Supplementary Information (SI) for Green Chemistry.

Selective one-pot chemical recycling of PET waste to xylene monomers: Insights into Ru/TiO_2 catalyst design and interfacial dynamics in a biphasic system

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1. Synthesis of the Ru/TiO_2 catalyst

The Ru-based nano catalysts were prepared using polyol, wet impregnation and incipient wetness impregnation method with an appropriate amount of an aqueous solution of $RuCl_3.xH_2O$. The obtained samples were dried at 100 °C for 12 h and then reduced in flowing 10 % H_2/Ar at 400 °C for 4 h.

1.1 Synthesis of size-controlled Ru/TiO_2 polyol catalyst

A sequence of small Ru colloidal nanoparticles (0.5-2.2nm) were produced through an in-situ reduction process with ethylene glycol. Initially, $RuCl_3.xH_2O$ was dissolved in ethylene glycol (Sigma–Aldrich), incorporating approximately 1 g of TiO_2-P25 (Sigma–Aldrich), were added to the mixture, followed by sonication at room temperature for 1 h. The pH of the solution was adjusted to 6 by the addition of NaOH solution. The solution was underwent purged with a gas mixture of 95:5 Ar: H_2 and sonication was carried out under a slow flow of this gas at room temperature for 1h. Then the mixture solution was subjected to heat at 180 °C for 10 min with vigorous string under a 95:5 Ar: H_2 atmosphere. After quenching the reaction, the suspension was subjected to ice bath, followed by ethylene glycol was removed by dilution the suspension with 0.3 M $NaNO_3$ (Sigma–Aldrich) aqueous solution. Then the solid phase was collected by filtration, washed multiple times with double distilled water and dried at room temperature in vacuum condition. Then the dried samples were reduced in 10 % H_2/Ar at 400 °C for 4 h.

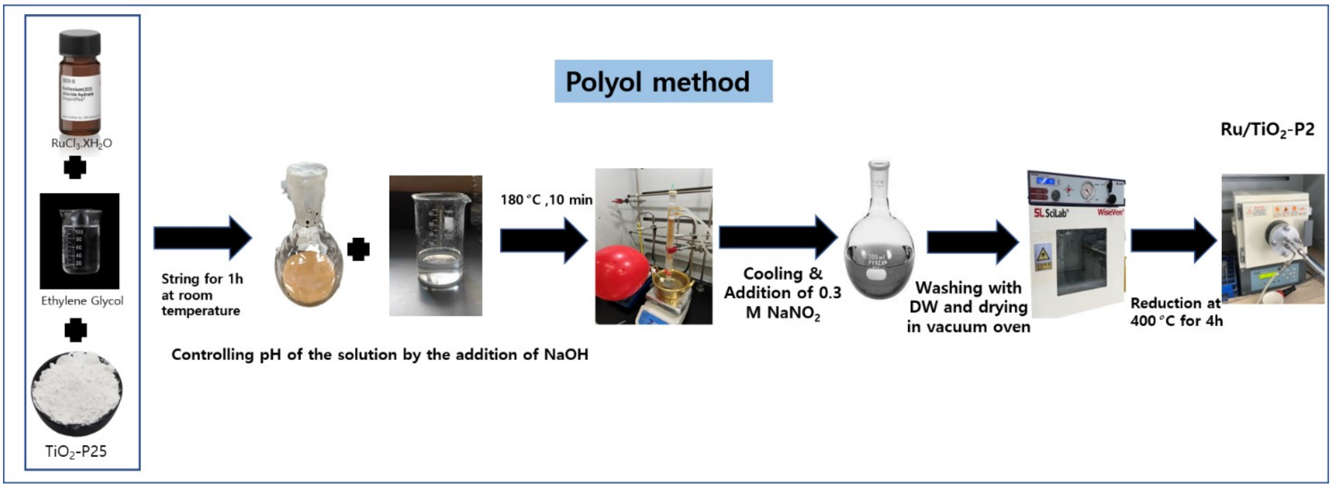


Fig.S1 Catalyst synthesizes using Polyol method

1.1.2 Synthesis of TiO_2-np and TiO_2-meso supports

TiO_2-np: First, 5.0 g of titanium(IV) butoxide (Sigma–Aldrich) was mixed with 50 mL of ethylene glycol (99%, Sigma–Aldrich) and agitated at 25 °C for 24 h. Subsequently, 340 mL of acetone and 2.7 mL of deionized water were added, and the mixture was stirred vigorously for an additional 1.5 h at the same temperature. The resulting suspension was centrifuged to separate the solid material from the solvent. The solid was then rinsed thoroughly with ethanol and deionized water to remove residual impurities and dried in an oven at 105 °C overnight. Subsequently, 1 g of the obtained white powder was dispersed in 200 mL of deionized water and heated to 90°C for 1 h with continuous stirring. The suspension was filtered to isolate the solid, which was washed with ethanol and deionized water to ensure purity. The solid was then dried in an oven at 105°C for 24 h. Finally, the dried solid was calcined at 400°C for 3 h to achieve the desired crystalline structure and composition.

TiO_2-meso: In a typical synthesis of mesoporous TiO_2 (TiO_2-meso), 4 mL of titanium butoxide (Sigma–Aldrich) was mixed with 40 mL of distilled water. The mixture was stirred vigorously for 30 min to ensure complete homogenization of the precursors. The resulting suspension was then sealed in a 60 mL Teflon-lined autoclave and heated at 200°C for 3 h. After the hydrothermal process, the obtained solid was separated by centrifugation, washed with distilled water, and dried overnight at 100 °C in an oven. Finally, the dried solid was calcined at 400°C for 3 h.

The produced supports were then used for the synthesis of Ru/TiO_2 catalysts using the polyol method in section 2.2.1 (2 wt% Ru/TiO_2-np-400 and 2 wt% Ru/TiO_2-meso-400).

1.1.3 Synthesis of Ru/TiO_2 catalysts by impregnation

Ru-based nanocatalysts were also prepared using the wetness impregnation (Wet) and incipient wetness impregnation (IWI) methods with an aqueous solution of $RuCl_3 \cdot xH_2O$ for comparosion with the polyol method. The samples were dried at 100°C for 12 h and then reduced in a 10% H_2/Ar flow at 400 °C for 4 h.

1.1.4 Preparation of Pickering emulsions using Ru/TiO_2 catalysts

Deionized water and *n*-dodecane were used as the aqueous and organic phases, respectively, to prepare emulsions with various nanohybrid catalysts. First, the catalyst (0.05 g) was dispersed in water (for hydrophilic catalysts) by sonication at 25% amplitude for 15 min. Subsequently, 2.5 mL of *n*-dodecane was added to achieve a water ratio of 1:1 (v/v). The resulting mixture was then sonicated at 50% amplitude for an additional 15 min.[1]

2. Calculation methods for the conversion of PET and selectivity of different products in PET HDO reaction.

The PET conversion and selectivity of products were calculated according to the following equations.

$$Conversion\ of\ PET\ waste\ (\%) = \frac{Initial\ weight\ of\ PET\ waste - The\ Weight\ of\ unreacted\ PET}{Initial\ weight\ of\ PET\ waste} * 100 \qquad (1)$$

$$The\ weight\ of\ unreacted\ PET = The\ weight\ of\ residual\ solid\ (g) - Introduced\ catalyst\ amount\ (g) \qquad (2)$$

$$Selectivity\ [\ \%\ C] = \frac{Amount\ of\ each\ products\ [\ mol - C]}{\Sigma\ Amount\ of\ products\ [\ mol - C]} * 100 \qquad (3)$$

$$Yield\ [\%\ C] = \frac{Conersion * Selectivity}{100} \qquad (4)$$

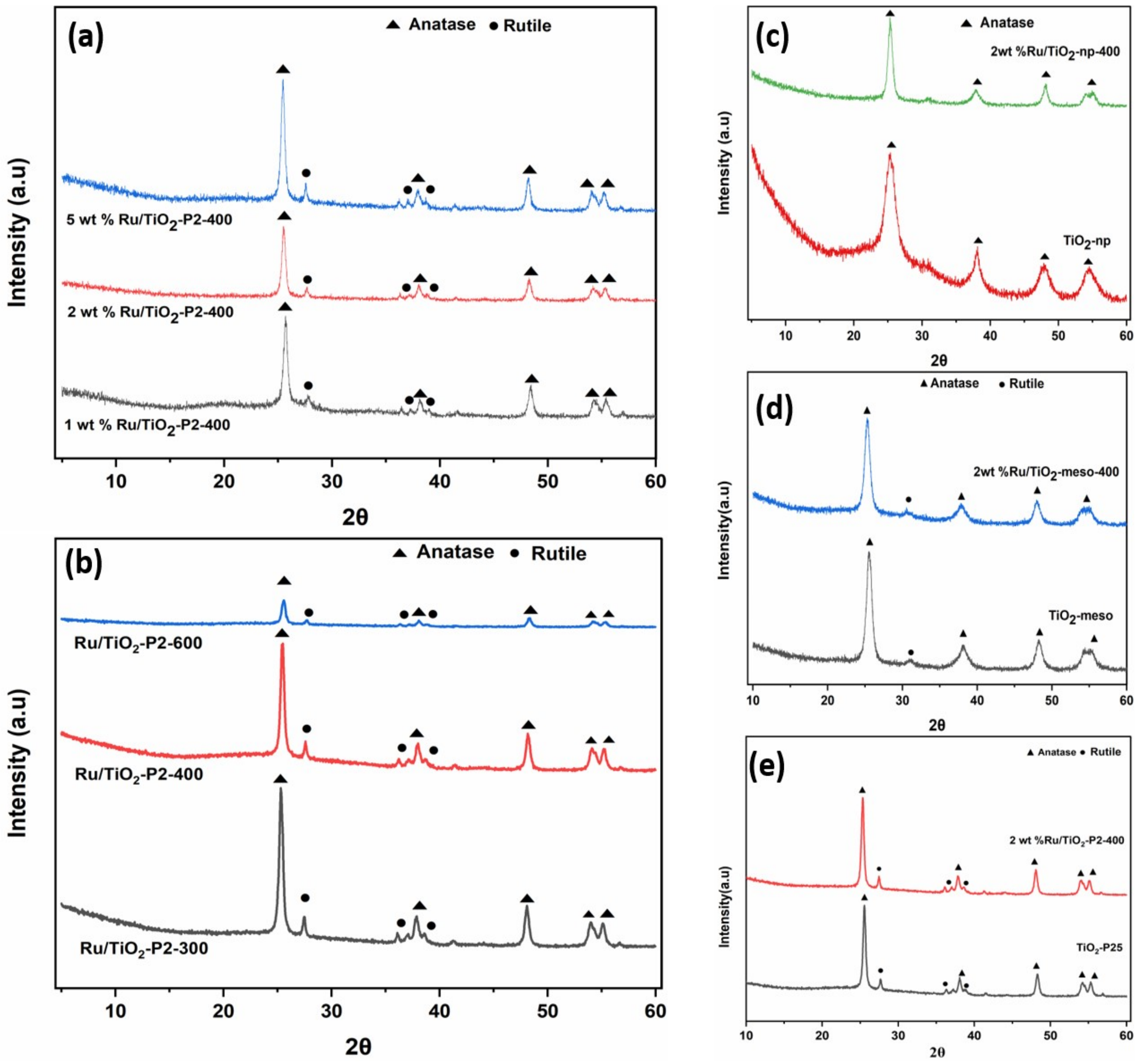


Fig. S2 XRD patterns of: a) 1, 2, and 5 wt% Ru/TiO_2-P2-400, b) 2 wt% Ru/TiO_2-P2-(300,400,600), c) 2 wt% Ru/TiO_2-np-400, d) 2 wt% Ru/TiO_2-meso-400, and e) 2 wt% Ru/TiO_2-P2-400.

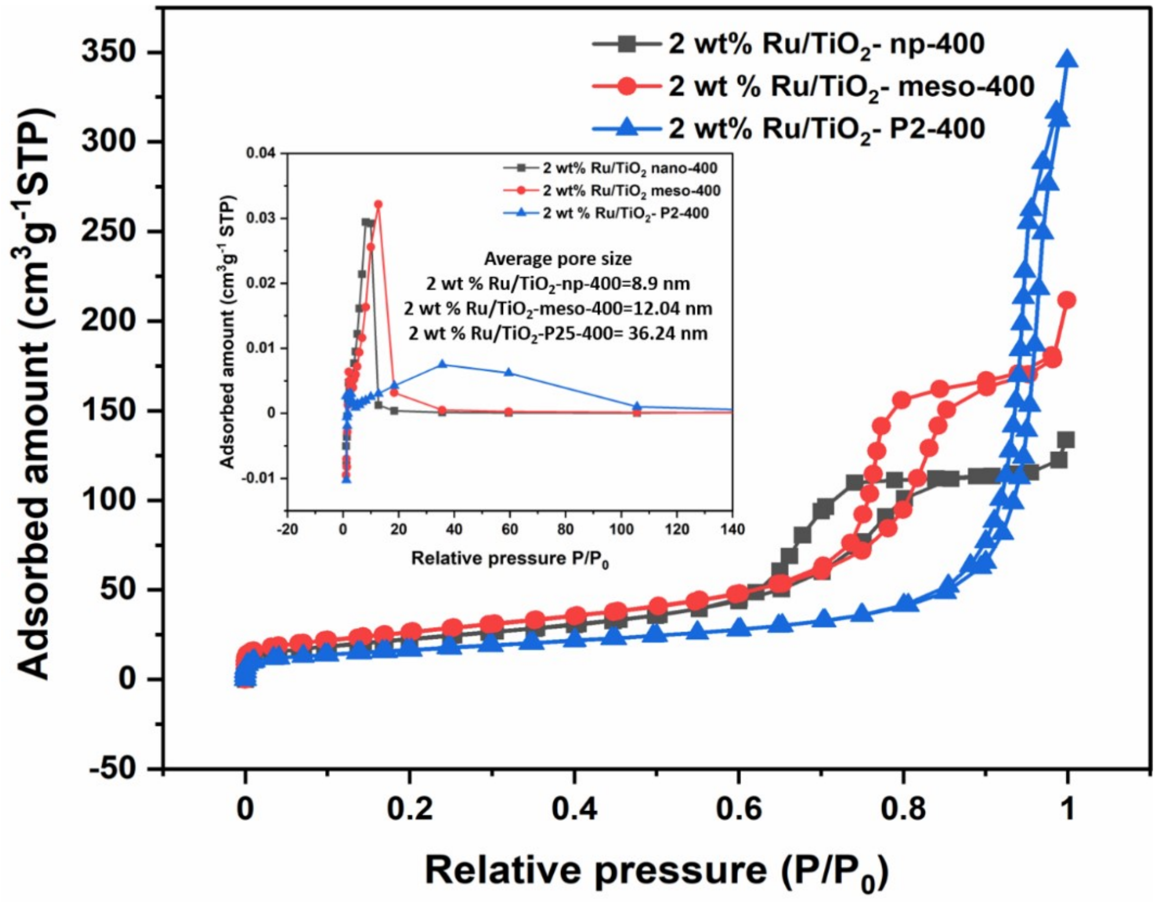


Fig. S3 N_2 adsorption–desorption isotherms and BJH pore size distributions of 2 wt% Ru/TiO_2-(np,meso,P2)-400.

Table S1 Textural properties of Ru/TiO_2 catalysts estimated from N_2 adsorption–desorption isotherms.

Catalyst	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_{meso} (nm)
5 wt % Ru/TiO_2-P2-400	63.95	0.48	-	0.48	30.35
2 wt % Ru/TiO_2-P2-400	58.66	0.48	-	0.48	36.24
1 wt % Ru/TiO_2-P2-400	54.67	0.56	-	0.56	33.38
2 wt % Ru/TiO_2-P2-300	57.18	0.46	-	0.46	33.43
2 wt % Ru/TiO_2-P2-600	36.64	0.44	-	0.44	41.32
2 wt % Ru/TiO_2-np-400	85.18	0.38	0.18	0.2	8.9
2 wt % Ru/TiO_2 – meso-400	79.29	0.3	0.1	0.29	12.04

-S_{BET}: *BET surface area*

-V_{pore}: *Single-point-desorption total pore volume (P/P_0 = 0.99).*

-V_{micro}: *Single-point-desorption micropore volume (P/P_0 = 0.20).*

-V_{meso}: $V_{pore} - V_{micro}$

-D_{meso}: *Mean mesopore diameter obtained via the BJH method.*

Table S2 Properties of emuslion droplets in Ru/TiO_2 supports.

Catalyst	Mean droplet distance (µm)	Mean droplet size(µm)
2wt % Ru/TiO_2-np-400	35.82	4.5
2wt % Ru/TiO_2-meso-400	14.64	9
2wt % Ru/TiO_2-P2-400	8.12	25

The droplet distance and droplet size was measured using the optical spectoscope softwere.

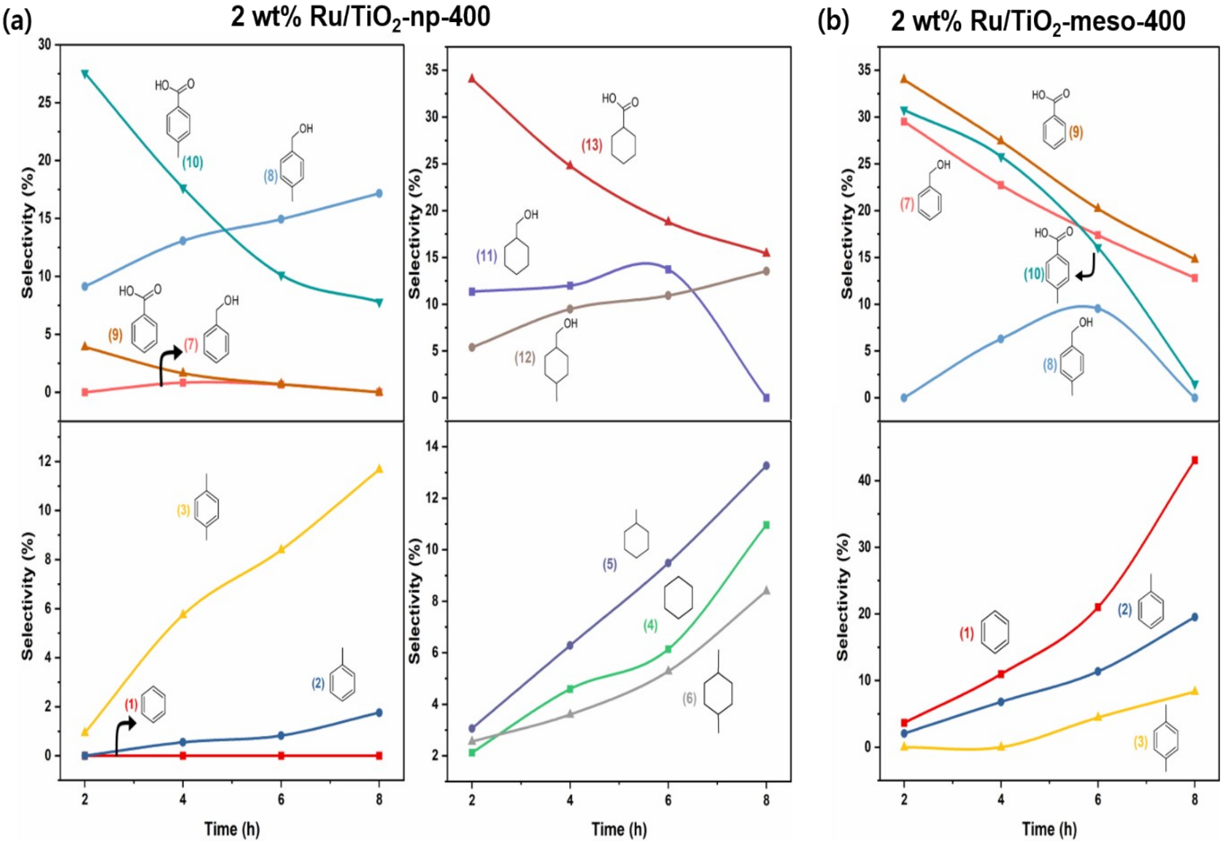
Table S3 Product distribution for PET hydrogenolysis over monophasic and biphasic systems. (Reaction condition: 0.5 g catalyst + 0.5 g PET water (monophasic and biphasic (water: n-dodecane (1:1) system), 220 °C, 10 bar H_2, 12 h. Selectivity of the product (C mol %).

No	Catalyst	Ben	Tol	Xyl	Cyclohexane (Cyc)	Methyl Cyc	Dimethyl Cyc	Cyc Methanol	4-Methyl Cyc Methanol	Cyc Dicarboxylic Acid	Conv. (%)
1	2wt % Ru/TiO_2-np-400	0	1.46	22.81	21.92	41.74	10.46	0	0	0	88.34
2	2wt %Ru/TiO_2-P2-400	13	49.47	29.11	5.2	3.2	0	0	0	0	81.52
3	2wt % Ru/TiO_2-Meso-400	67.07	26.35	6.57	0	0	0	0	0	0	64.34
4	1 wt % Ru/TiO_2-P2-400	37.54	49.47	12.9	0	0	0	0	0	0	71.56
5	5 wt % Ru/TiO_2-P2-400	22.76	52.58	10.81	13.85	0	0	0	0	0	88.52
6	2wt % Ru/TiO_2-imp-400	0	25.42	32.18	17.83	20.41	2.56	0.74	0.84	0	84.62
7	2 wt % Ru/TiO_2-Wet-400	9.2	7.64	2.13	0	0	0	0	0	81.02	90.71
8	2wt % Ru/TiO_2-P2-300	55.83	37.68	6.47	0	0	0	0	0	0	86.6
9	2wt % Ru/TiO_2-P2-600	34.07	44.12	8.11	13.6	0	0	0	0	0	84.2

3. Product distribution for PET HDO over 2 wt% Ru/TiO_2-np-400 and 2 wt% Ru/TiO_2-meso-400

To understand the product distribution for PET HDO over 2 wt% Ru/TiO_2-np-400 and 2 wt% Ru/TiO_2-meso-400, we conducted a time series analysis. (Fig. S4) shows the product distributions for these Ru/TiO_2 catalysts over a period of 2–8 h. The kinetic profile for the 2 wt% Ru/TiO_2-np-400 catalyst (Fig. S4a) indicates that PET conversion reached 64.32% after 8 h. During the initial stage of the reaction (2 h), the primary products were a mixture of oxygenated aromatic and cyclic hydrocarbons, specifically product 13 (cyclohexane carboxylic acid) and product 10 (*p*-toluic acid), with selectivities of 34.0% and 27.6%, respectively. As the reaction progressed to 4 h, the selectivities for products 10 and 13 gradually decreased, whereas those for products 12, 11, and 8 increased, indicating hydrogenolysis of the acid groups to form the corresponding alcohols. At this stage, the total selectivity for oxygenated cyclic hydrocarbons (~46.2%) was higher than that for oxygenated aromatics (~33.2%), suggesting that ring hydrogenation of oxygenated aromatics was favored. At 6 h, ring hydrogenation became more pronounced, and hydrogenolysis resulted in the formation of deoxygenated cyclic hydrocarbons (products 4–6) with a selectivity of 20.9%, which increased to 32.61% at 8 h. The total selectivity for cyclic hydrocarbons (32.61%) was much higher than that for BTX (~13%, mainly xylenes), suggesting that the small size of TiO_2-np enhanced the rate of ring hydrogenation. In addition, the cyclohexane selectivity was quite high (~10.22%), indicating that a high degree of decarboxylation occurred on TiO_2-np. The reaction network for PET HDO is shown in (Fig. S4 c). Based on the time evolution of the intermediates with the TiO_2-np support, PET is initially converted to a decarboxylated product (mainly benzoic acid) and subsequently undergoes ring hydrogenation to form cyclohexane carboxylic acid, which further decarboxylates and undergoes hydrogenolysis to produce cyclohexane and methyl cyclohexane.

In the case of 2 wt% Ru/TiO_2-meso-400 (Fig. S4b), PET conversion reached 42.57% after 8 h. During the initial 2 h period, the major products were products 10 and 9 (benzoic acid) with selectivities of 30.8% and 33.9%, respectively. The high selectivity for product 9 indicates that large number of hydroxyl groups on the TiO_2-meso support enhanced the decarboxylation rate. After 4 h, the selectivity for BTX gradually increased. However, the selectivity for benzene was higher compared to xylene and toluene, suggesting that decarboxylation was greatly enhanced on the TiO_2-meso support. At 8 h, the benzene selectivity was 41.92%, while the selectivities for toluene and xylene were 19.0% and 8.1%, respectively. This demonstrates that TiO_2-meso effectively promoted the formation of decarboxylated products rather than promoting hydrogenolysis.



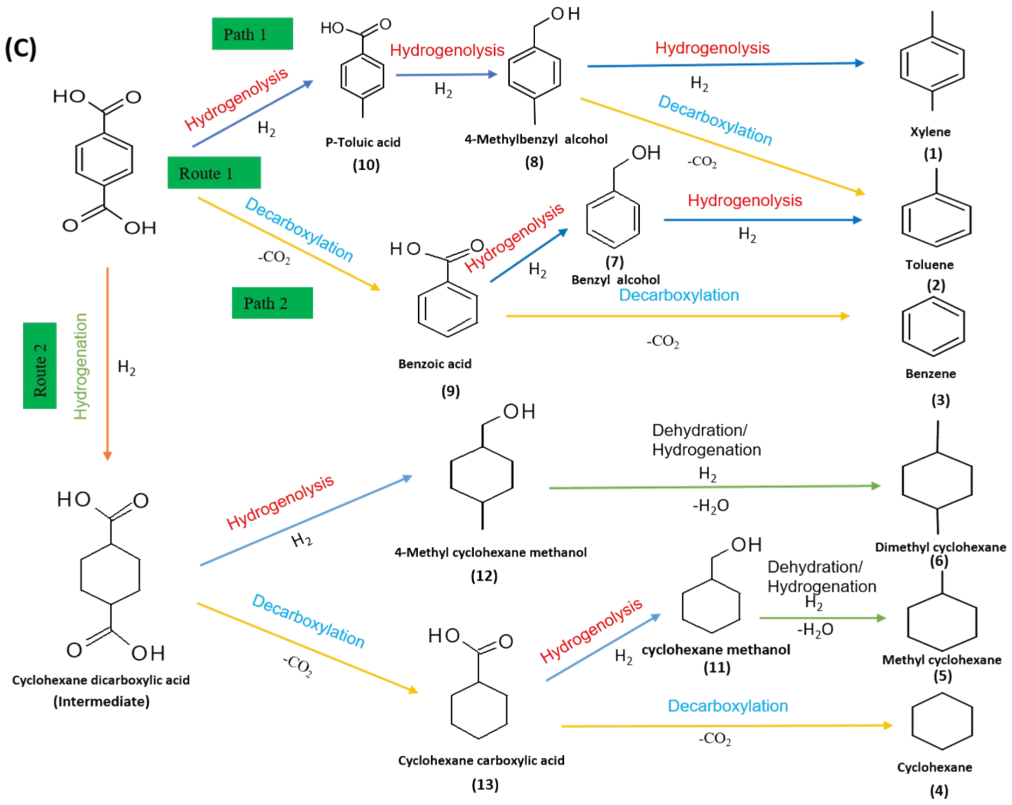


Fig. S4 Time series analysis of the effect of different TiO_2 supports on the PET HDO reaction: (a,b) product distribution for PET hydrogenolysis in a biphasic system (water:*n*-dodecane (1:1, v/v)) over 2 wt% Ru/TiO_2-np-400 and 2 wt% Ru/TiO_2-meso-400 (reaction conditions: 0.5 g of catalyst and 0.5 g of PET in 50 g of water + *n*-dodecane, 220 °C, 10 bar H_2, 8 h). (c) Reaction pathway of PET HDO over Ru/TiO_2-(np,meso).

4. PET HDO reaction

We conducted to understand the catalytic activity of Ru/TiO2 catalyst in a biphasic system.for understanding more detail, the obtained product were classified as 0-Os hydrocarbons.aromatics, 1-Os hydrocarbons, or 2–4-Os hydrocarbons, as shown in Fig. S3.

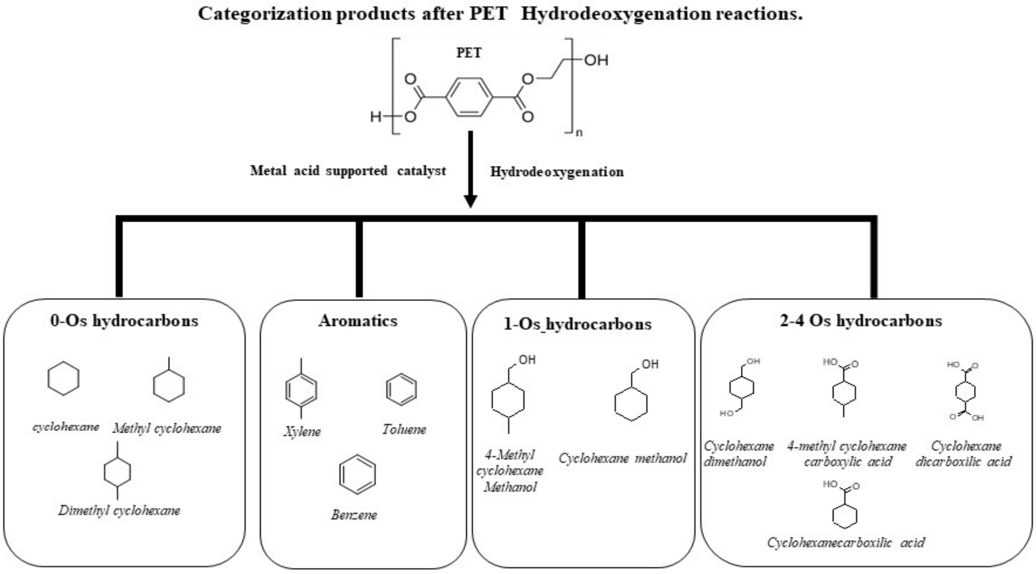


Fig.S5 Categorization of product after PET HDO reaction

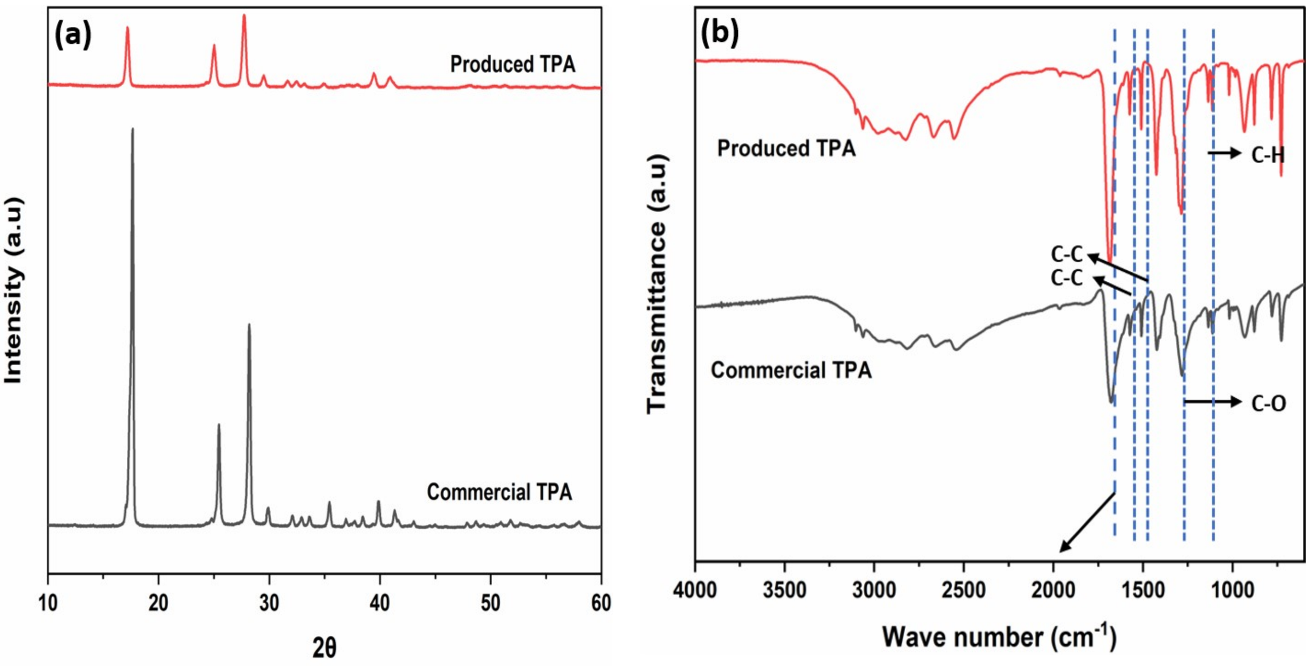


Fig. S6 a) XRD data of TPA produced by Ru/TiO_2 catalyst in water phase, b) FTIR data of produced TPA by Ru/TiO_2 catalyst in water phase.(*Reaction condition: 0.5 g PET + 0.5 g catalyst ,220 ° C, 2 h, 10 bar* $H_{2,}$ *50 g water)*

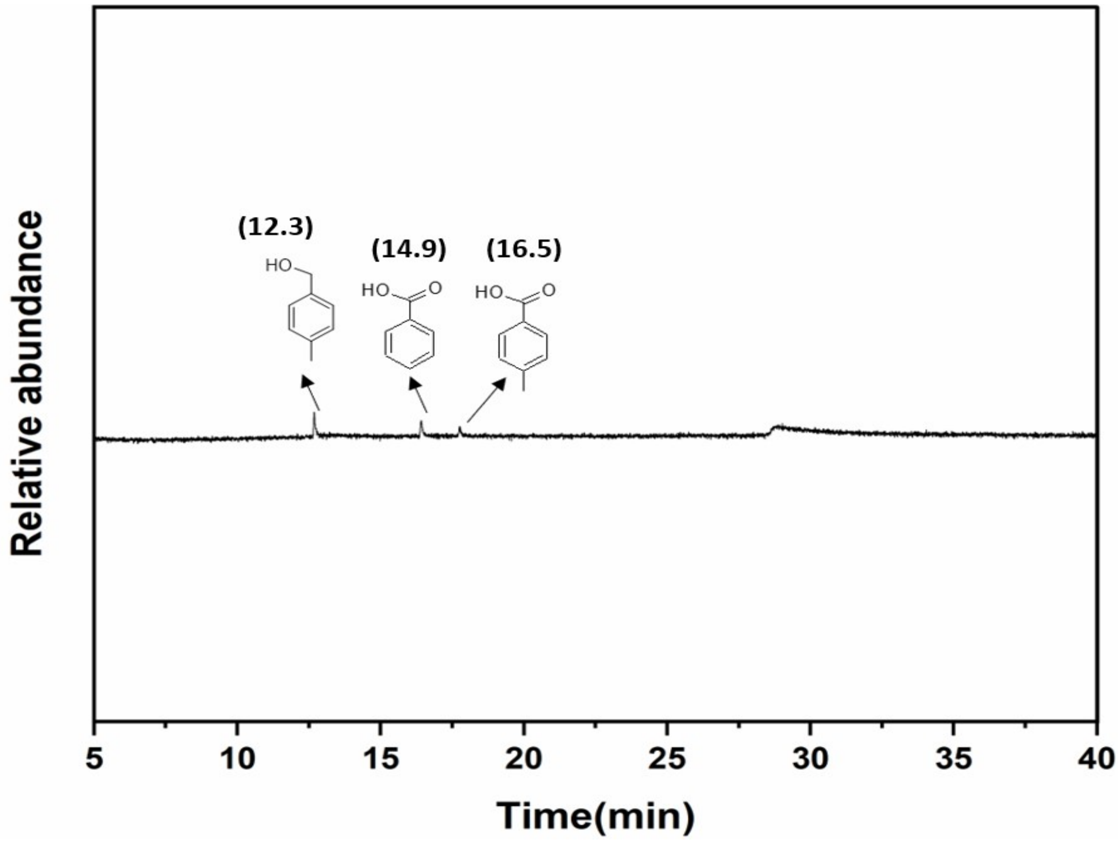


Fig. S7 GC-MS analysis of the PET HDO over Ru/TiO_2 catalyst in water phase system. .(*Reaction condition: 0.5 g PET + 0.5 g catalyst ,220 ° C, 4 h, 10 bar* $H_{2,}$ *water : n-dodecane (1:1)*

5. Hydrogen solubility in water and dodecane.

The solubility of hydrogen in water phase at room temperature is relatively high.At standared condition (25 and 1 atm pressure) The solubility of hydrogen in dodecane is relatively low. According to the previous studes. We formaulate the table of solubilites of hydrogen in water and dodecane phase.(Table. S2)

Table S4 Solvent polarity index and H2 solubility in different solvent (25 C and 1 atm pressure)[2, 3]

Solvent	Polarity	H_2 solubility (mol cm^{-3})	ref
Water	9.0	$7.8*10^{-7}$	2, 3
n-Dodecane	0.3	$4.7*10^{-6}$	4

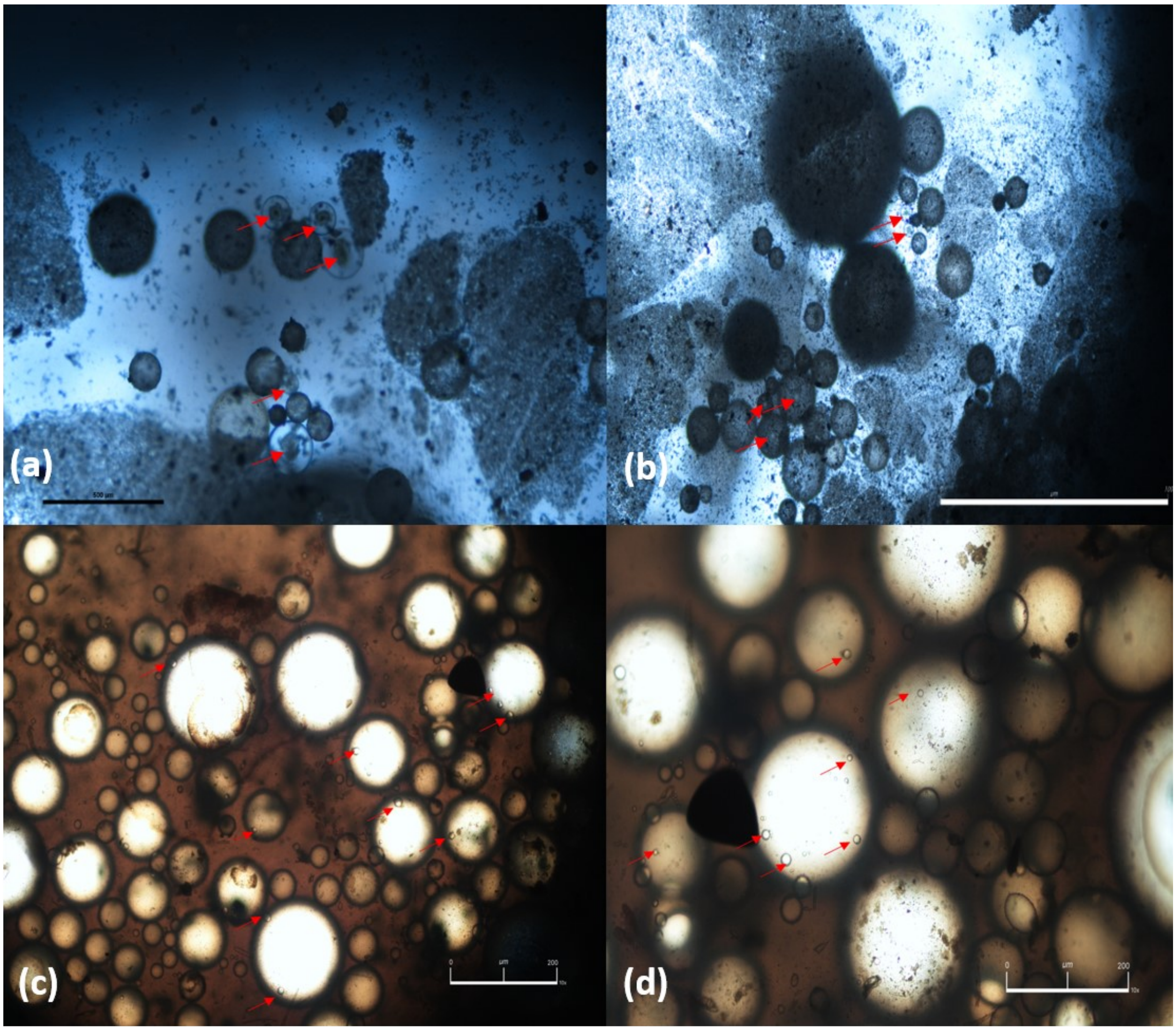


Fig. S8 Microscopic observation of o/w Pickering emulsion in Ru/TiO_2. (a-b) 2wt % Ru/TiO_2-np-400 (c-d) 2wt % Ru/TiO_2-P2-400 The red arrow indicating the location of H_2 bubbles

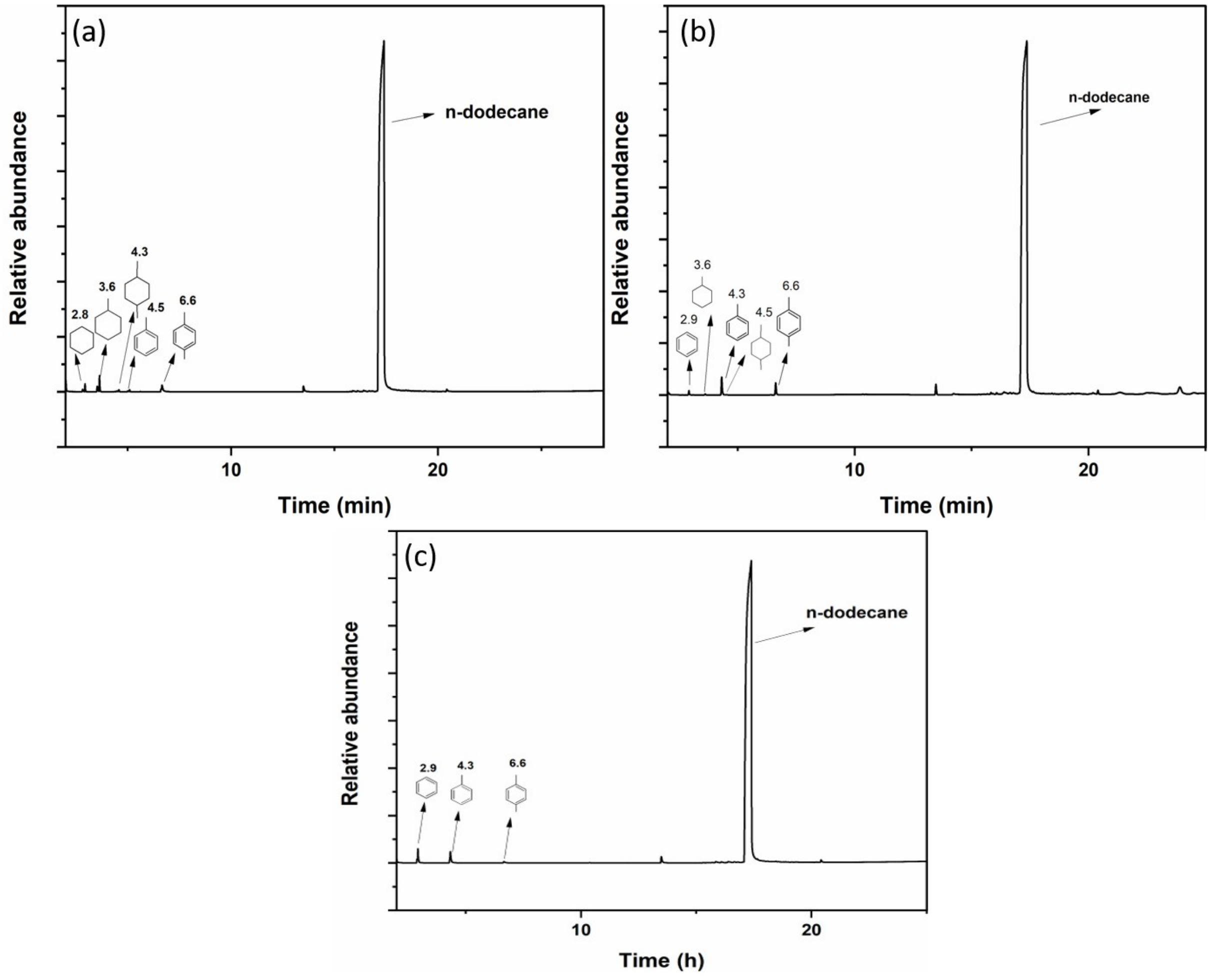


Fig. S9 GC-MS chromatogram of the PET HDO catalyst in biphasic system, a) 2 wt% Ru/TiO_2-np-400, b) 2 wt% Ru/TiO_2-P2-400, c) 2 wt% Ru/TiO_2-meso-400.

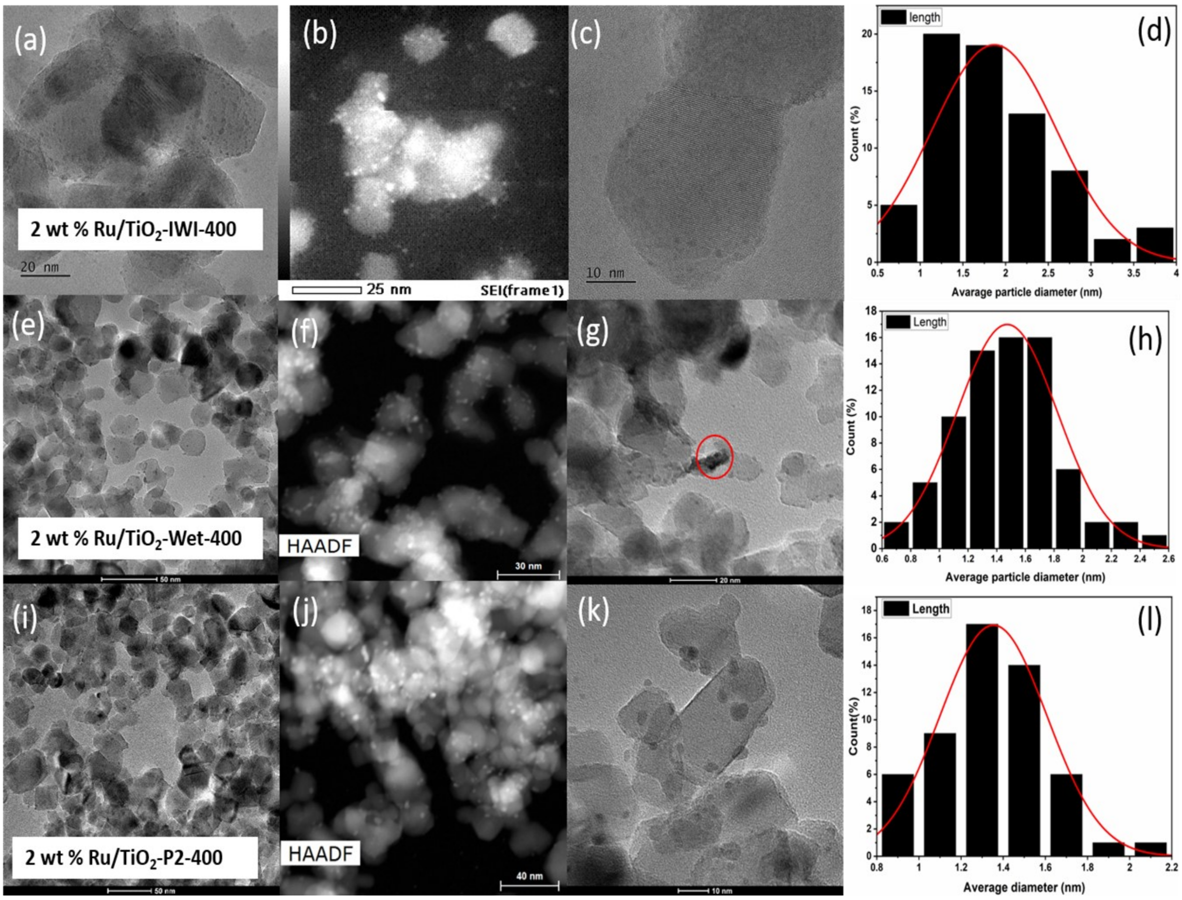


Fig. S10 TEM and STEM images of Ru/TiO_2 catalysts fabricated using different methods: (a–c) 2 wt% Ru/TiO_2-IWI-400, (e–g) 2 wt% Ru/TiO_2-Wet-400, (i–k) 2 wt% Ru/TiO_2-P2-400, and (d,h,i) corresponding particle size histograms.

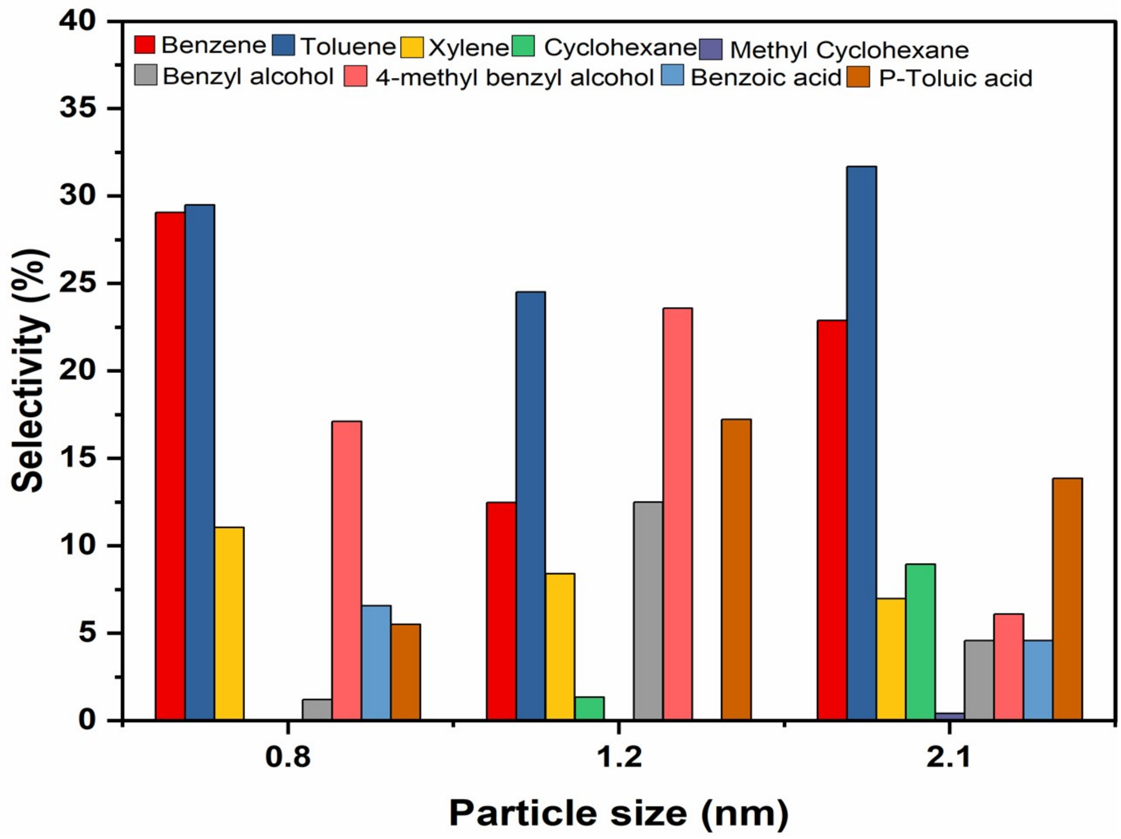


Fig. S11 Selectivities for major products as a function of Ru particle size at ~50 % PET conversion. Reaction conditions: 0.5 of g catalyst, 0.5 g of PET, 50 g of water + *n*-dodecane, 220 °C, 10 bar H_2, 8 h

Table S5 Solublity of different intermediate products in water and dodecane medium.

No.	Products	Solubility in water medium	Solubility in dodecane medium
1	Terepathallic acid	Insoluble	Insoluble
2	Benzoic acid	Slighlty soluble	Soluble
3	4-Methylbenzyl alcohol	Slighlty soluble	Soluble
4	Benzyl alcohol	Slighlty soluble	Soluble
5	Dimethyl cyclohexane	Insoluble	Soluble
6	Methyl cyclohexane	Insoluble	Soluble
7	Cyclohexane	Insoluble	Soluble
8	Toluene	Insoluble	Soluble
9	Xylene	Insoluble	Soluble
10	p-Toluic acid	Insoluble	Soluble

Table S6 Surface area of different TiO_2 supports

Catalyst	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_{meso} (nm)
TiO_2-np	84.12	0.33	0.13	0.2	9.42
TiO_2-meso	78.74	0.44	0.16	0.28	12.93.
TiO_2-P25	41.48	0.35	0.1	0.34	25.29

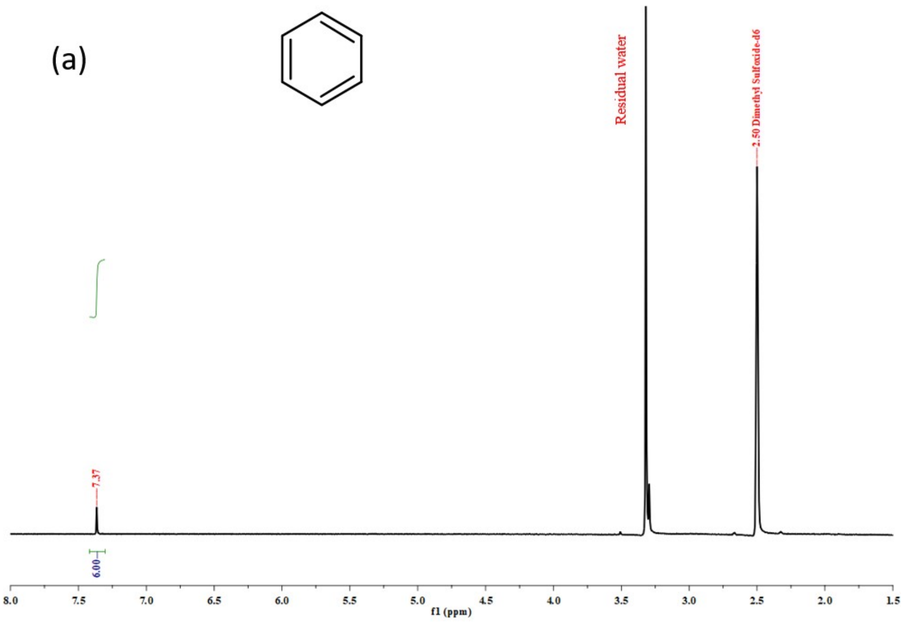
-S_{BET}: *BET surface area*

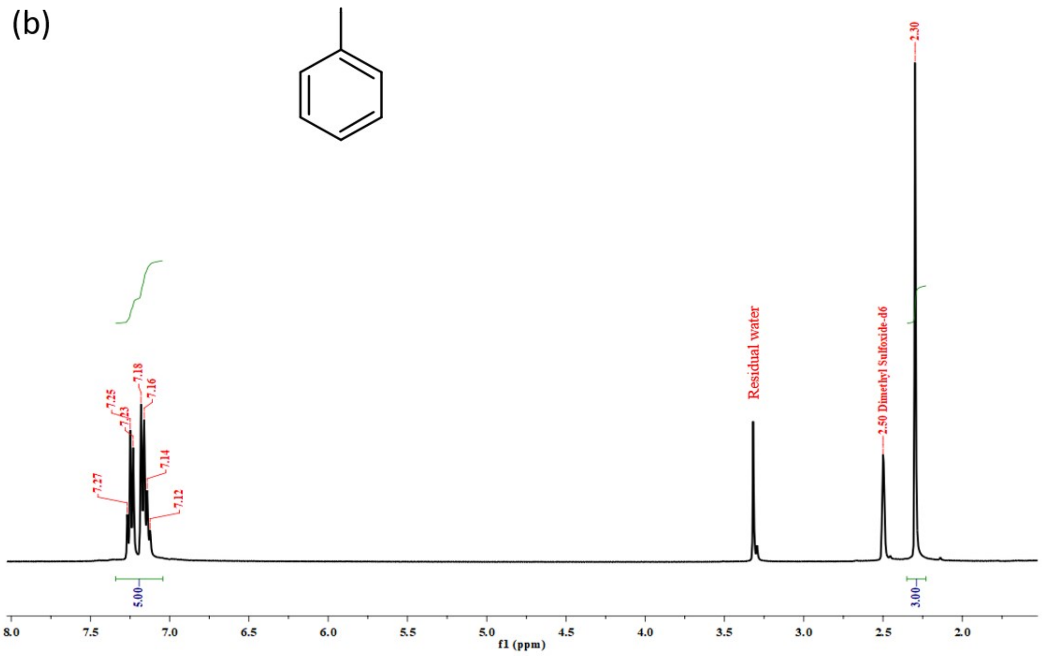
-V_{pore}: *Single-point-desorption total pore volume ($P/P_0 = 0.99$).*

-V_{micro}: *Single-point-desorption micropore volume ($P/P_0 = 0.20$).*

-V_{meso}: $V_{pore} - V_{micro}$

-D_{meso}: *Mean mesopore diameter obtained via the BJH method.*


(a)
Residual water
2.50 Dimethyl Sulfoxide-d6
7.37
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


(b)
2.30
Residual water
2.50 Dimethyl Sulfoxide-d6
7.27
7.25
7.23
7.18
7.16
7.14
7.12
5.00
3.00
8.0
7.5
7.0
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4.5
4.0
3.5
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2.5
2.0
f1 (ppm)

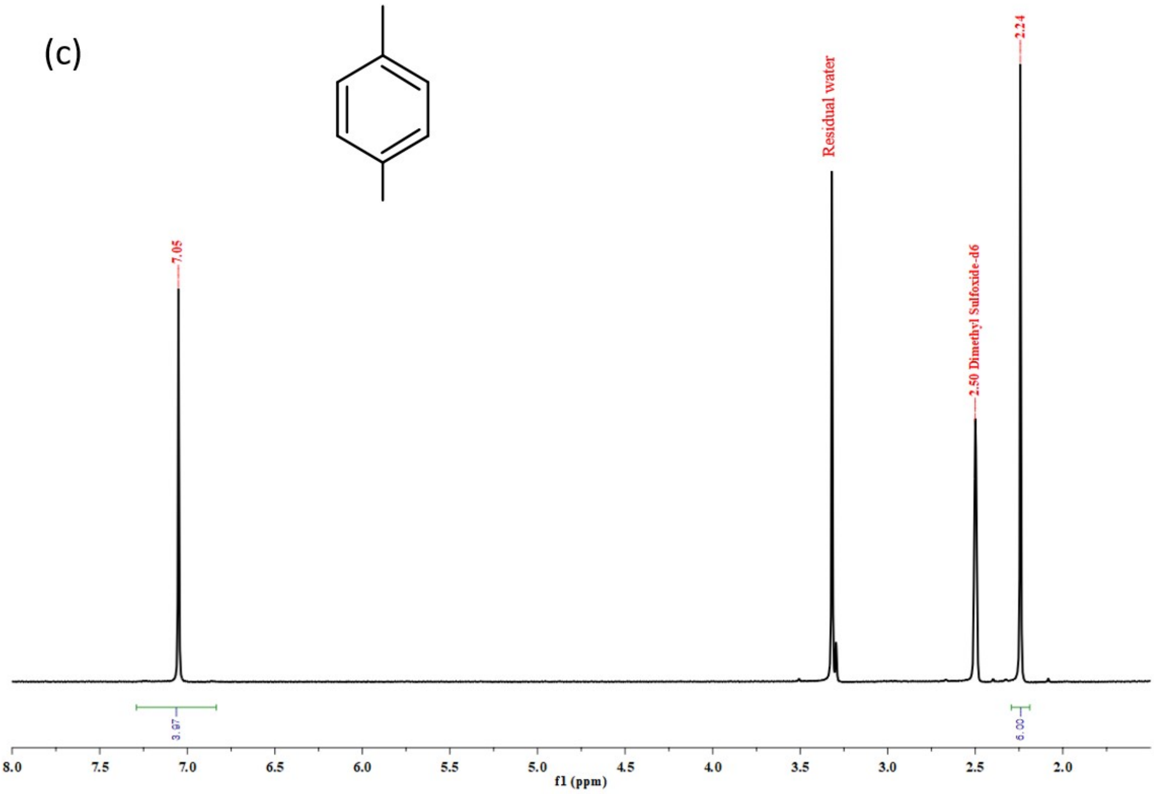

Fig. S12 ^{1}H NMR spectrum of BTX after product separation, a) Benzene, b) Toluene, c) Xylene dissolved in Dimethyl sulfoxide-d6.

Table S7 Summary of main results in literature and parallel work for PET conversion.

Catalyst	Temp (°C)	Reaction time (min)	Solvent /PET mass ratio	Catalyst /PET mass ratio	Products	Yield of arenes/C6-C8 cyclic hydrocarbons (%)	Energy economy (ε) (°C^{-1}*min^{-1})	Environmental factor (E) (a.u)	Carbon Footprint analysis (Kg of tCO$_2$/ton waste)	Environmental Energy Impact (ξ)(°C*min)	Ref.
Ru/TiO$_2$	220	720	50	1	Arenes	89.34	5.55E-04	13.21	3.38	23801.80	This work
Ru/TiO$_2$	220	720	50	1	Naphthenes	87.92	5.55E-04	15.04	3.22	27099.10	Previous work
Ru/Nb$_2$O$_5$	200	720	100	1	Arenes	87.01	5.68E-04	22.36	3.19	39353.6	5
Ru/ZrO$_2$	200	720	100	1	Arenes	40	2.52E-04	48.64	1.46	193016.0	5
Ru/Nb$_2$O$_5$	320	960	66.6	1	Arenes	78.9	2.57E-04	22.40	2.89	87238.57	5
Ru/Cu/SiO$_2$	400	1320	40	0.25	Naphthenes	94	1.78E-04	17.29	3.44	97134.83	6
Ru/NiAl$_2$/O$_3$	220	720	75	1	Arenes	65	4.10E-04	30.30	2.38	109393.14	7
Ru/Nb$_2$O$_5$	220	720	75	1	Arenes	85	5.37E-04	22.63	3.11	42189.19	7
Nickel phosphate	400	360	10	0.6	Arenes	84	5.34E-04	33.68	3.08	63071.2	8

<Calculation method>

T is the reaction temperature in degrees Celsius, Y is the yield of the main monomer in mass fraction, t is the reaction time (in minutes). MM and m represent the molar mass (g mol^{-1}) and mass (g) of the polymers respectively.

$$\varepsilon = \frac{y}{T * t} \qquad (5)$$

$$Efactor = \frac{\left[0.1 \times \left(\frac{solvent}{PET} ratio\right) + \left(\frac{catalyst}{PET} ratio\right) + \left(\frac{other\ subst}{PET} ratio\right)\right] \times mPET}{mProduct} \qquad (6)$$

$$mProduct = yieldProduct \times \frac{MMProduct\ E}{MMPET} \times mPET \qquad (7)$$

Combine equation (2) and (3)

$$Efactor = \frac{\left[0.1 \times \left(\frac{solvent}{PET} ratio\right) + \left(\frac{catalyst}{PET} ratio\right) + \left(\frac{other\ subst}{PET} ratio\right)\right] \times mPET}{yieldProduct \times \frac{MMProduct\ E}{MMPET} \times mPET} \qquad (8)$$

$$\xi = \frac{Efactor}{\varepsilon} \qquad (9)$$

$$Carbon\ foot\,print\ anaylysis = \frac{(Yield\ of\ product\ in\ wt\ \% \ * \ molar\ mass\ of\ CO_2)}{molar\ mass\ of\ C} \qquad (10)$$

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