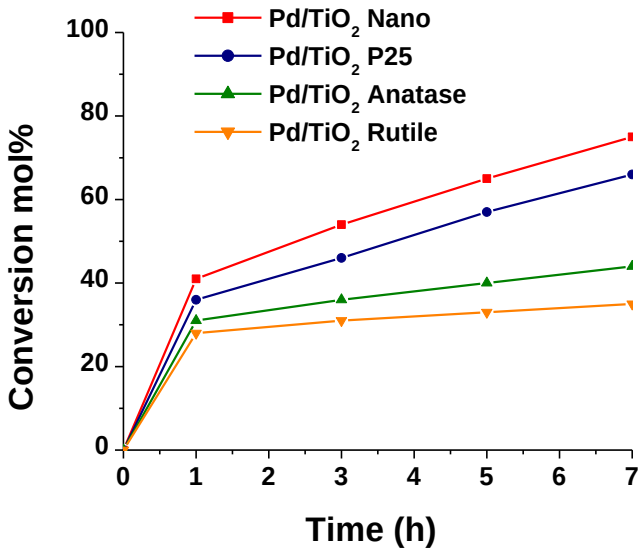

Figure S8. Conversion vs time for different TiO_2-supported Pd catalysts in tars mild hydrotreatment. Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, at 250 °C and 30 bar of H_2 during 7 h.

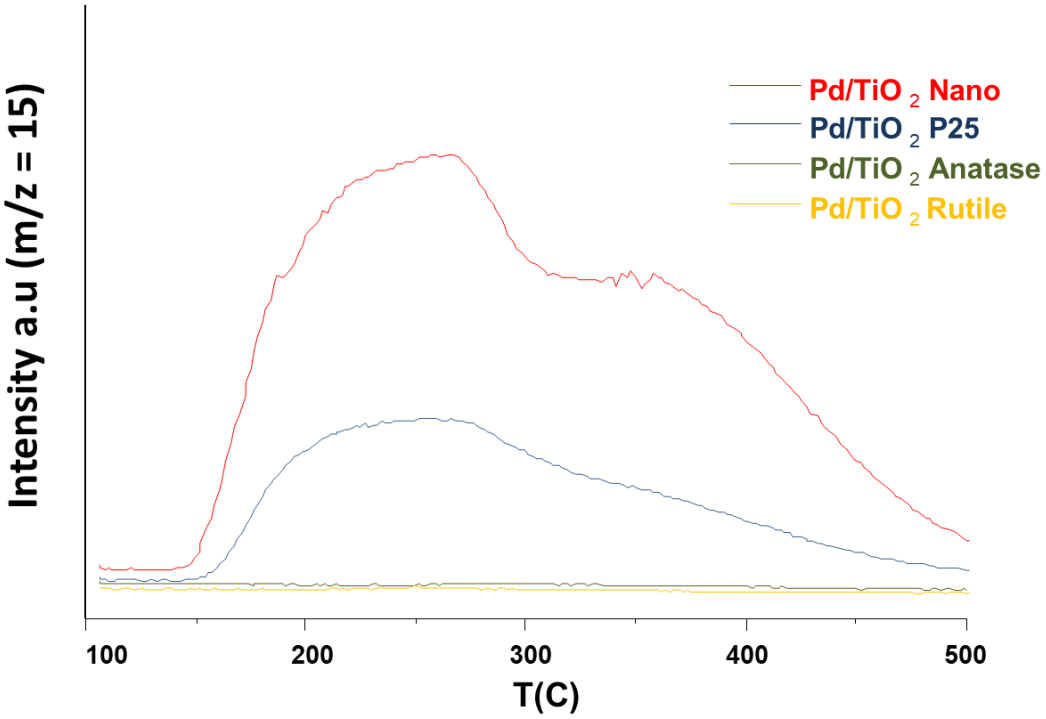

Figure S9. NH_3-TPD profiles for different TiO_2-supported Pd catalysts.

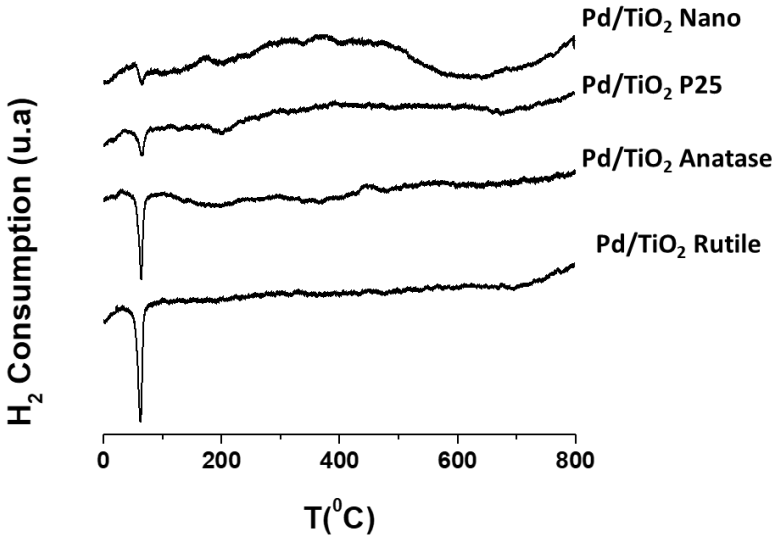

Figure S10. H_2-TPR profiles for different TiO_2-supported Pd catalysts.

Effect of reaction conditions for Pd/TiO_2 Nano catalyst

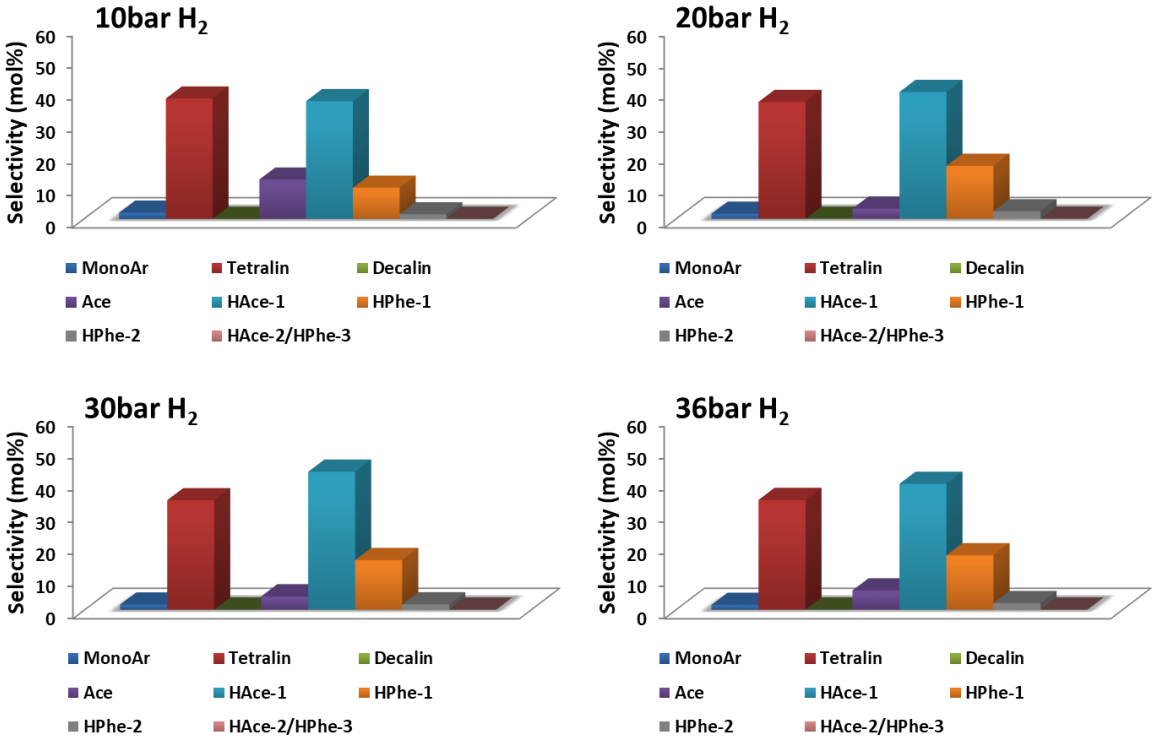

Figure S11. Selectivity to the different groups of products (compared at ≈53% conversion) for 1.3wt%Pd/TiO_2 Nano catalyst by using different H_2 pressures. Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, 0.2 g of catalyst, at 275 °C during 7 h.

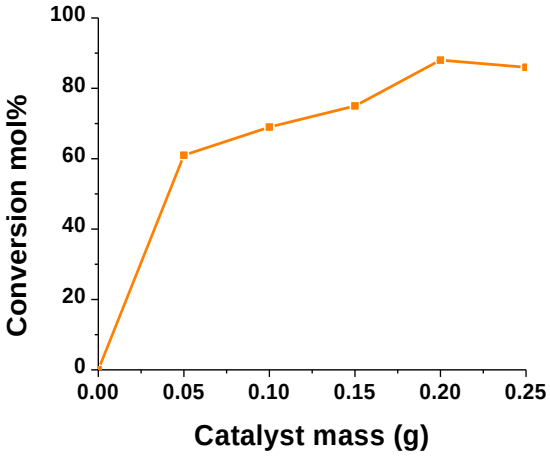

Figure 12. Catalyst loading optimization in tars mild hydrotreatment over 1.3wt%Pd/TiO_2 Nano. Reaction conditions: 0.5 g of tars-type compounds, 4 g of n-hexadecane, at 275 °C and 30 bar of H_2 during 7 h.

Reusability tests

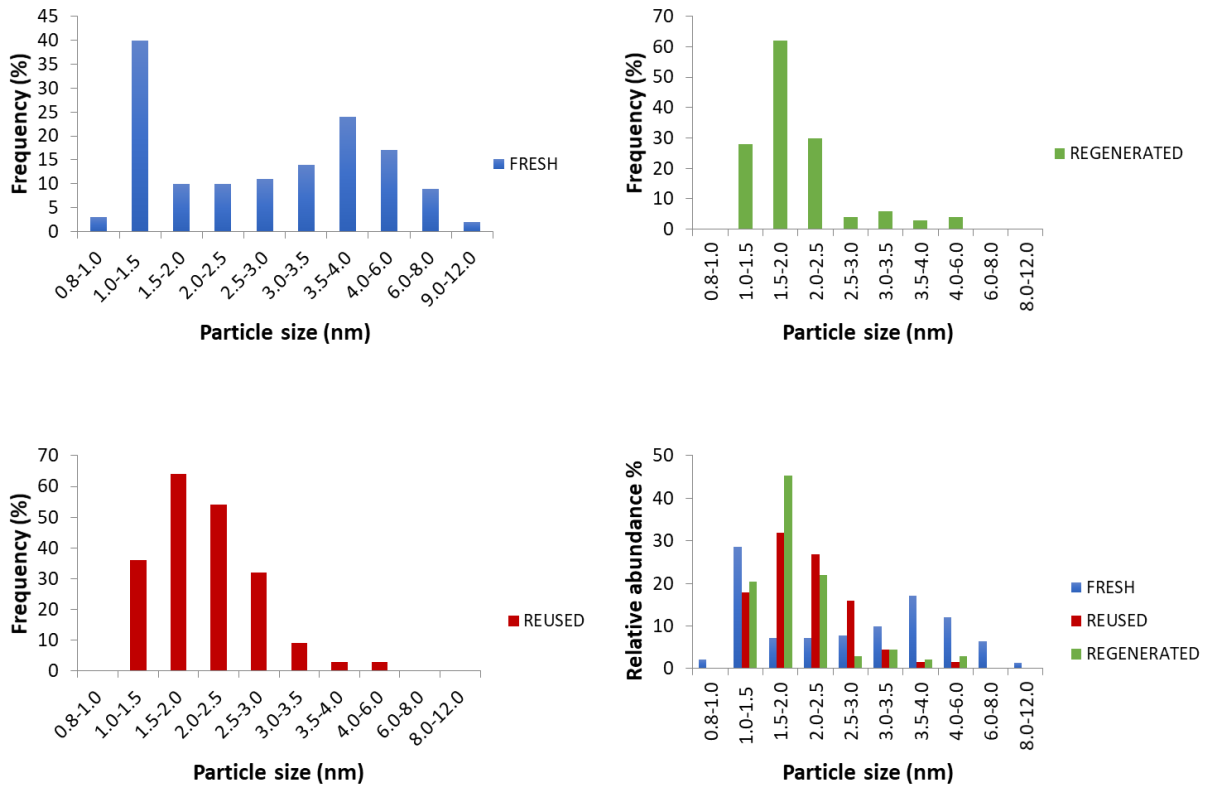

Figure S13. Pd particle size distribution of fresh, reused and regenerated samples of Pd/TiO_2 Nano catalyst.

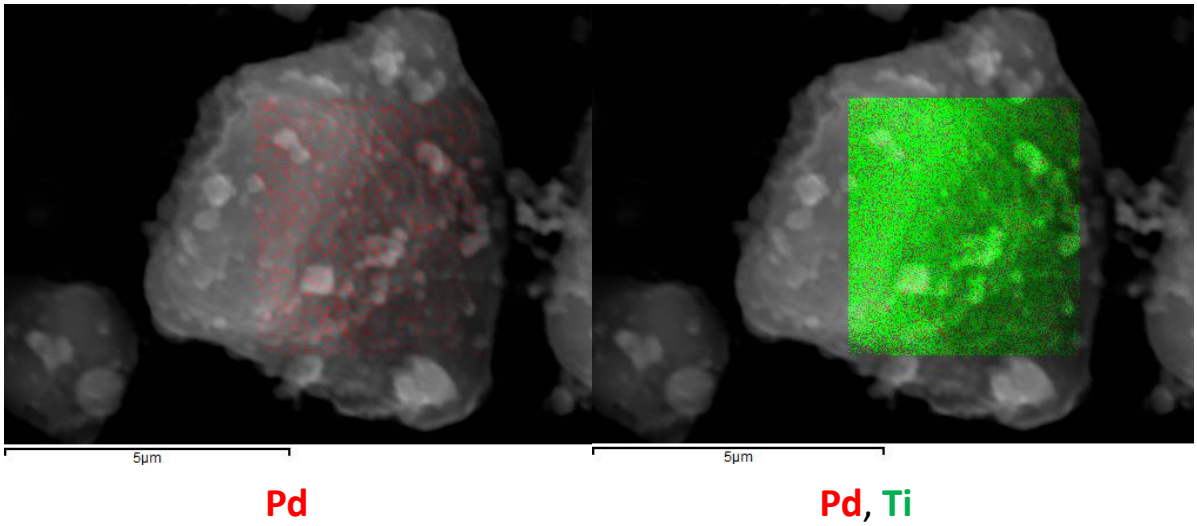

Figure S14. SEM-EDX for the fresh sample of Pd/TiO_2 Nano catalyst.

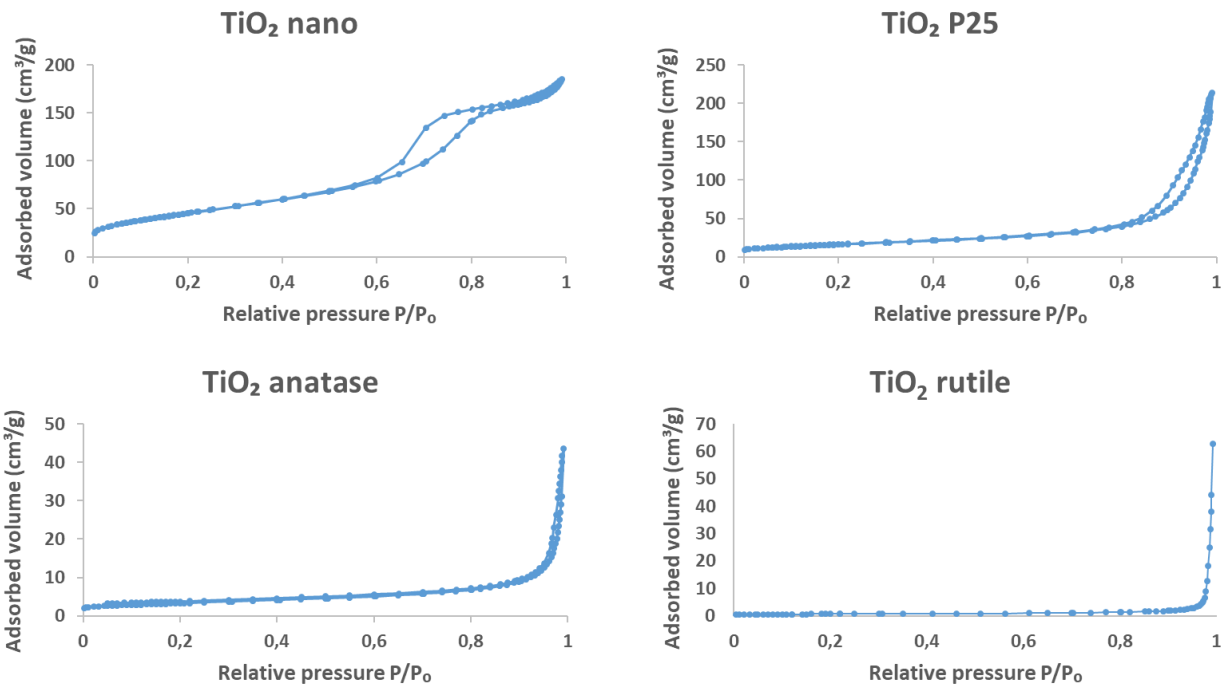

Figure S15. Nitrogen adsorption-desorption isotherms for different TiO_2 materials.

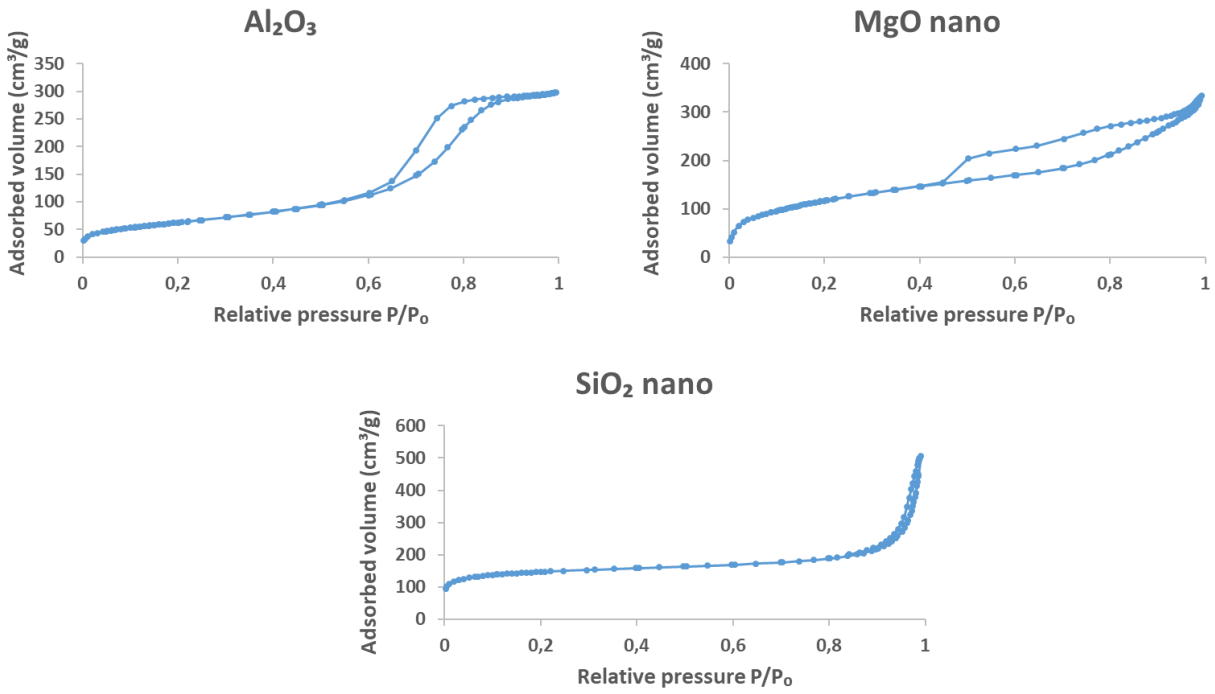

Figure S16. Nitrogen adsorption-desorption isotherms for different metal oxides materials.