Supplementary material for

Upcycling of waste polyethylene terephthalate to dimethyl terephthalate over solid acid under mild conditions

Authors:

Boyong Ye [a], Ruru Zhou [a], Zixin Zhong [a], Songlin Wang [b], Han Wang [b], Zhaoyin Hou [a,b,*]

Address:

[a] Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemistry, Zhejiang University, Hangzhou 310028, China.

[b] Zhejiang Hengyi Petrochemical Research Institute Co., Ltd., Hangzhou 311200, China.

* Corresponding author

Zhaoyin Hou

Tel/Fax: 86-571-88273283

Email: zyhou@zju.edu.cn

Synthesis of SiO_2 or TiO_2: 180 μL triethanolamine was added to 100 mL of deionized water, heated in an oil bath at 80 °C and stirred for 30 min. After that, 0.74 g of sodium salicylate and 1.52 g of CTAB were added, and the mixture was stirred for 30 min at a constant temperature. Then tetraethyl orthosilicate (TEOS, 4.16 g, 0.02 mol) was added, and stirring was continued at 80 °C for 9 h. After the reaction was stopped, the mixture was centrifuged (10000 rpm, 4 min), and the collected solids were dried in an 80 °C oven. The obtained solid powder was roasted for 4 h in a muffle furnace at 550 °C, and the resulting material was denoted as SiO_2. Titanium tetraisopropanolate (TTIP, 5.68 g, 0.02 mol) was instead of TEOS to obtain TiO_2.

Synthesis of TiO_2/SiO_2-5/5: 180 μL triethanolamine was added to 100 mL of deionized water, heated in an oil bath at 80 °C and stirred for 30 min. After that, 0.74 g of sodium salicylate and 1.52 g of cetyltrimethylammonium bromide (CTAB) were added, and the mixture was stirred for 30 min at a constant temperature. Then 1.2 g of SiO_2 (0.02 mol, Sigma Aldrich Trading Co., Ltd, the average particle size is 50 nm) was added and stirred for 1 h. Thereafter, titanium tetraisopropanolate (TTIP, 5.68 g, 0.02 mol) was added dropwise, and stirring was continued at 80 °C for 9 h. After the reaction was stopped, the mixture was centrifuged (10000 rpm, 4 min), and the collected solids were dried in an 80 °C oven. The obtained solid powder was roasted for 4 h in a muffle furnace at 550 °C, and the resulting material was named TiO_2/SiO_2-5/5.

Synthesis of SiO_2/TiO_2-5/5: 180 μL triethanolamine was added to 100 mL of deionized water, heated in an oil bath at 80 °C and stirred for 30 min. After that, 0.74

g of sodium salicylate and 1.52 g of CTAB were added, and the mixture was stirred for 30 min at a constant temperature. Then 1.6 g of TiO_2 (0.02 mol, Sigma Aldrich Trading Co., Ltd) was added and stirred for 1 h. Thereafter, tetraethyl orthosilicate (TEOS, 4.16 g, 0.02 mol) was added dropwise, and stirring was continued at 80 °C for 9 h. After the reaction was stopped, the mixture was centrifuged (10000 rpm, 4 min), and the collected solids were dried in an 80 °C oven. The obtained solid powder was roasted for 4 h in a muffle furnace at 550 °C, and the resulting material was named SiO_2/TiO_2-5/5.

NH_3-TPD: The sample was first heated at 700 °C for 1 h in N_2 and then the reactor was cooled to 50 °C. The sample was exposed to NH_3 for 30 min, and then purged by Ar for 3 h at 50 °C to eliminate the physically adsorbed NH_3. NH_3-TPD was conducted by heating to 700 °C with a ramp of 15 °C/min, and the effluent was measured on the online quadrupole mass spectrometer.

Pyridine-IR: Pyridine-IR spectra was obtained on Tensor 27 (Bruker, Germany) using self-supporting wafers of approximately 20 mg (1.3 cm diameter). Prior to the measurements, the wafers were pretreated under vacuum at 300 °C for 1 h inside a home-built IR cell with ZnSe windows, exposed to pyridine at 150 °C, and then evacuated at the same temperature to remove the physisorbed pyridine. IR spectra were collected at 150 °C (32 scans with a resolution of 2 cm^{-1}).

Gel permeation chromatography (GPC) analysis: The average molecular weight of remaining solids during the alcoholysis of PET was detected using GPC with a refractive index detector. PET solid was dissolved using hexafluoroisopropanol

(HFIP) and prepared into a solution of 2.23 mg/mL. The column temperature was 35 °C, the mobile phase was hexafluoroisopropanol (HFIP) at a flow rate of 0.5 mL/min and the injection volume was 100 μL. The GPC was calibrated and the standard curve was established using standard polymethyl methacrylate (PMMA) samples.

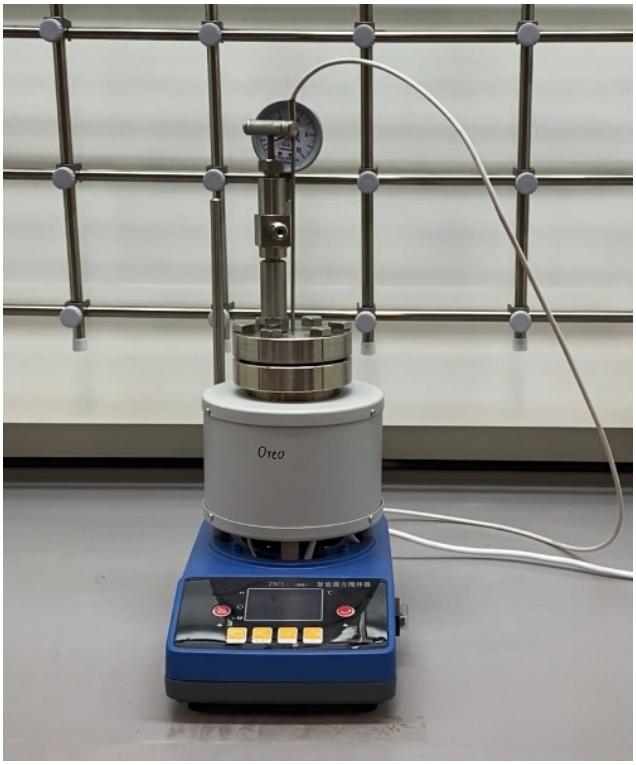

Fig. S1. The photograph of the high-pressure reactor and electric heating apparatus.

Table S1. The physical and chemical properties of various materials.

Materials	S_{BET} (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
SiO_2	526	1.4, 13.3	2.5
SiO_2/TiO_2-5/5	264	1.4, 4.8	1.1
TiO_2/SiO_2-5/5	137	1.4, 4.7	0.8
TiO_2	34	8.4	0.2

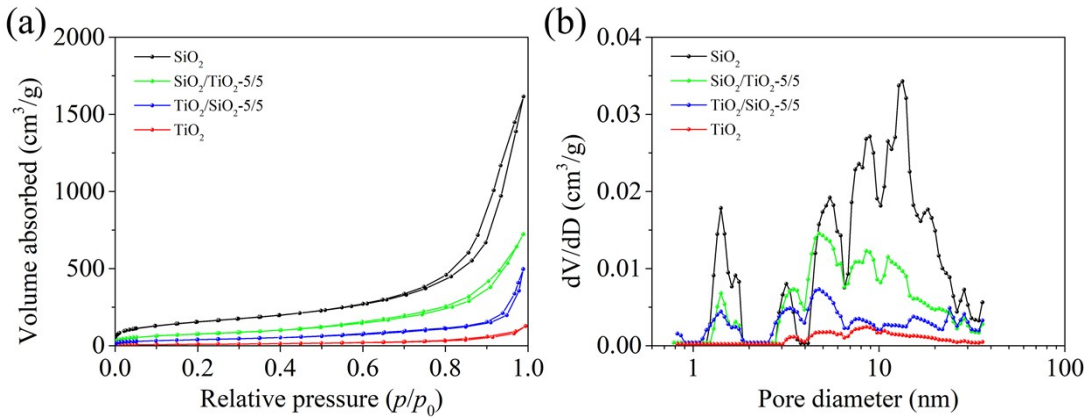

Fig. S2. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of various materials.

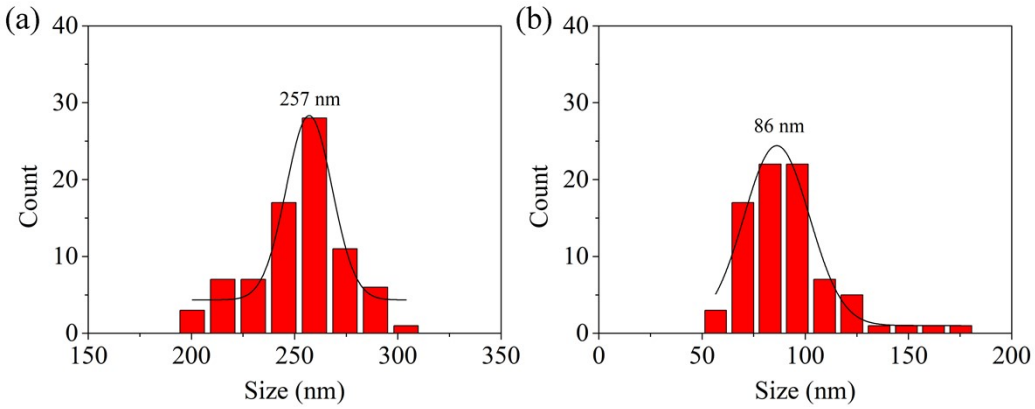

Fig. S3. Particle size distributions of (a) $Ti_{0.1}Si_{0.9}O_2$ and (b) $Ti_{0.5}Si_{0.5}O_2$.

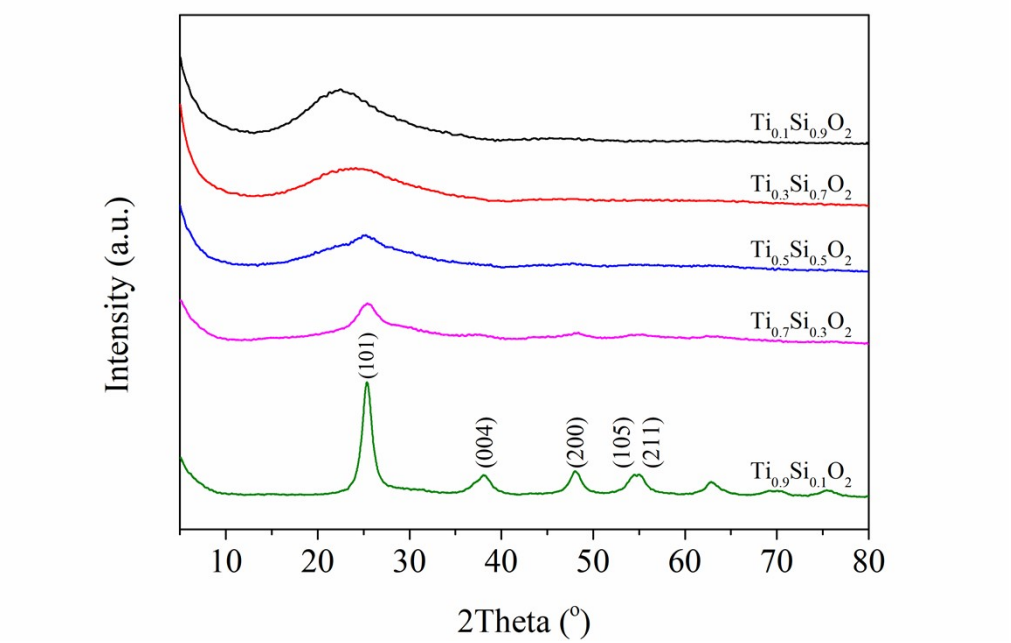

Fig. S4. XRD patterns of $Ti_xSi_{1-x}O_2$ catalysts.

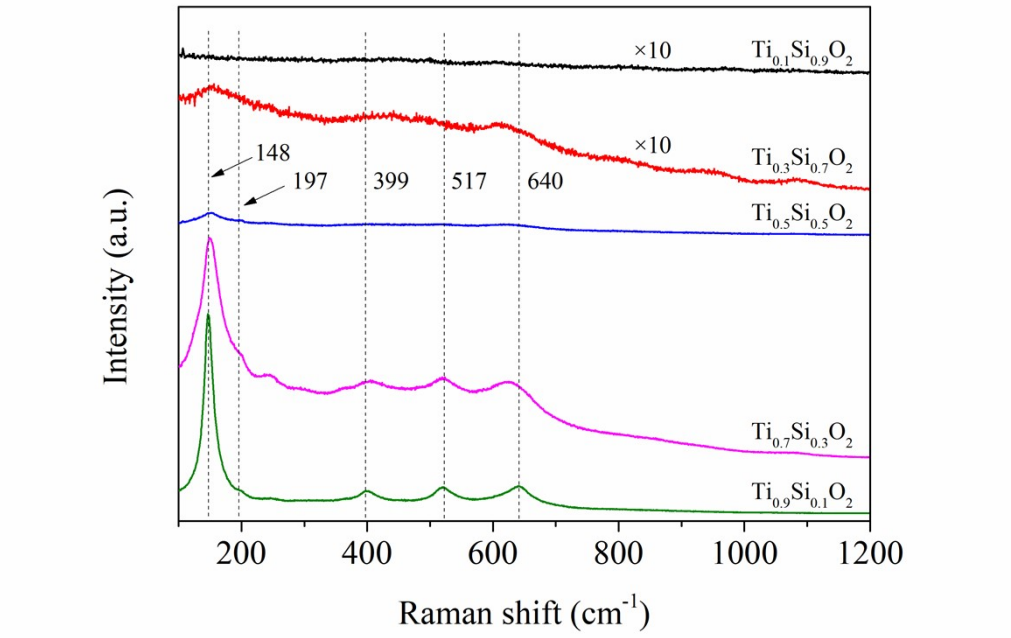

Fig. S5. Raman spectra of $Ti_xSi_{1-x}O_2$ catalysts.

Table S2. Values for the chemical shift, the full individual line width at half height and the percentage of Q^n obtained from the analysis of ^{29}Si MAS NMR.

Catalyst	Structural type	-δ (ppm)	FWHH (ppm)	Q^n (%)
$Ti_{0.5}Si_{0.5}O_2$	Q_4	-110.0	8.5	43.9
	Q_3	-101.3	10.0	53.4
	Q_2	-92.2	4.4	2.7

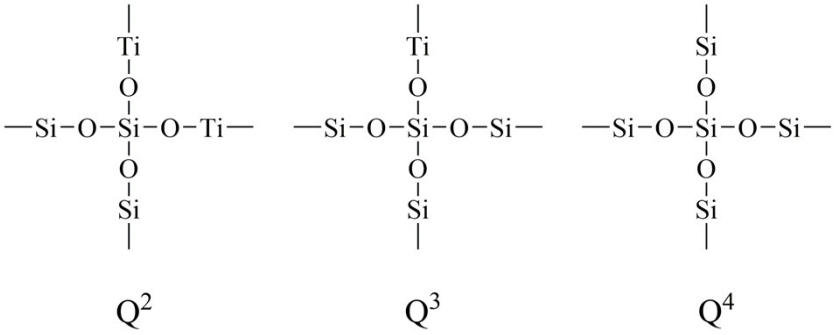

Fig. S6. Schematic diagram of Q^n structural unit.

Table S3. Binding energies of $Ti_xSi_{1-x}O_2$.

Catalysts	Ti $2p_{3/2}$ (eV)	Ti $2p_{1/2}$ (eV)	Si $2p$ (eV)	O $1s$ (eV)
$Ti_{0.1}Si_{0.9}O_2$	459.2	464.8	103.7	530.7, 533.0
$Ti_{0.3}Si_{0.7}O_2$	459.0	464.7	103.5	530.6, 532.8
$Ti_{0.5}Si_{0.5}O_2$	459.0	464.7	103.2	530.6, 532.7
$Ti_{0.7}Si_{0.3}O_2$	458.9	464.6	102.7	530.3, 532.2
$Ti_{0.9}Si_{0.1}O_2$	458.8	464.5	102.4	530.1, 532.0

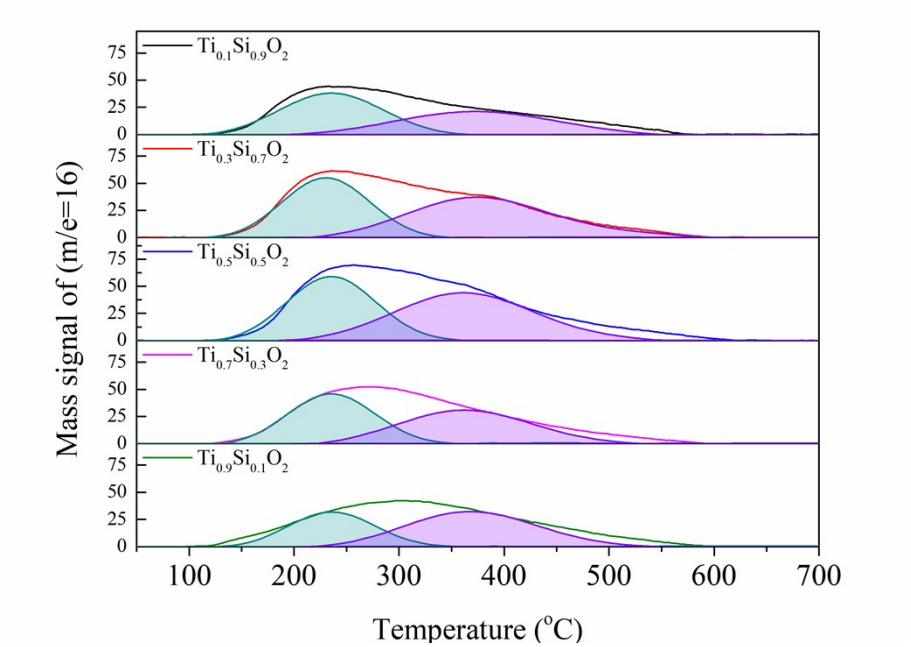

Fig. S7. NH_3-TPD profiles of $Ti_xSi_{1-x}O_2$ catalysts.

Table S4. Catalytic performance of catalysts for the PET alcoholysis to DMT[a].

Catalysts	PET conversion (%)	DMT yield (%)	MHET yield (%)
$Ti_{0.4}Si_{0.6}O_2$	87.0	77.5	4.1
$Ti_{0.5}Si_{0.5}O_2$	87.3	79.0	3.8
$Ti_{0.6}Si_{0.4}O_2$	80.5	71.9	5.6
H_2SO_4	8.3	4.2	1.3
$AlCl_3$	4.6	1.5	0.8
TiO_2/SiO_2-5/5	36.4	8.8	5.1
SiO_2/TiO_2-5/5	8.8	1.7	1.1
TiO_2	<1.0	0.1	<0.1
SiO_2	<1.0	0.1	<0.1

[a] Reaction conditions: 1 g PET, 0.025 g catalyst, 10 mL MeOH, 150 °C, 2 h.

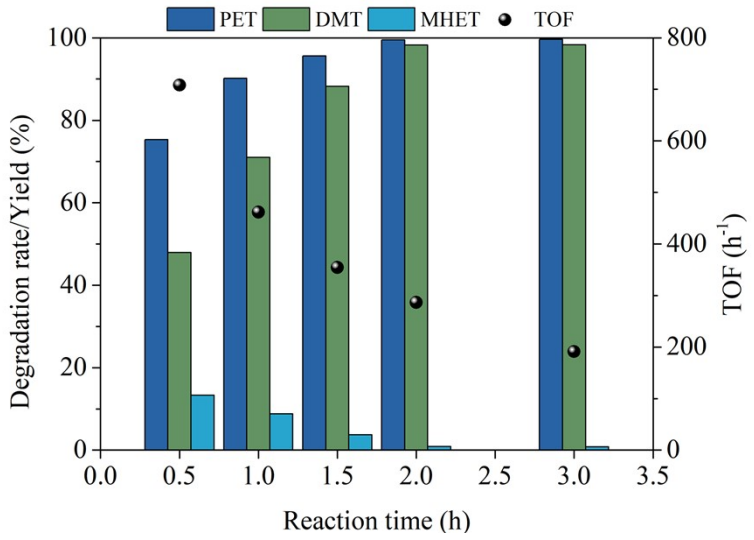

Fig. S8. Performance of $Ti_{0.5}Si_{0.5}O_2$ under different reaction times. Reaction conditions: 1 g PET, 0.025 g $Ti_{0.5}Si_{0.5}O_2$, 10 mL methanol, 160 °C.

Table S5. The comparison of fresh and spent $Ti_{0.5}Si_{0.5}O_2$.

Catalyst	W_{Ti} (%) [a]	W_{Si} (%) [a]	n(Ti/Si) [b]	Acidity (mmol/g) [c]
Fresh $Ti_{0.5}Si_{0.5}O_2$	38.70	21.13	1.07	0.36
Spent $Ti_{0.5}Si_{0.5}O_2$	38.29	21.12	1.06	0.35

[a] Measured by ICP-OES.
[b] Calculated according to ICP-OES results.
[c] Measured via acid-base titration.

Table S6. The physical properties of fresh $Ti_{0.5}Si_{0.5}O_2$ and spent $Ti_{0.5}Si_{0.5}O_2$.

Catalysts	S_{BET} (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
Fresh $Ti_{0.5}Si_{0.5}O_2$	407	1.5, 5.1	1.06
Spent $Ti_{0.5}Si_{0.5}O_2$	334	1.7, 4.9	0.79

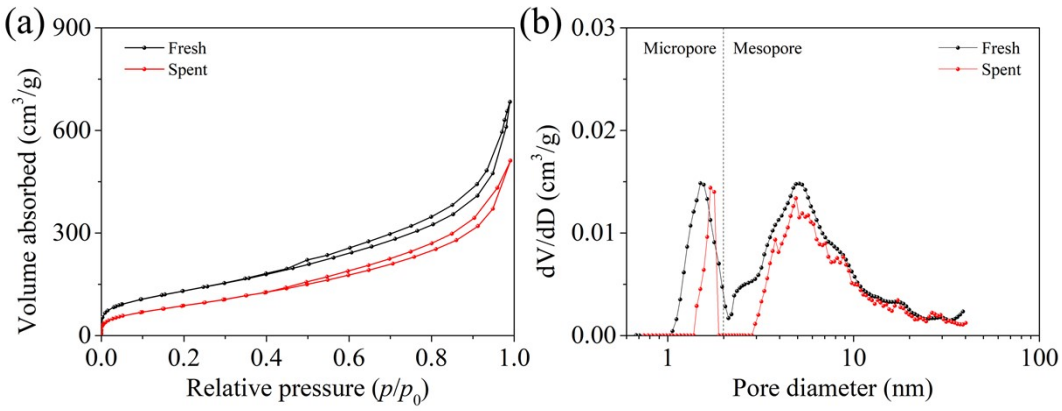

Fig. S9. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of fresh $Ti_{0.5}Si_{0.5}O_2$ and spent $Ti_{0.5}Si_{0.5}O_2$.

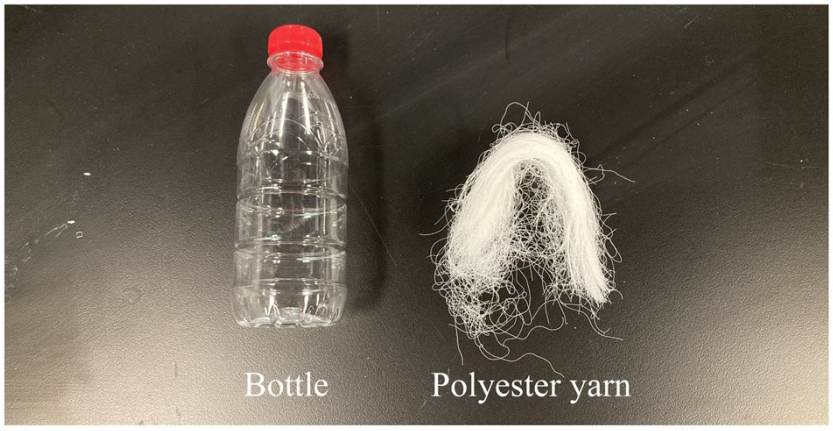

Fig. S10. Alcoholysis of PET bottle and Polyester yarn over $Ti_{0.5}Si_{0.5}O_2$. Reaction conditions: 1 g PET-based product, 0.025 g $Ti_{0.5}Si_{0.5}O_2$, 10 mL MeOH, 160 °C, 3 h.

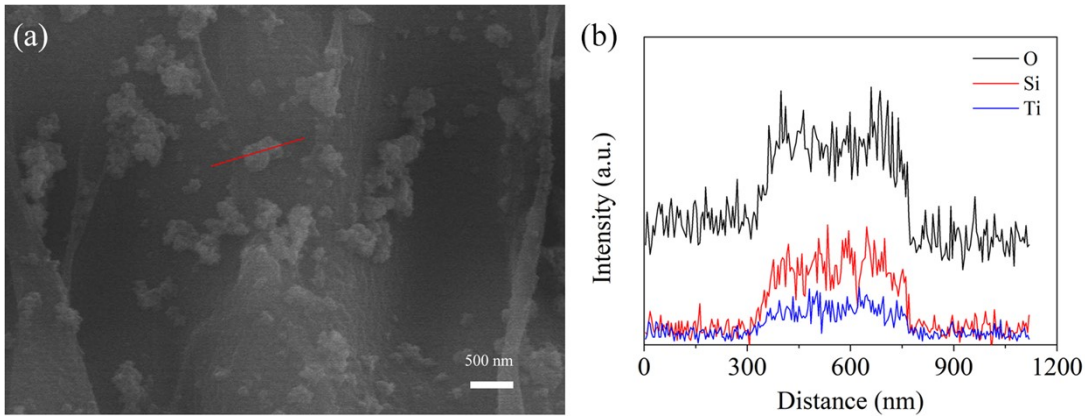

Fig. S11. (a) SEM image and (b) line-eds of PET and $Ti_{0.5}Si_{0.5}O_2$.

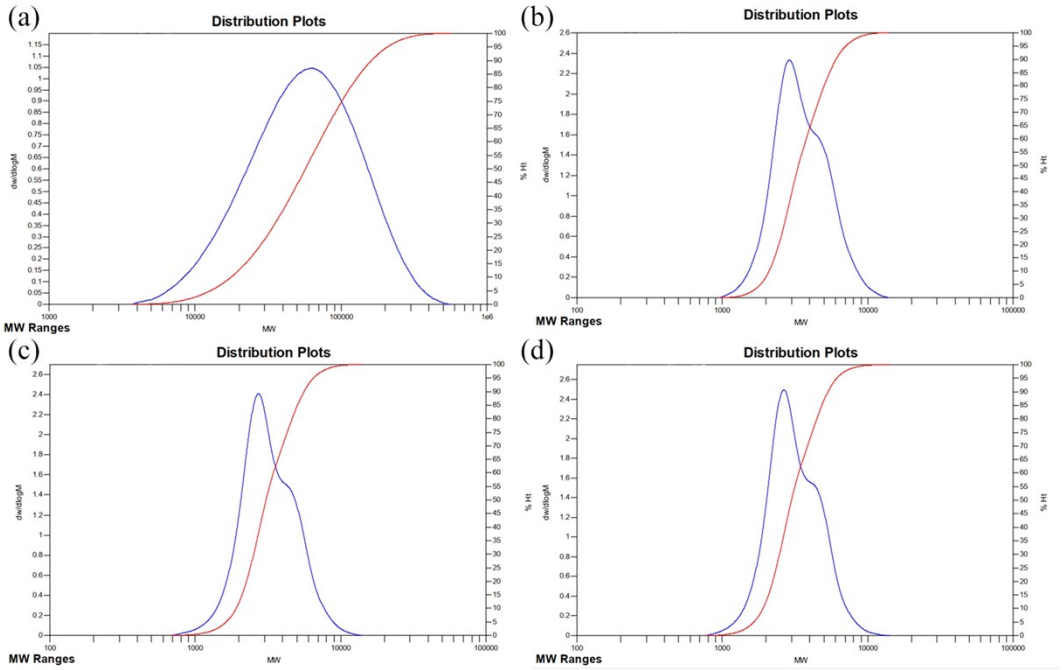

Fig. S12. Molecular weight of (a) raw PET and the remaining solid after different reaction times (b) 0.5 h, (c) 2 h and (d) 4 h.

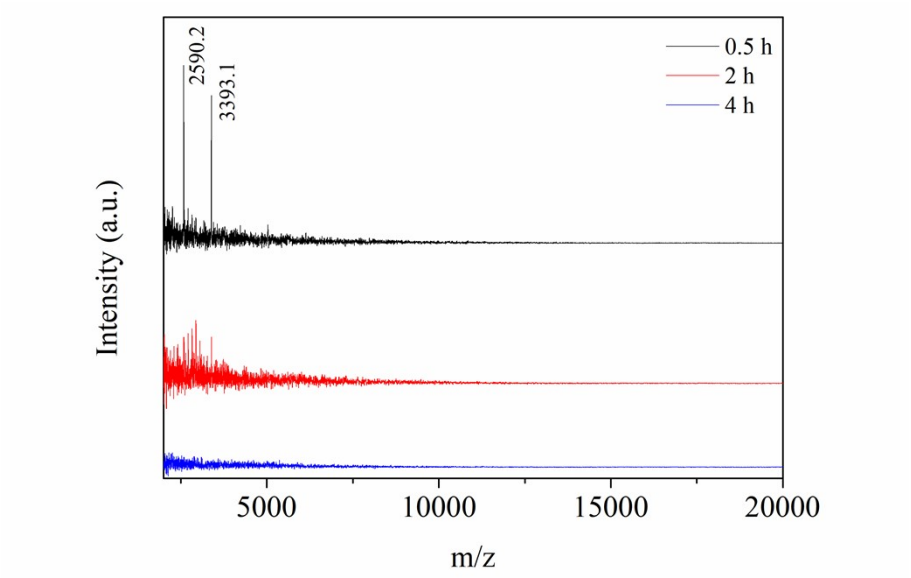

Fig. S13. MALDI-TOF-MS spectra of the reaction solution. Reaction conditions: 1 g PET, 0.025 g $Ti_{0.5}Si_{0.5}O_2$, 10 mL methanol, 150 °C.