Supporting information for

Water-assisted single-step catalytic hydrodeoxygenation of polyethylene terephthalate into gasoline- and jet fuel-range cycloalkanes over supported Ru catalysts in a biphasic system

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1. Catalyst synthesis

All the Ru-based nano catalysts were prepared by IWI method with an appropriate amount of aqueous solution of $RuCl_3.xH_2O$. The obtained samples were dried at 100 °C for 12 h.

Table S1 Conditions used for the synthesis of Ru/S, (S=Support) catalyst

No	Catalyst Type	Drying condition	Calcination condition	Reduction condition
1	Ru/TiO_2	100 °C, 12 h	-	400 °C, 4 h
2	Ru/HZSM-5	100 °C, 12 h	500 °C, 5 h	250 °C, 2 h
3	Ru/C	80 °C, 12 h	-	400 °C, 4 h
4	Ru/HY(30)	100 °C, 12 h	500 °C, 4 h	400 °C, 4 h
5	Ru/ZrO_2	100 °C, 12 h	500 °C, 5 h	450 °C, 4 h

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

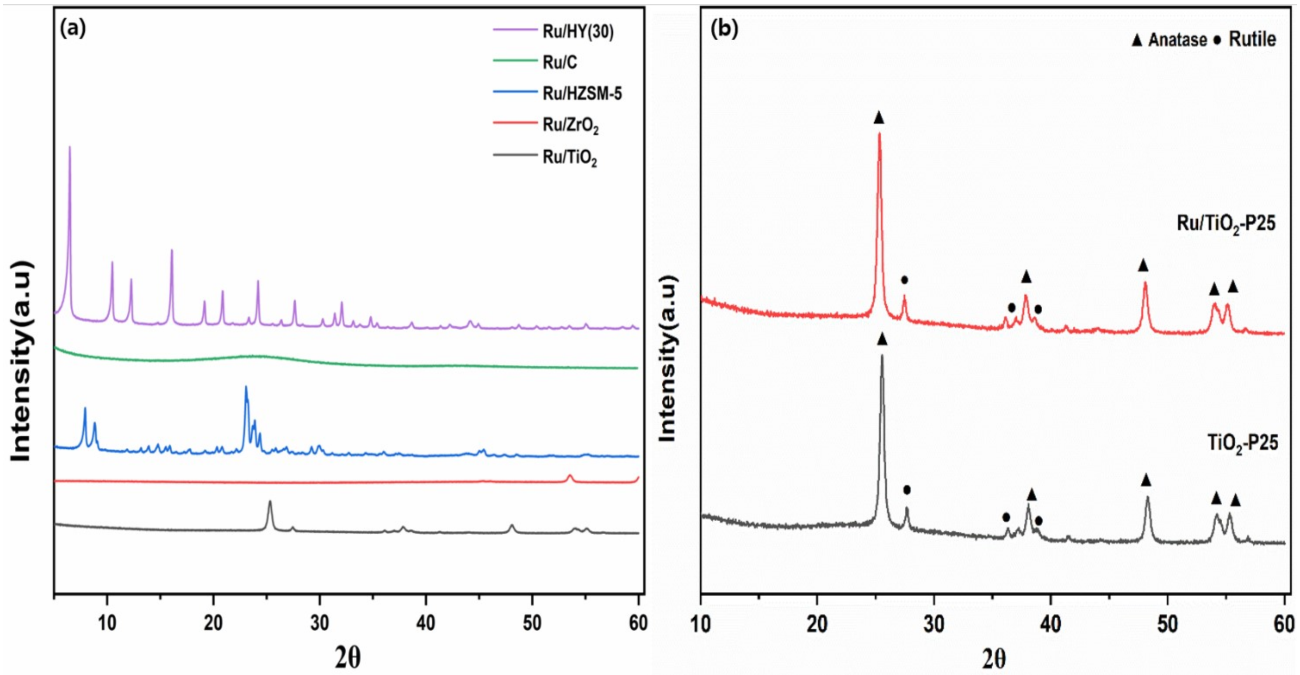
The PET conversion and selectivity of products were calculated according to the following equations.

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

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

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

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



3. Catalyst characterization

Fig. S1 The XRD pattern a) Ru/S (support) b) Ru/TiO_2 and TiO_2-P25.

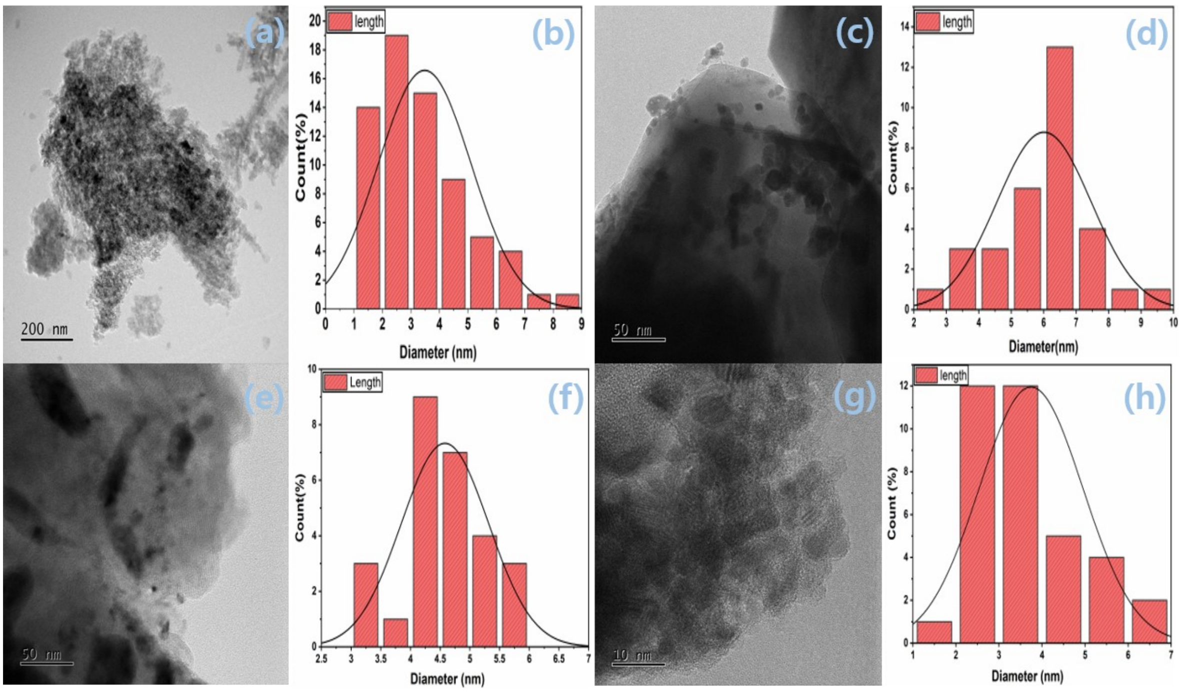


Fig. S2 TEM micrograph image and histogram of different catalysts: (a,b) Ru/C , (c,d) Ru/ZrO_2, (e,f) Ru/HY(30), (g,h) Ru/HZSM-5

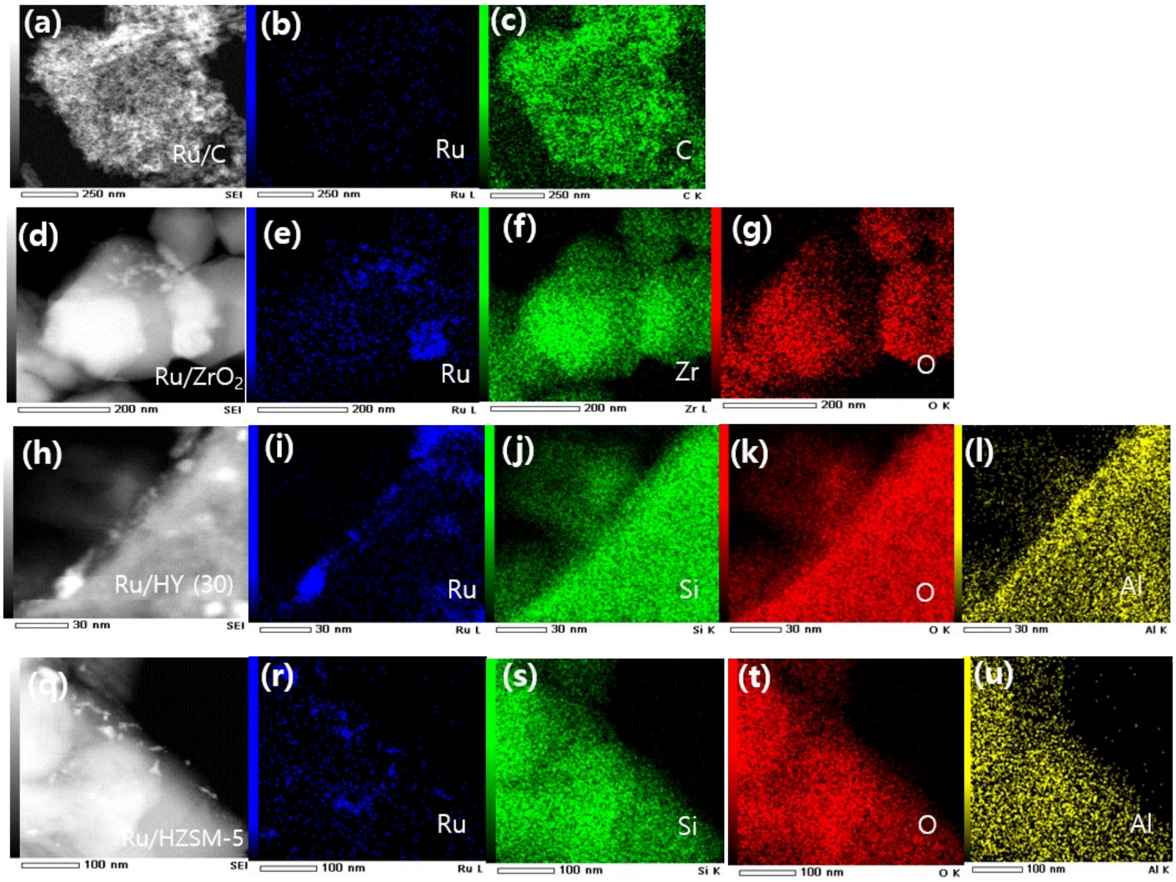


Fig. S3 TEM-EDS mapping of prepared catalysts: (a-c) Ru/C, (d-g) Ru/ZrO_2, (h-l) Ru/HY (30), (q-u) Ru/HZSM-5.

Table S2 Ru (wt%) content in metal supported catalysts based on the EDS mapping data.

Catalyst	Ru wt(%)
Ru-TiO_2	1.89
Ru-C	1.58
Ru-ZrO_2	1.88

Ru-HZSM-5	1.8
Ru-HY(30)	1.66

4. Contact angle measurements

To investigate the wettability of Ru-supported catalysts, here we chose Ru/C, Ru/TiO_2 and Ru/HZSM-5 (neutral, medium and strong acidic supports) as the reference samples. The contact angle of water on the surface of the catalyst was measured and the results were shown in (Fig. S3). From the study the Ru/TiO_2 catalyst has a contact angle of 45.4 °, indicating a very hydrophilic character. Whereas the catalyst Ru/HZSM-5 assigned the contact angle of 89.9 ° indicating an amphiphilic behavior and the Ru/C showed a contact angle > 90 ° signifying high hydrophobic behavior.

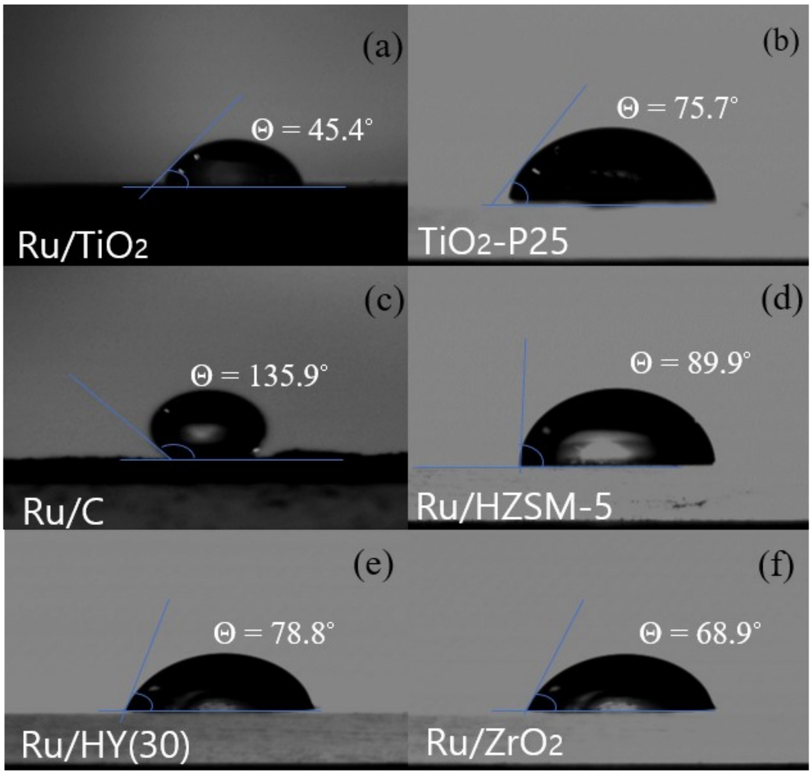


Fig. S4 Contact angle of different catalyst support a) Ru/TiO_2, b) TiO_2-P25, c) Ru/C, d) Ru/HZSM-5, e) Ru/HY(30) , f) Ru/ZrO_2

Table S3 The contact angle of different catalyst supports

Catalyst	**Contact angle (θ)**
Ru/TiO_2	45.4 °
TiO2-P25	75.7 °
Ru/HZSM-5	89.9 °
Ru/C	135.9 °
Ru/ZrO_2	68.9 °
Ru/HY(30)	78.8°

5. PET hydrogenolysis results

Table S4 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, 50 bar H_2, 12 h)

Entry	Catalyst	0-Os HCs C mol (%)	Aromatics C mol (%)	1-Os HCs C mol (%)	2-4-Os HCs C mol (%)	Conversion (%)
1	Ru/TiO_2 - monophasic	2.11	0.8	97.1	0	85.3
2	Ru/TiO_2 - biphasic	96.8	0	3.2	0	86.16
3	Ru/C -monophasic	13.1	0	86.87	0	82.11
4	Ru/C - biphasic	43.54	0	20.59	35.58	46.06
5	Ru/ZrO_2 - monophasic	16.64	11.58	14.43	57.32	35.22
6	Ru/ZrO_2 -biphasic	73.76	0	26.24	0	14.06
7	Ru/HZSM-5 - monophasic	2.03	0.58	74.58	22.12	89.26
8	Ru/HZSM-5 - biphasic	41.87	0	1.38	53.9	95.08
9	Ru/HY(30) - monophasic	1.91	0.29	4.88	92.87	92.89
10	Ru/HY(30) - biphasic	13.58	12.01	0	74.39	94.18
11	Ru/TiO_2+HZSM-5 - monophasic	3.96	0	56.42	38.7	84.3
12	Ru/TiO_2+HZSM-5 - biphasic	74.39	0.44	8.69	16.48	77.96

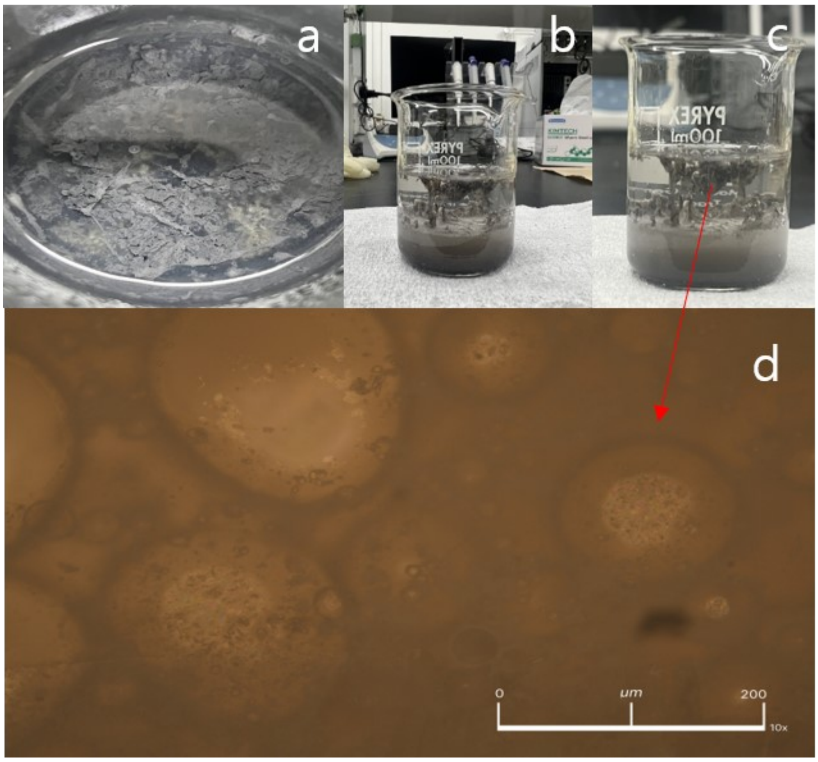


Fig. S5 Photograph a-c) Photo of Pickering emulsion (O/W) system of Ru-TiO_2 Catalyst, d) optical microscope image of O/W emulsion of Ru/TiO_2 catalyst.

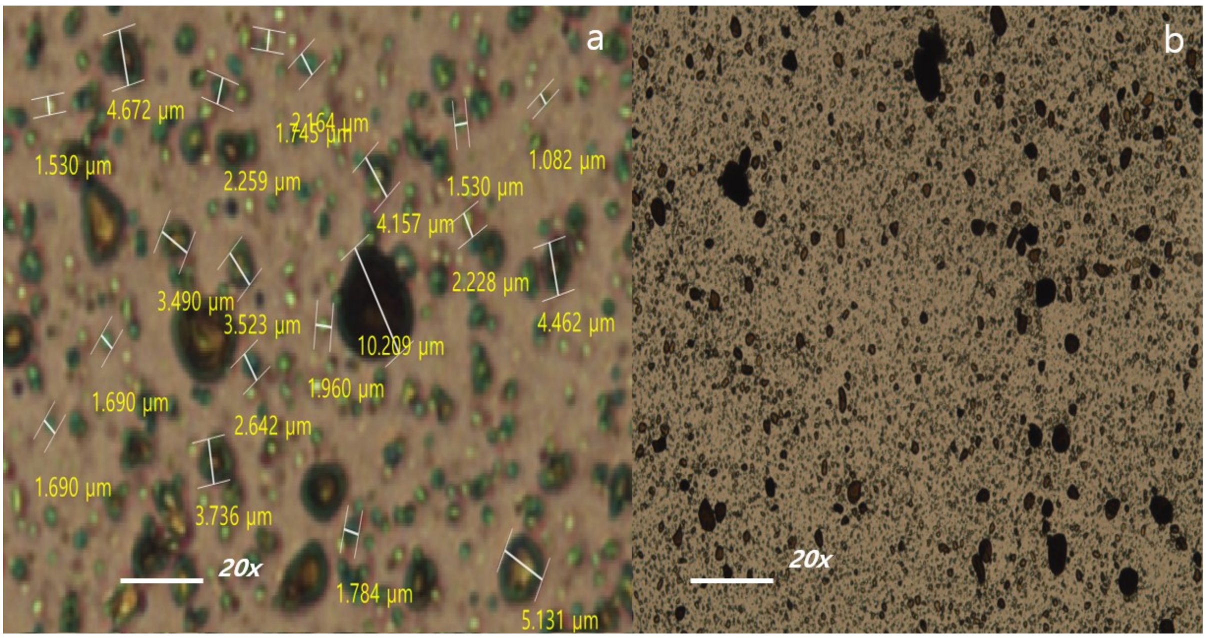


Fig. S6 (a-b) Optical microscopy images of W/O emulsion droplets stabilized over Ru/TiO_2 Catalyst in 4:1 (water: n-dodecane) biphasic system.

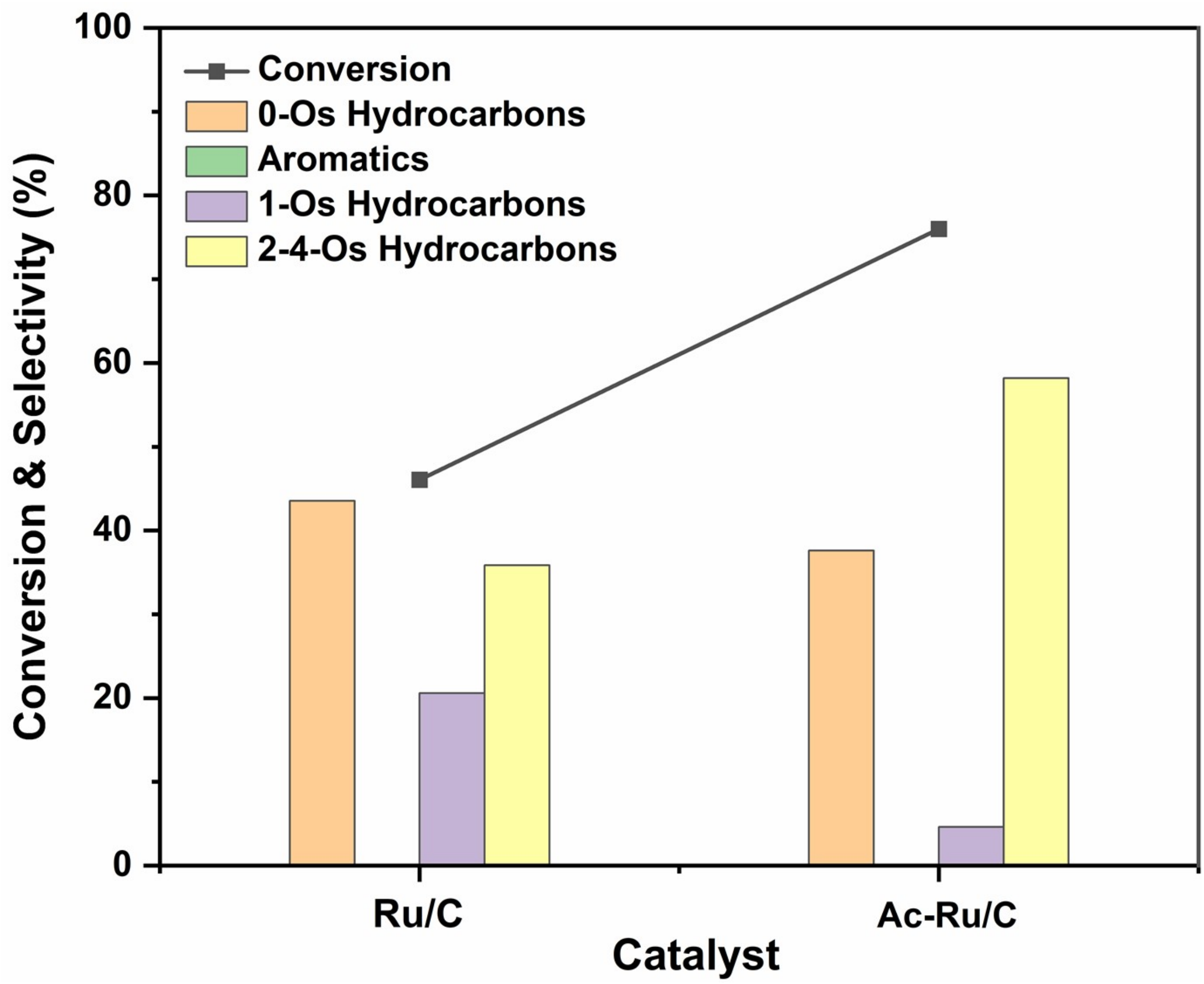


Fig. S7 Effect of hydrophilic catalyst in PET hydrogenolysis reaction. Reaction condition: 0.5 g catalyst + 0.5 g PET in (biphasic system),220 °C, 50 bar H_2, 12 h.

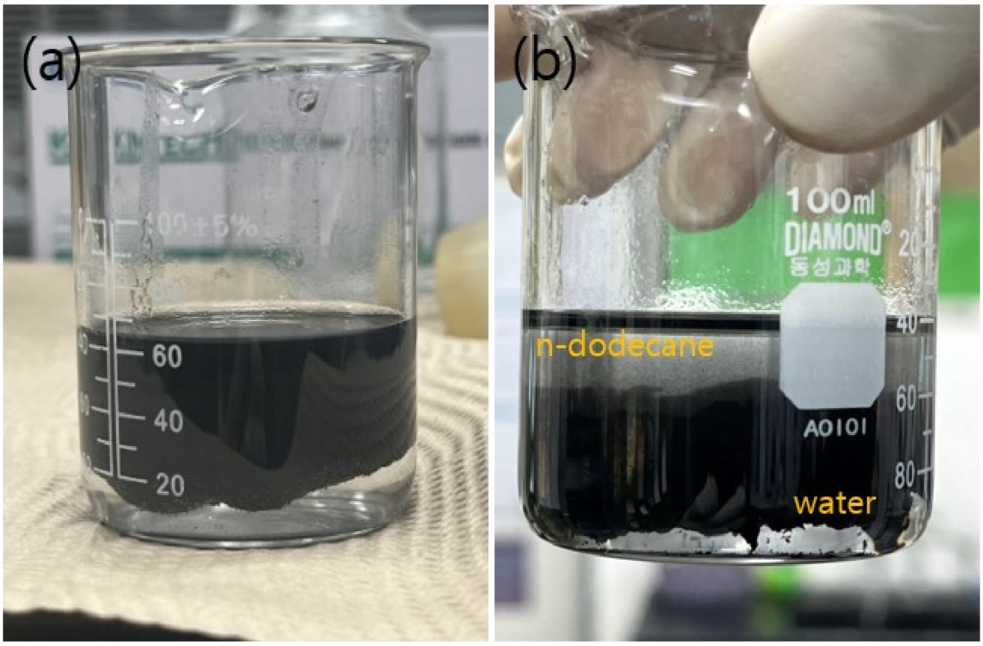


Fig. S8 Photograph of a) (W/O) system of Ru/C, b) (O/W) emulsion system of Ac-Ru/C

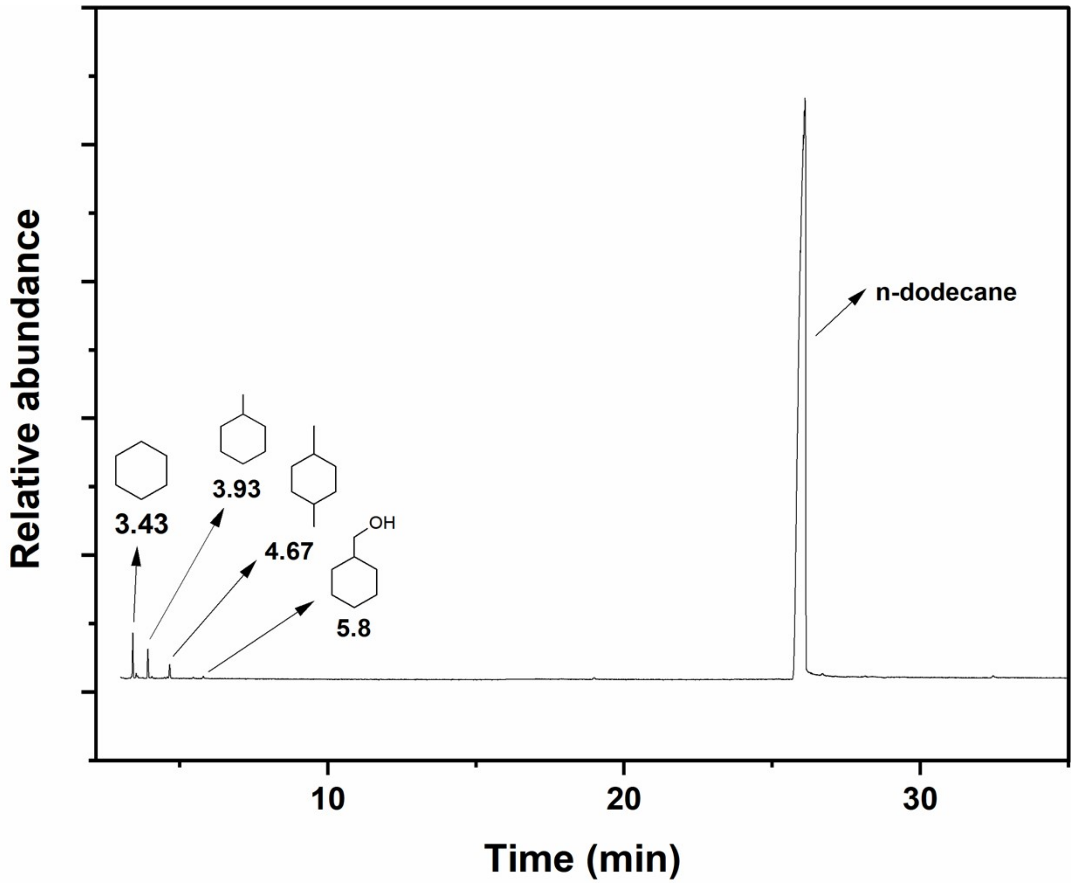


Fig. S9 GC-MS analysis of the PET HDO over Ru/TiO_2 catalyst in biphasic system.

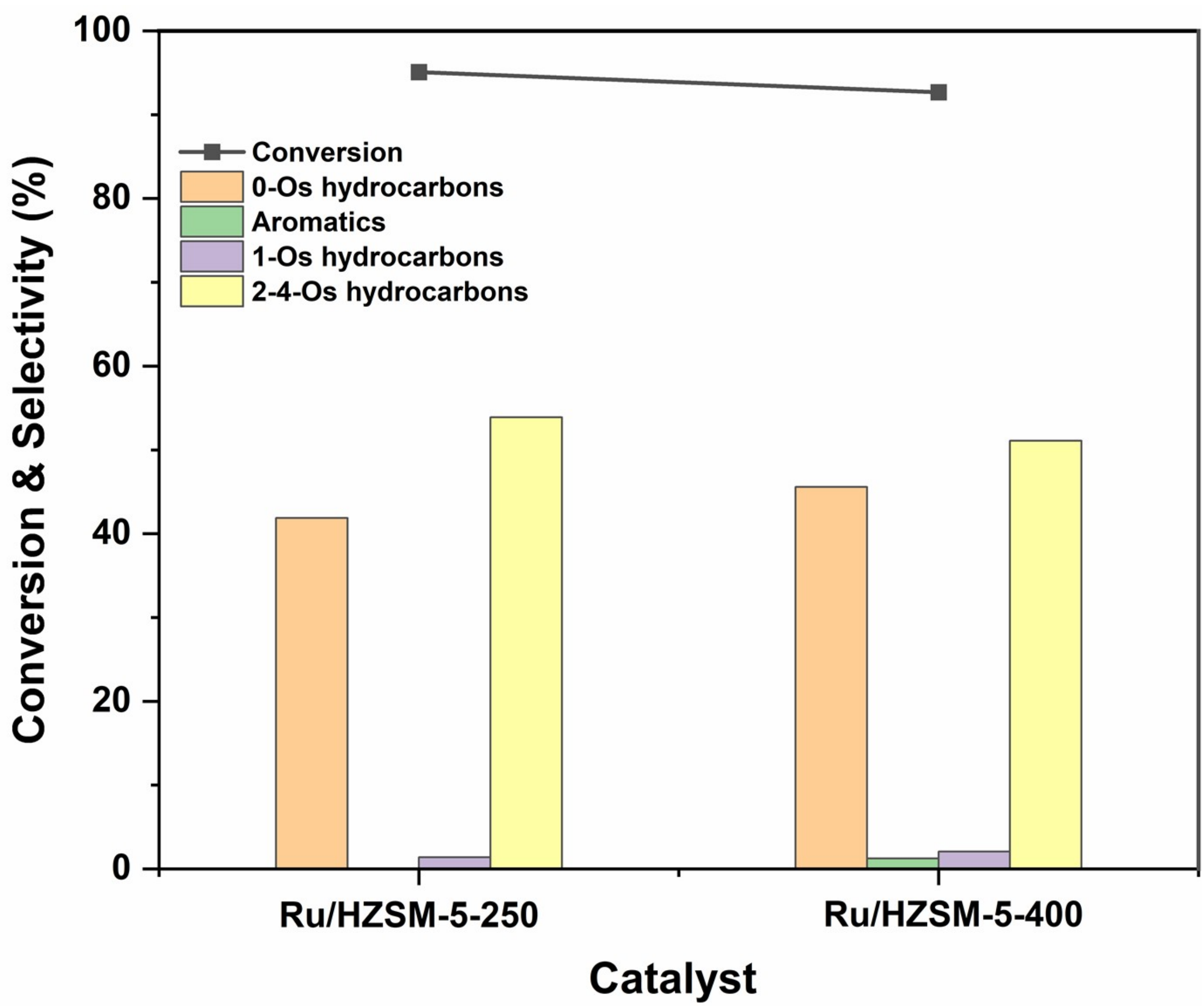


Fig. S10 Effect of reduction temperature in PET hydrogenolysis reaction over Ru/HZSM-5. Reaction condition: 0.5 g catalyst + 0.5 g PET in (biphasic system),220 °C, 50 bar H_2, 12 h.

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	Cyclohexane dicarboxylic acid	Slighlty soluble	Soluble
3	4-Methylcyclohexane carboxylic acid	Slighlty soluble	Soluble
4	Cycliohexane carboxylic acid	Slighlty soluble	Soluble
5	4-Methyl cyclohexane methanol	Insoluble	Soluble
6	Cyclohexane methanol	Insoluble	Soluble
7	Dimethyl cyclohexane	Insoluble	Soluble
8	Methyl cyclohexane	Insoluble	Soluble
9	Cyclohexane	Insoluble	Soluble
10	Toluene	Insoluble	Soluble
11	Xylene	Insoluble	Soluble
12	p-Toluic acid	Insoluble	Soluble

Table S6 leaching test results) Catalyst (ICP-OES

	First Run	**Second Run**
Ru Concentration (μ/L)	Ru	Ru
water layer	0	0
Oil layer	0	0

6. Calculation of Energy economy coefficient (ε)

The energy economy coefficient (ε) is a useful parameter to identify the advanced process for PET hydrodeoxygenation. The advanced process would tend to possess high ε.

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

Y=yield of the main monomer,

T=temperature of the reaction in celsious

t=the reaction time in minutes.

Table S7 Calculation of energy economy factor.

Catalyst	T (˚C)	Reaction time (min)	Products	Yield of arenes or C6-C8 cyclic hydrocarbon or TPA (%)	Energy economy (ε) (˚C^{-1}*min^{-1})	Ref.
Ru/TiO_2	220	720	Cyclic hydrocarbon	87.92	5.55E-04	This work
$Ru\text{-}TiO_2$	220	720	Cyclic hydrocarbon	83.41	5.27E-04	This work
Ru/Nb_2O_5	320	960	Areans	85	2.77E-04	1
$Ru/NiAl_2O_3$	320	960	Areans	80	2.60E-04	1
Co/TiO_2	320	1440	Areans	75.2	1.36E-04	2
$Ru/Cu/SiO_2$	400	1320	Cyclic hydrocarbon	94	1.78E-04	3
Ru/ZrO_2	220	720	Areans	40	2.52E-04	4
$Pt/NiAl_2O_3$	220	720	Areans	3.6	2.27E-05	4
$Pd/NiAl_2O_3$	220	720	Areans	21	1.33E-04	4
Single site C/MoO_2	260	1440	TPA	87	2.32E-04	5
Nickel phosphade catalyst	400	360	Areans	84	5.34E-04	6
CoMo/NC	260	600	TPA	91	5.34E-04	7

7. Product and catalyst separation

Table S8 Boiling points of solvents and major products.

Substance	Boiling point (°C)
n-dodecane	216.2
Cyclohexane	80.75
Methyl cyclohexane	101
Dimethyl cyclohexane	124-125

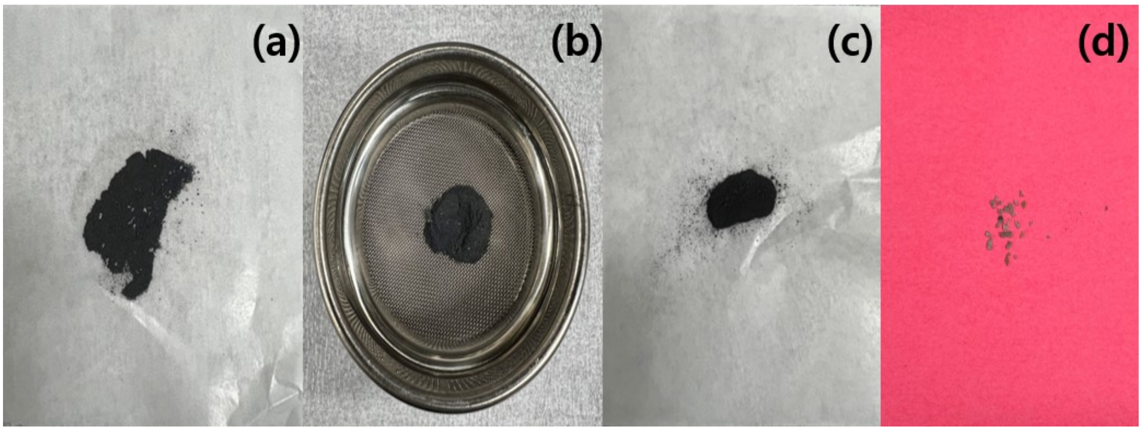


Fig. S11 Photograph of a) Catalyst after reaction (residual PET + catalyst), b) sieve process, c) Catalyst after sieving, d) Separated residual PET.

8. References

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