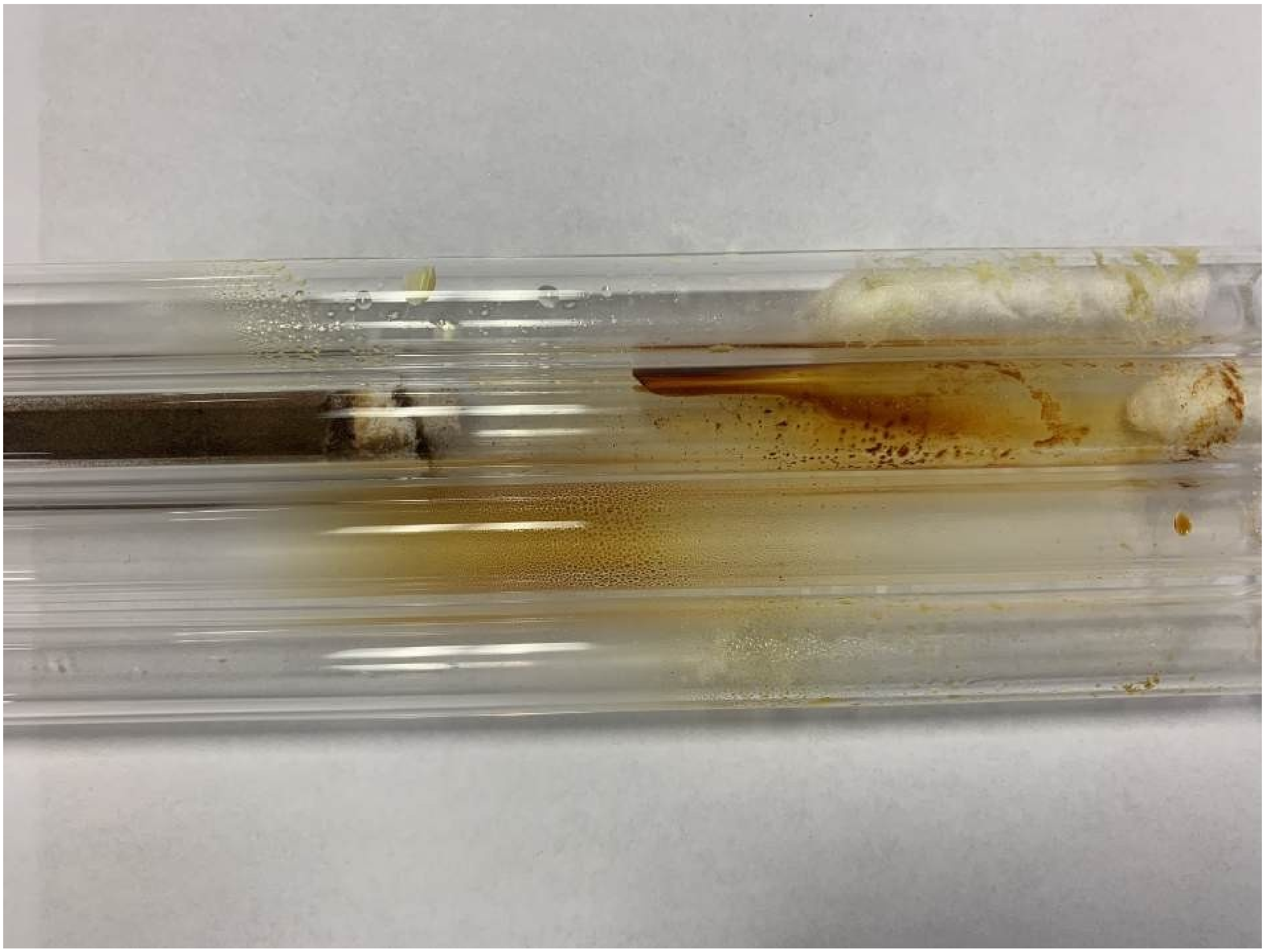
Supplementary Information (SI) for Reaction Chemistry & Engineering.

Supplementary Documents

Supplementary Table 1 Carbon balance of PMMA hydrolysis over di erent zeolites

Samples	T	$X_{PMMA}{}^{a}$	Y_{MAA}	Y_{MeOH}	Y_{MMA}	$Y_{Acetone}$	S_{MAA}	S_{MeOH}	S_{MMA}	$S_{Acetone}$	C in residues[b]	CO	CO_2	CH_4	Recovered C
	°C	%	%	%	%	%	%	%	%	%	mol %	mol %	mol %	mol %	mol %
HY(80)	350	97	54	15	2	3	56	15	3	3	10	3.4	0.8	0.0	88
HY(80)-rep	350	97	56	16	3	2	58	16	3	2	10	3.4	0.9	0.0	91
HY(80)	330	74	43	12	1	3	58	16	1	5	32	3.3	0.8	0.0	95
HY(80)	370	99	55	14	4	2	56	14	4	2	6	3.5	0.9	0.1	86
HY(60)	350	96	49	14	2	5	51	15	2	5	15	3.9	0.8	0.0	89
HY(30)	350	96	41	13	2	5	42	14	2	5	20	4.2	0.9	0.0	86
Hβ(360)	350	92	51	14	2	6	55	16	2	6	15	3.6	0.7	0.0	92
HZSM-5(200)	350	96	45	13	3	11	47	14	3	12	6	4.5	1.0	0.0	84
HZSM-5(80)	350	98	24	7	1	13	25	7	1	13	6	7.5	0.9	0.0	60
HMOR(20)	350	98	40	2	3	3	41	2	3	3	13	4.5	0.9	0.1	67
R-HY(80)	350	95	51	15	2	2	53	15	3	2	12	3.4	0.8	0.0	86
M0.5	350	98	21	7	19	0	21	8	19	0	7	3.4	0.9	0.0	59
M1	350	99	18	5	25	0	18	5	25	0	5	3.3	0.8	0.0	57
M2	350	98	19	7	17	0	20	8	18	0	7	3.4	1.3	0.0	56
HY(80) on PMMA[c]	350	97	47	6	0	0	48	6	0	0	6	5.8	1.5	0.0	66
PMMA (blank)	350	95	0	0	56	0	0	0	59	0	5	0.0	0.7	0.0	61

Note: T-temperature, rep.-repetition, a-determined by TGA, b-measured by LECO, c-HY(80) layer covered on the surface of PMMA powder.
Liquid products detected by GCMS contains MAA, methanol, MMA and acetone. GC-TCD quantified CO, CO_2 and CH_4 in the gas phase. LECO measured total carbon residues for carbon balance and TGA determined the amount of unreacted PMMA and coke for conversion calculation.



Supplementary Fig. 1 MMA repolymerization byproducts in PMMA-to-MMA recycling routes. The yellow repolyermzaition residues that formed in reactors and condensers during PMMA catalytic/non-catalytic pyrolysis reduced MMA yield and resulted in higher MMA puri cation cost.

Supplementary Table 2 Physico-chemical properties of fresh zeolites, regenerated HY(80), desilicated HY(80) and coked HY(80) zeolites

Sample	Si/Al[a]	S_{BET}	V_{tot}	Average D_v	V_{micro}	S_{micro}	S_{meso}	d_p[b]			
								Medium size	Mean size	D[10]	D[90]
		$m^2\ g^{-1}$	$cm^3\ g^{-1}$	Å	$cm^3\ g^{-1}$	$m^2\ g^{-1}$	$m^2\ g^{-1}$	μm	μm	μm	μm
Commercial zeolites											
HY(80)	102	741	0.59	15	0.26	498	242	2.87	3.00	2.03	4.18
HY(60)	-	767	0.58	15	0.26	504	263	4.08	4.82	2.33	8.39
HY(30)	-	731	0.58	19	0.27	523	208	3.25	4.54	1.89	9.10
Hβ(360)	150	550	0.39	17	0.21	413	137	1.04	1.10	0.84	1.38
Activated zeolites											
HZSM-5(200)	104	381	0.24	15	0.06	110	270	2.18	2.23	1.76	2.78
HZSM-5(80)	-	403	0.29	17	0.12	242	161	1.68	1.71	1.22	2.21
HMOR(20)	11	440	0.36	17	0.19	384	56	2.67	4.12	1.54	9.11
Regenerated HY zeolite											
R-HY(80)	107	786	0.60	15	0.27	534	252	-	-	-	-
Desilicated HY zeolites											
M0.5	58	128	0.43	39	0.004	10	118	2.49	3.38	1.51	6.73
M1	46	43	0.29	86	0.003	6	37	2.17	2.42	1.37	3.77
M2	27	82	0.45	87	0.004	10	72	2.34	2.49	1.70	3.45
M3	6	95	0.21	17	0.003	8	87	2.60	2.66	2.05	3.36
Coked HY zeolite											
C-HY(80)	58	-	-	-	-	-	-	-	-	-	-

Note: d_p-particle size; a-calculated by XPS; b-measured by PSD

Supplementary Table 3 Acidic properties of fresh, regenerated, coked, and desilicated Zeolite Y ($\mu molg^{-1}$).

Sample	Weak[a]	Medium strong[a]	Brønsted[b]	Lewis[b]	B/L ratio	Brønsted[b]	Lewis[b]	B/L ratio
				150 °C			350 °C	
HY(80)	95	52	15	170	0.09	6.4	49	0.13
HY(60)	240	340	-	-	-	-	-	-
HY(30)	850	910	-	-	-	-	-	-
R-HY(80)	150	210	8.8	250	0.04	3.2	62	0.05
M0.5	300	0	20	53	0.37	8.3	18	0.46
C-HY(80)	230	0	3.4	83	0.04	2.7	12	0.21

Note: a-measured by NH_3-TPD; b-measured by Py-IR

Supplementary Table 4 Pore dimension of di erent zeolites

Zeolite	Framework Type	Channel diameter, Å
Zeolite Y	FAU	12-ring [111] channels: 7.4 × 7.4
Zeolite β	BEA	12-ring [100] channels: 6.6 × 6.7
Zeolite β	BEA	12-ring [001] channels: 5.6 × 5.6
Mordenite	MOR	12-ring [001] channels: 6.5 × 7.0
Mordenite	MOR	8-ring [001] channels between 12-ring channels: 2.6 × 5.7
ZSM-5	MFI	10-ring [010] channels: 5.3 × 5.6
ZSM-5	MFI	10-ring [100] channels: 5.1 × 5.5

Data source: Database of Zeolite Structures (http://www.iza-structure.org/databases/)

Supplementary Table 5 Molecular weight of PMMA in reacted HY(60) sample

PMMA residues in	M_n	M_w	Dispersity
HY(60)	18000	39000	2.15

Supplementary Table 6 XPS elemental identi cation and quanti cation in HY(80)

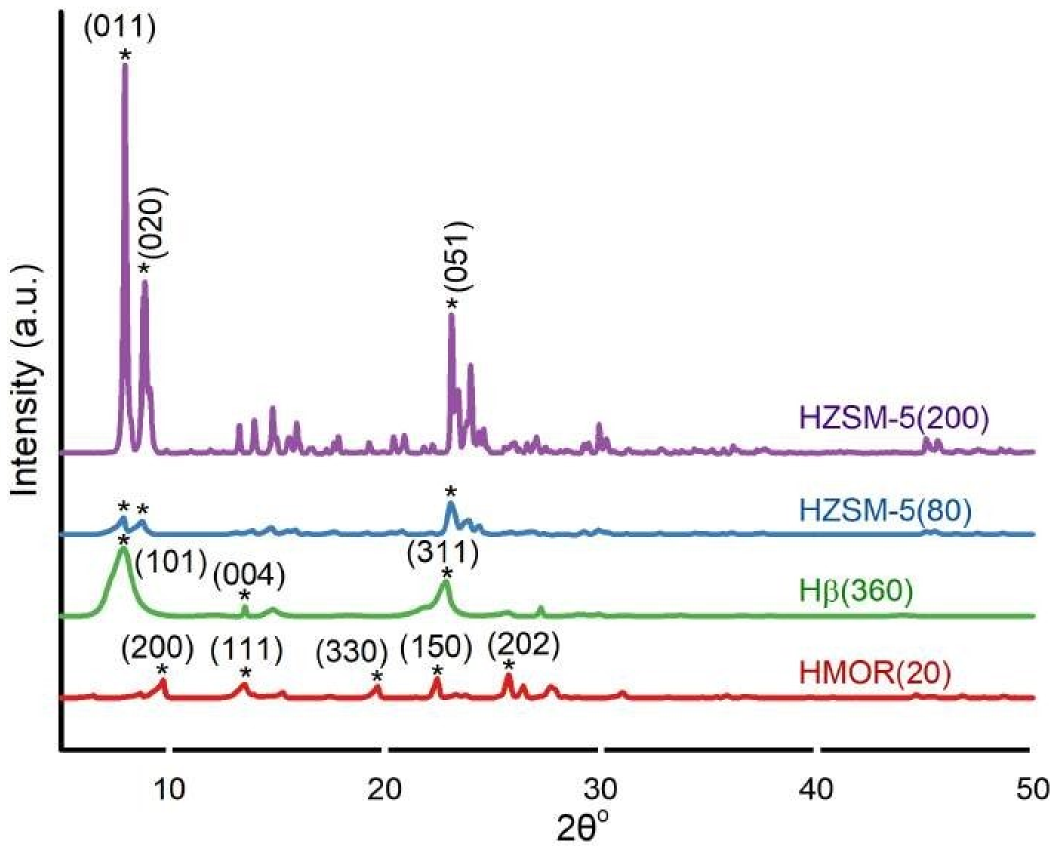
Name	Structure	Peak BE eV	FWHM eV	Area (P), CPS eV	Atomic %
Al2p	Al in zeolite	74.7	2.46	542	0.3
Si2p3	Si in zeolite	103.3	1.71	50300	30.7
C1s A	C−C and/or C−C	284.1	1.65	7740	2.9
C1s B	C−O	285.4	1.65	2980	1.1
C1s C	C−O and/or O−C−O	287.5	1.65	796	0.3
O1s A	O in zeolite	533.0	2.01	440000	61.6
O1s B	Adsorbed H_2O	535.4	2.01	21600	3.0

Abbreviations: BE, binding energy; FWHM, full-width-at-half-maximum; CPS, counts per second

Supplementary Table 7 XPS elemental identi cation and quanti cation in R-HY(80)

Name	Structure	Peak BE eV	FWHM eV	Area (P), CPS eV	Atomic %
Al2p A	Al in zeolite	74.9	2.60	540	0.3
Si2p3	Si in zeolite	103.3	1.60	5660	32.0
C1s A	C-C and C=C	284.2	1.89	3570	1.2
C1s B	C-O	286.0	1.89	1320	0.5
C1s C	O-C=O	288.5	1.89	490	0.2
O1s A	O in zeolite	533.1	1.94	484000	62.8
O1s B	Adsorbed H_2O	535.6	1.94	23500	3.0

Abbreviations: BE, binding energy; FWHM, full-width-at-half-maximum; CPS, counts per second

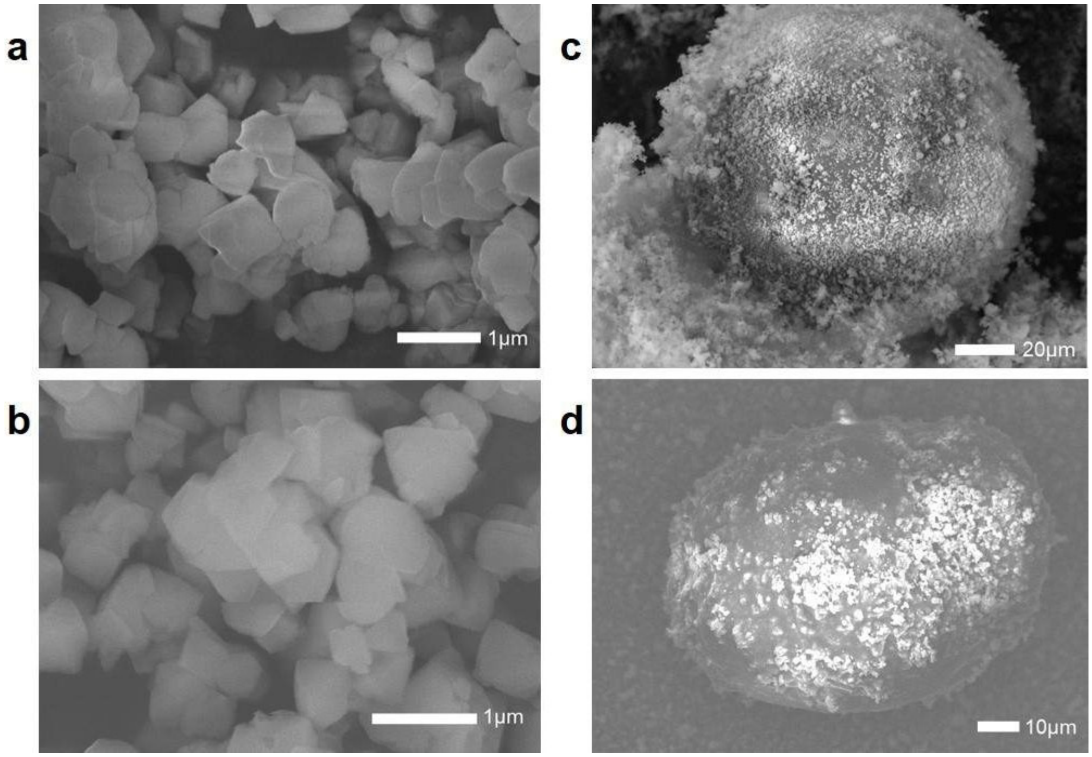


Supplementary Fig. 2 X-ray powder di raction over HZSM-5(200), HZSM-5(80), Hβ(360) and HMOR(20)

Supplementary Table 8 XPS elemental identi cation and quanti cation in C-HY(80)

Name	Structure	Peak BE eV	FWHM eV	Area (P), CPS eV	Atomic %
Al2p A	Al in zeolite	74.4	2.43	570	0.4
Si2p3	Si in zeolite	103.3	1.73	50000	29.2
C1s A	C-C and C=C	284.2	1.68	17000	6.0
C1s B	C-O	285.9	1.68	3240	1.2
C1s C	O-C=O	288.3	1.68	1670	0.6
O1s A	O in zeolite	532.8	1.82	470000	62.7

Abbreviations: BE, binding energy; FWHM, full-width-at-half-maximum; CPS, counts per second



Supplementary Fig. 3 SEM images of fresh HY(80) (a), R-HY(80) (b), unreacted PMMA sphere covered by HY(80) particles (c), and PMMA sphere covered by HY(80) particles preheated at 350 °C for 2 min under steam atmosphere (d).

Supplementary Table 9 XPS elemental identi cation and quanti cation in M0.5

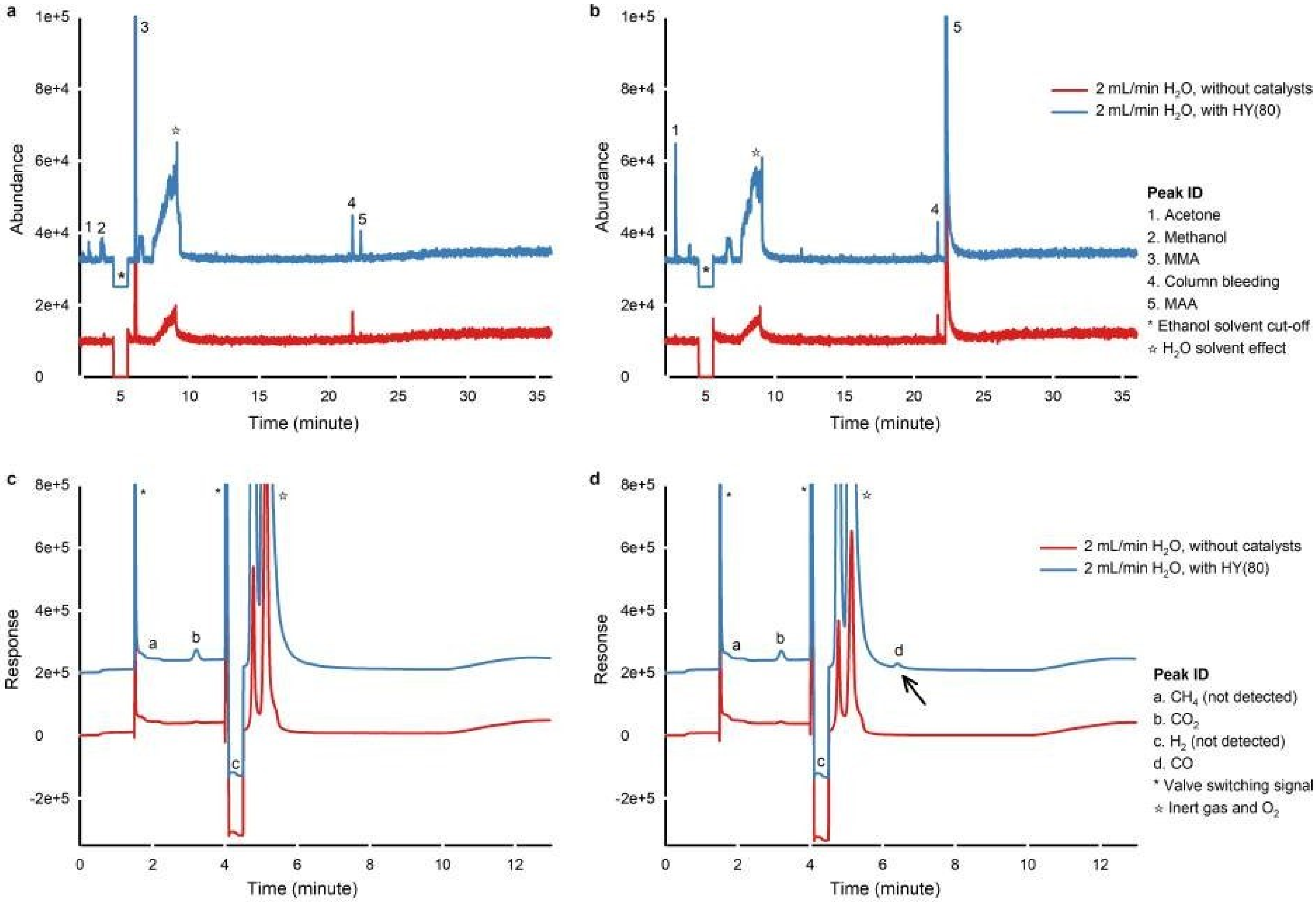
Name	Structure	Peak BE eV	FWHM eV	Area (P), CPS eV	Atomic %
Al2p A	Al in zeolite	75.4	2.91	1500	0.5
Si2p3 A	Si in zeolite	103.3	1.83	78000	25.1
Si2p3 B	Si in other forms	104.8	1.83	13500	4.4
C1s A	C-C	284.5	1.99	24000	4.9
C1s B	C-O	286.2	1.99	7700	1.6
C1s C	O-C=O	288.3	1.99	3600	0.7
O1s A	O in zeolite	532.9	2.18	800000	62.4
Na1s	Na from NaOH	1072.2	3.15	4400	0.1
N1s	N from NH_3NO_3	399.7	2.79	1300	0.2

Abbreviations: BE, binding energy; FWHM, full-width-at-half-maximum; CPS, counts per second

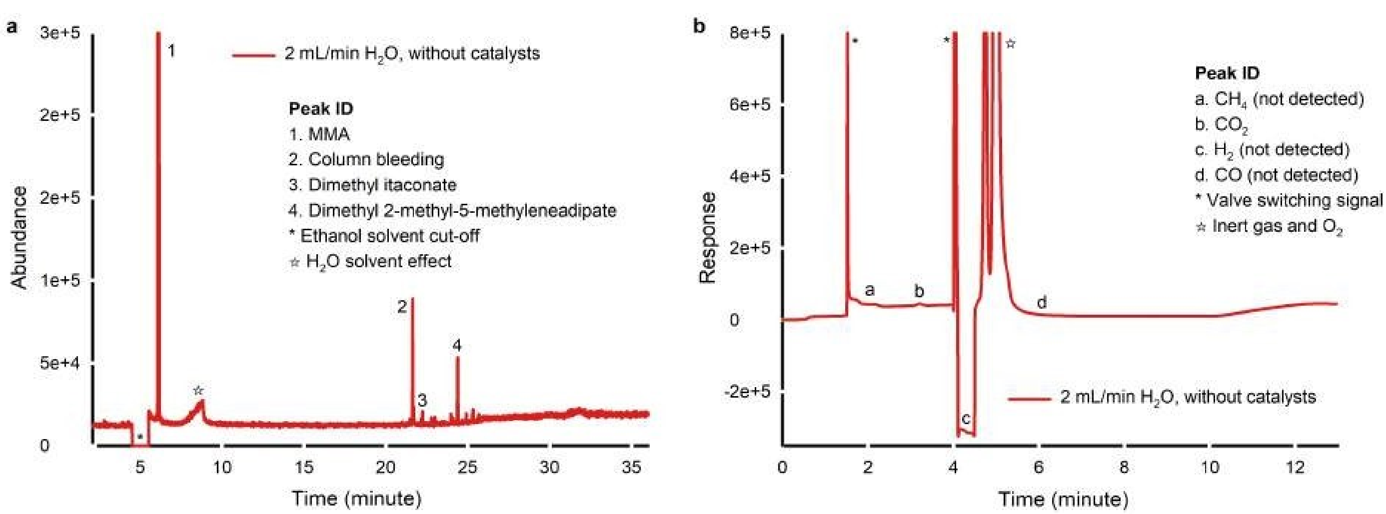
Supplementary Table 10 XPS elemental identi cation and quanti cation in M1

Name	Structure	Peak BE eV	FWHM eV	Area (P), CPS eV	Atomic %
Al2p	Al in zeolite	75.0	2.49	1900	0.7
Si2p3	Si in zeolite	103.3	1.82	92000	30.2
C1s A	C-C	284.9	1.99	11000	2.3
C1s B	C-O	286.6	1.99	4100	0.8
C1s C	O-C=O	288.8	1.99	1800	0.4
O1s A	O in zeolite	532.9	2.06	820000	65.0
Na1s	Na from NaOH	1072.8	2.46	5300	0.2
N1s	N from NH_3NO_3	402.5	2.65	600	0.1

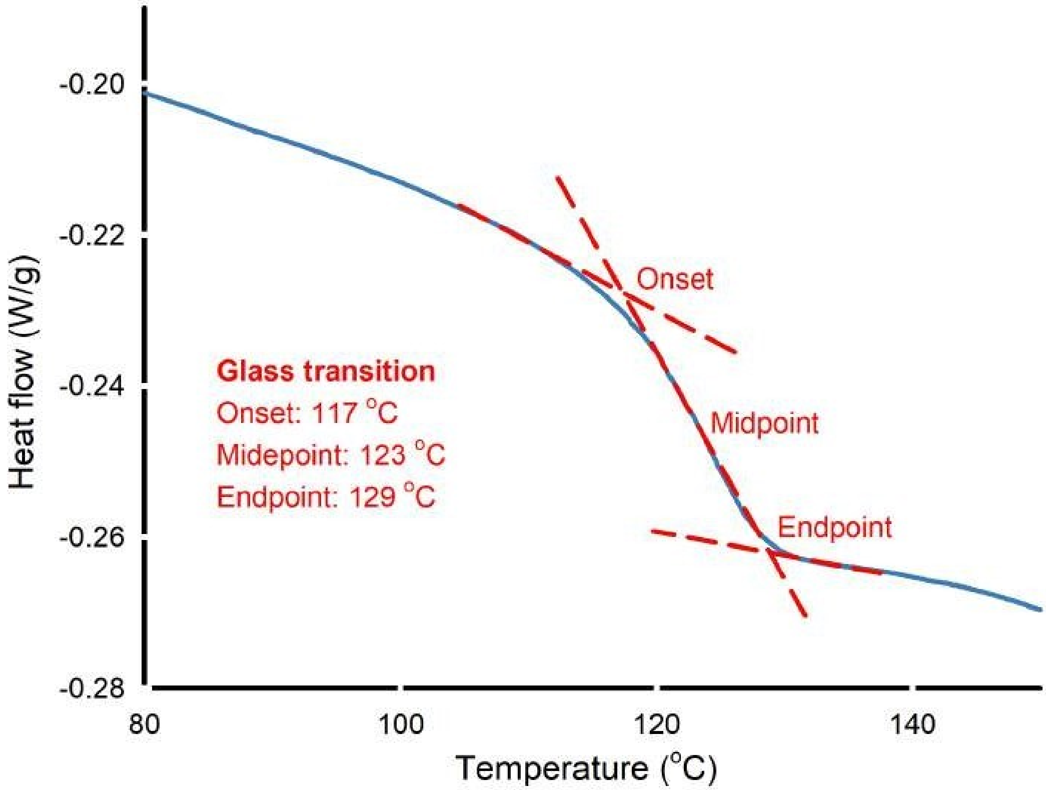
Abbreviations: BE, binding energy; FWHM, full-width-at-half-maximum; CPS, counts per second



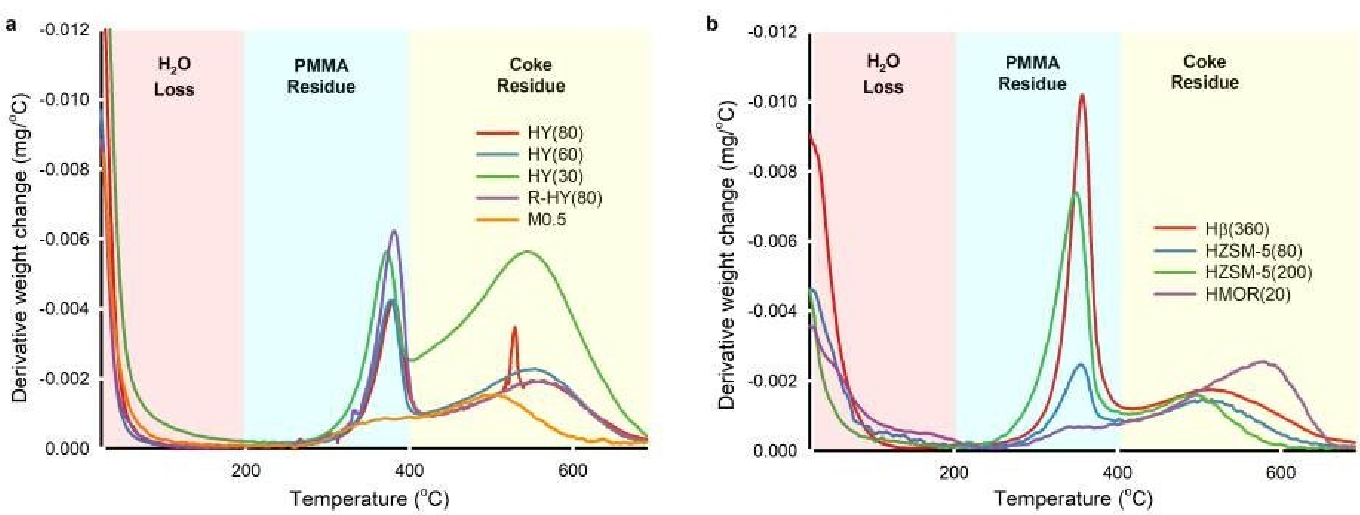
Supplementary Fig. 4 Catalytic and non-catalytic hydrolysis of MMA and MAA. a, GCMS results of MMA hydrolysis with and without HY(80) at 350 °C with 2 $mLmin^{-1}$ of water injection. b, GCMS results of MAA hydrolysis with and without HY(80) at 350 °C with 2 $mLmin^{-1}$ of water injection. c, GC-TCD gas detection results of MMA hydrolysis with and without HY(80) at 350 °C with 2 $mLmin^{-1}$ of water injection. Catalytic hydrolysis of MMA over HY(80) produced a small amount of CO_2. d, GC-TCD gas detection results of MAA hydrolysis with and without HY(80) at 350 °C with 2 $mLmin^{-1}$ of water injection. Catalytic hydrolysis of MAA over HY(80) produced a small amount of CO and CO_2.



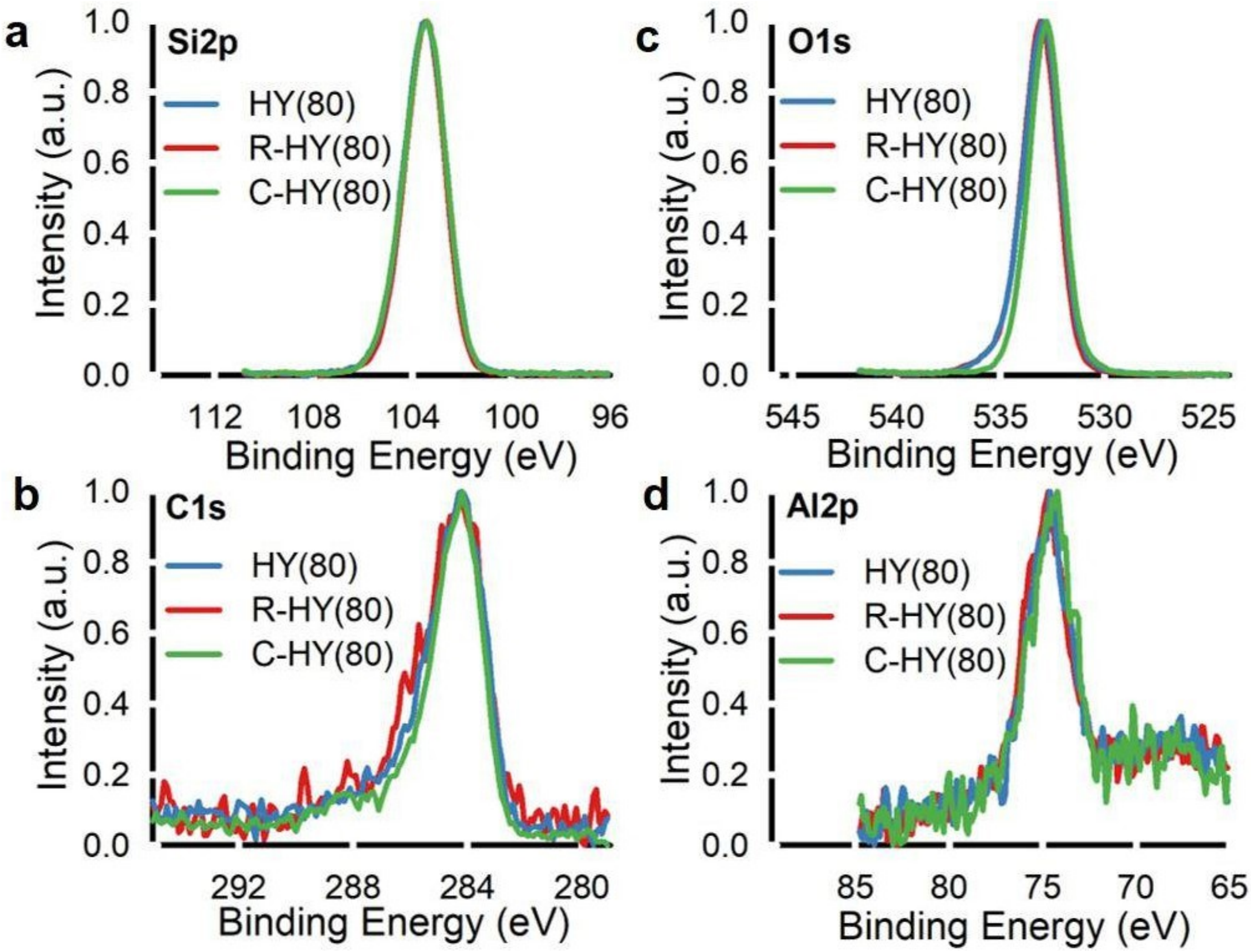
Supplementary Fig. 5 PMMA blank hydrolysis without catalysts at 350 °C under steam conditions (2 $mLmin^{-1}$ of water injection). a, GCMS results of PMMA non-catalytic degradation. b, GC-TCD gas detection results of PMMA non-catalytic degradation.



Supplementary Fig. 6 DSC results of PMMA powder showed onset T_g=117 °C, midpoint T_g=123 °C and endpoint T_g=129 °C.



Supplementary Fig. 7 The rst derivative of the TGA curves of solid residues for fresh, regenerated and desilicated zeolite Y reacted at 350 °C (a), and activated HZSM-5(200), HZSM-5(80), HMOR(20) and fresh Hβ (360) reacted at 350 °C (b) under air atmosphere (60 mLmin^{-1}) with a heating ramp of 5 °Cmin^{-1}. Weight loss under 200 °C was attributed to H_2O loss, while weight loss between 200 °C and 400 °C was attributed to PMMA residues. Coke residues corresponded to temperature higher than 400 °C.

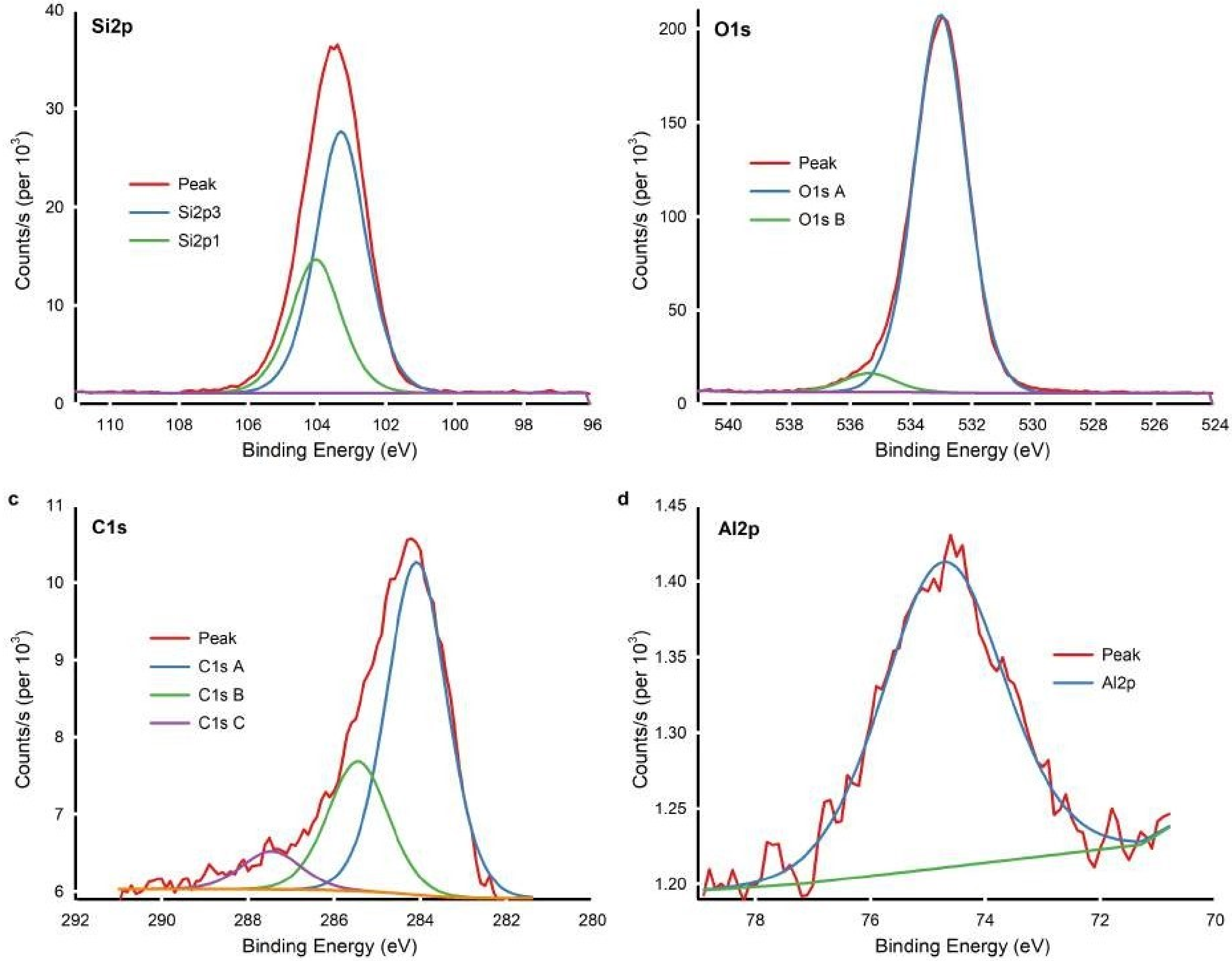


Supplementary Fig. 8 XPS spectra comparison for Si2p (a), C1s (b), O1s (c) and Al2p (d) over HY(80), R-HY(80), and C-HY(80).

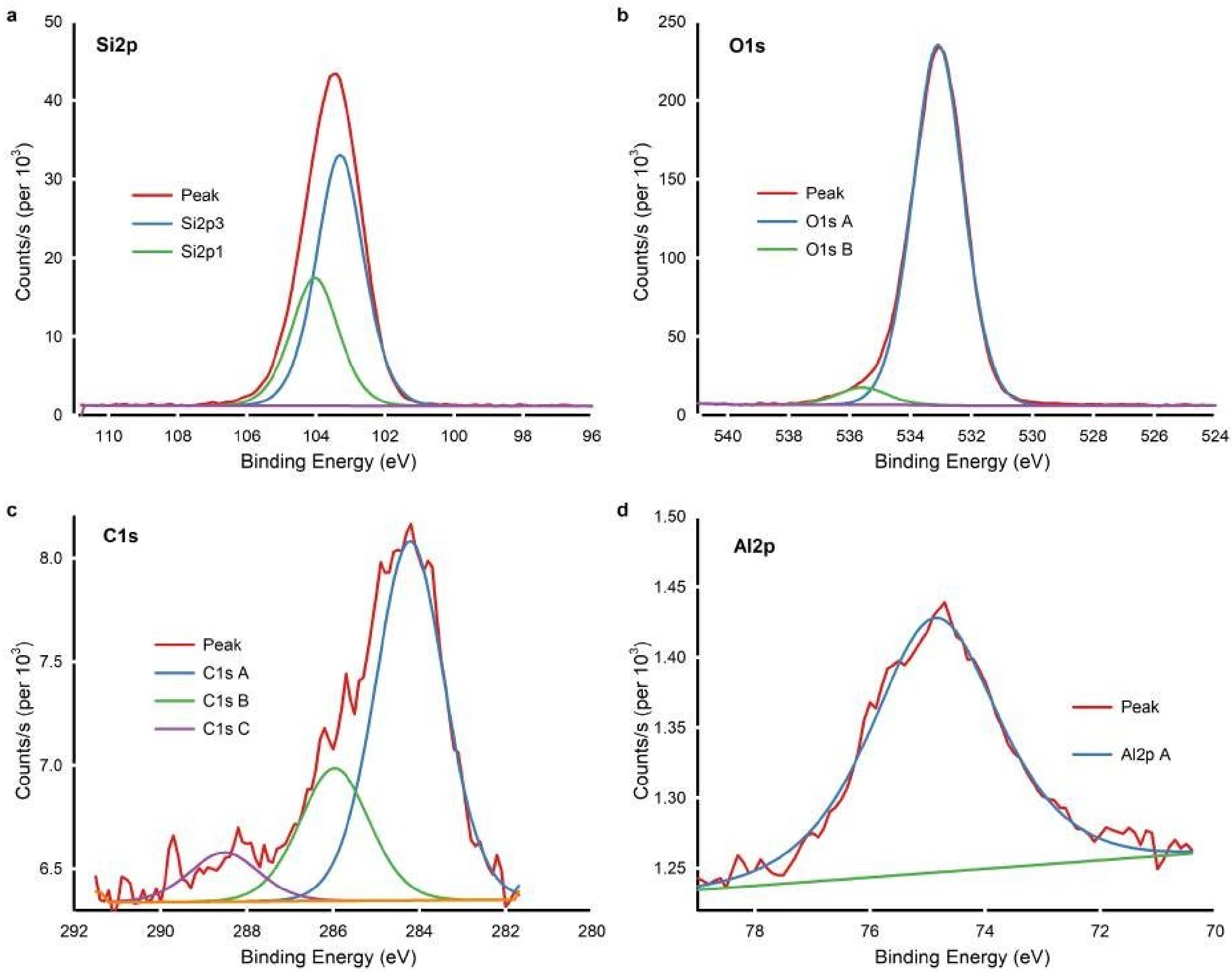
Supplementary Table 11 XPS elemental identi cation and quanti cation in M2

Name	Structure	Peak BE eV	FWHM eV	Area (P), CPS eV	Atomic %
Al2p	Al in zeolite	74.9	2.43	3200	1.1
Si2p3	Si in zeolite	103.1	1.97	92000	29.5
C1s A	C-C	284.5	1.74	10000	2.1
C1s B	C-O	285.9	1.74	5900	1.2
C1s C	C=O	287.7	1.74	2000	0.4
C1s D	O-C=O	289.3	1.74	1200	0.2
O1s A	O in zeolite	532.6	2.05	840000	64.8
Na1s	Na from NaOH	1072.5	2.61	13000	0.4
N1s	N from NH_3NO_3	401.5	3.35	1500	0.2

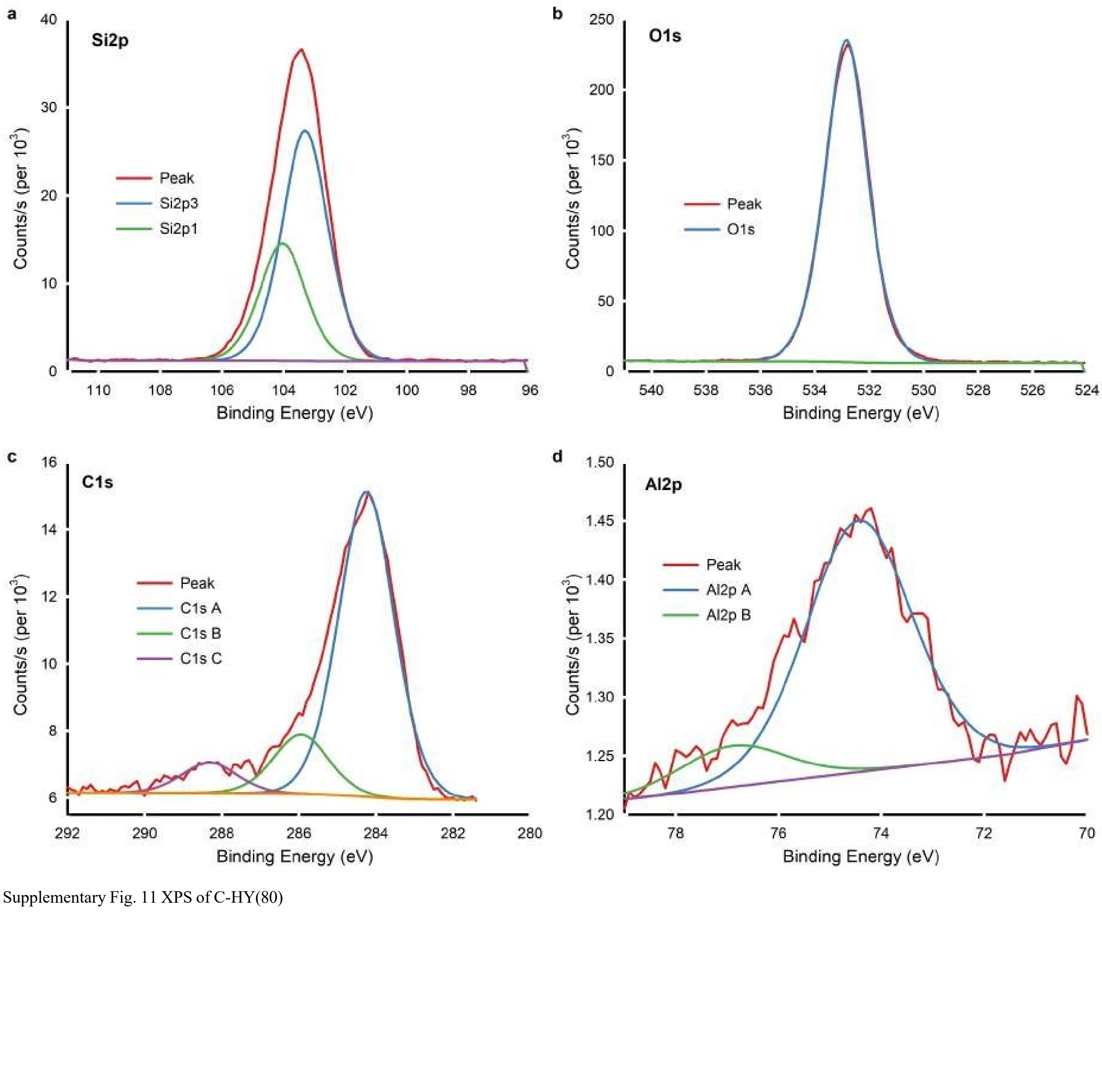
Abbreviations: BE, binding energy; FWHM, full-width-at-half-maximum; CPS, counts per second



Supplementary Fig. 9 XPS of HY(80)



Supplementary Fig. 10 XPS of R-HY(80)



Supplementary Fig. 11 XPS of C-HY(80)