Supporting Information

Investigating the interplay of hydrogen transfer, protolytic cracking, and dehydrogenation reactions over faujasite zeolites by using isooctane conversion as a probe

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S.1. Catalyst Characterization

(A) IPA-TPD profiles.

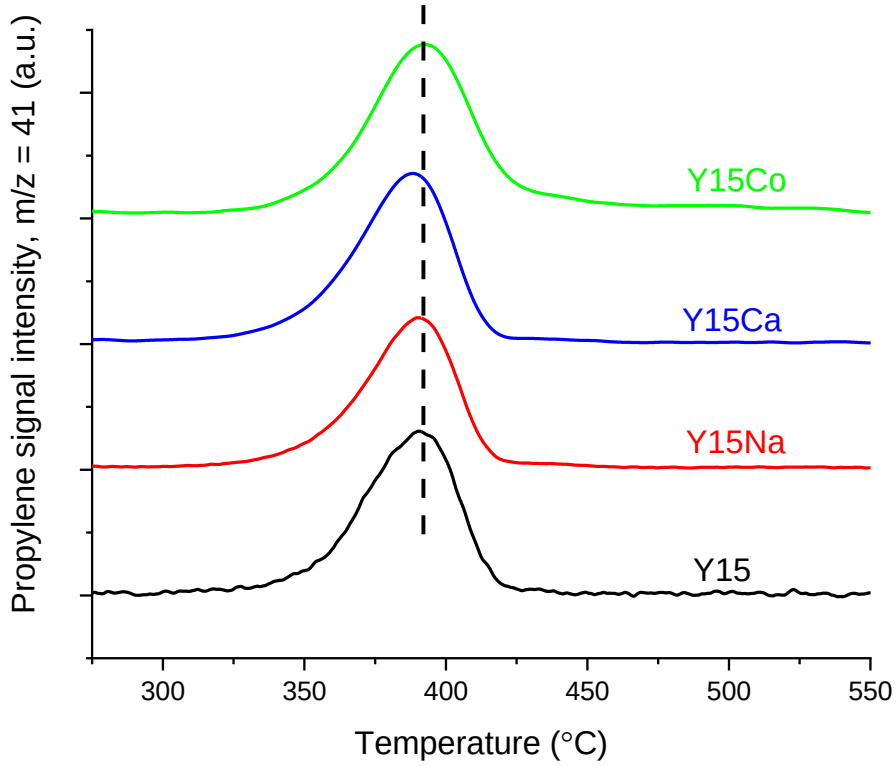

Figure S1. IPA-TPD profiles of Y15, Y15Na, Y15Ca, and Y15Co

(B) XRD. Powder X-ray diffraction (XRD) performed on a Rigaku Ultima IV diffractometer (Cu Kα radiation, λ =1.5406 Å) in the 2θ range of 5–70° under an operating voltage of 40 kV and a current of 44 mA. Each sample was pretreated in a vacuum oven at 80 °C to remove moisture.

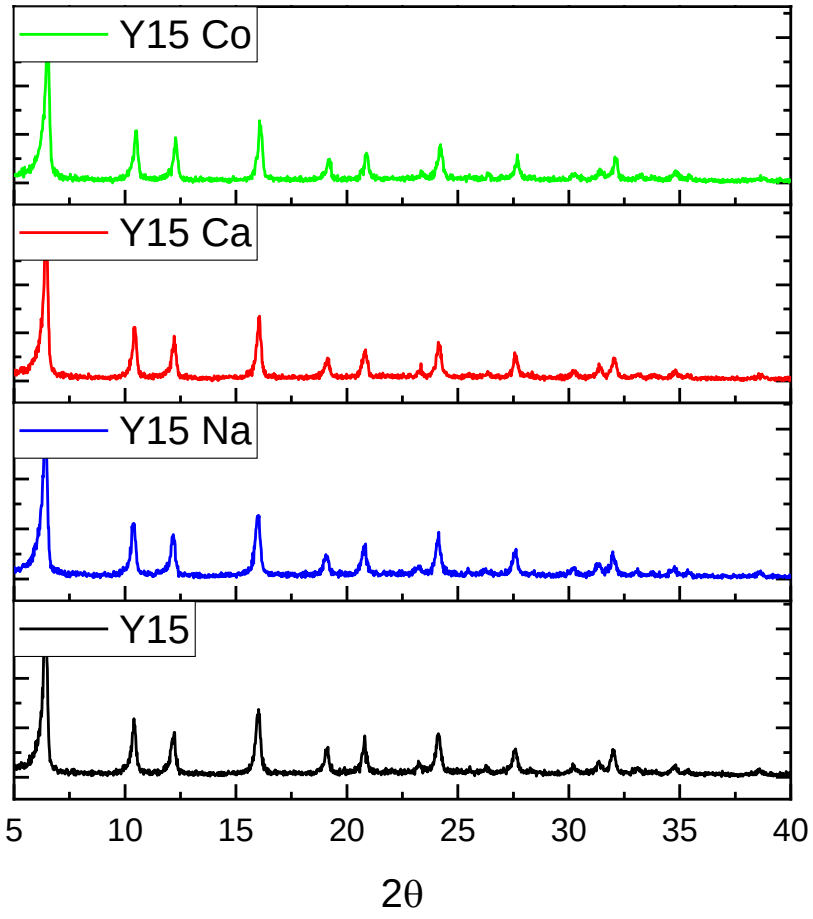

Figure S2. XRD patterns of Y15, Y15 Na, Y15 Ca, and Y15 Co

(C) SEM. The SEM images taken on a Thermo Fischer Quatro Environmental Scanning Electron Microscope (ESEM). The imaging was performed at 5kV accelerating voltage, 15,000x magnification, with an ETD detector.

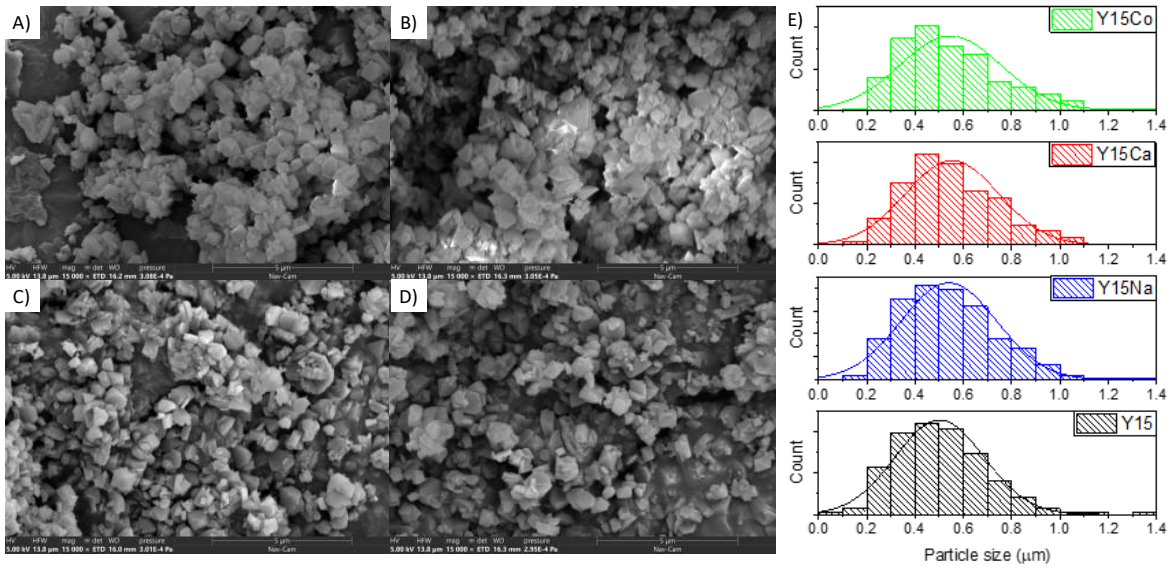

Figure S3. SEM images of Y15 (A), Y15 Na (B), Y15 Ca (C), Y15 Co (D), and the particle size distributions (E).

(D) Pore volume.

Table S1. Total pore volume, micropore volume, and mesopore volume of Y15, Y15Na, Y15Ca, and Y15Co.

	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
Y15	0.51	0.29	0.22
Y15Na	0.48	0.29	0.21
Y15Ca	0.49	0.28	0.21
Y15Co	0.49	0.28	0.21

S.2. Catalytic measurements.

Catalytic reactions over the zeolites were evaluated in a fixed-bed quartz tube reactor operated in either flow or micropulse mode by using a 6-port valve with constant loop volume of 500 μL. In flow-mode, a continuous and steady supply of reactants to the reactor was kept for a specified time on stream, whereas in micropulse mode, the 6-port valve set-up provides intermittent reactant injections to the reactor bed as the sample loop is filled with isooctane vapor in N_2. The reactant was fed using a syringe pump (KDS100, KD scientific) and vaporized before entering the N_2 stream (carrier gas) with the aid of heating tapes.

(A) Isooctane Cracking Product Distribution

Table S2. Product selectivity (mol%) isooctane cracking over Y15 zeolite, as well as the Na-,Ca- tritrated Y15 at varying conversion. Reaction conditions: Pulse mode, 2.7 kPa partial pressure of isooctane, 400 C, 1 atm

Sample zeolite	Conversion (%)	Molar selectivity (%)				
		C1	C3=	C4 (iC4)	C4= (iC4=)	C5+
Y15	15	25	25	13 (12)	34 (28)	3
	13	24	24	14 (14)	34 (28)	2
	12	26	26	12 (11)	34 (31)	2
	12	27	27	11 (11)	35 (32)	1
	11	26	26	12 (12)	34 (29)	2
	10	25	25	14 (13)	33 (31)	2
	9	25	25	13 (13)	34 (31)	2
	3	30	30	6 (6)	34 (28)	0
	3	31	31	7 (7)	34 (29)	0
	3	30	30	6 (6)	40 (33)	0
	2	30	30	6 (6)	38 (35)	0
	2	30	30	7 (7)	38 (32)	0
	1	30	30	7 (7)	38 (31)	0
Y15Na	16	28	28	6 (6)	38 (31)	0
	15	29	29	7 (7)	38 (33)	0
	15	29	29	6 (6)	40 (37)	0
	14	29	29	6 (6)	34 (28)	0
	13	29	29	6 (6)	34 (28)	0
	7	29	29	6 (6)	34 (31)	0
	7	23	23	14 (14)	35 (32)	1
	7	25	25	11 (11)	38 (32)	0
	6	24	24	13 (12)	38 (36)	0

	5	25	25	12 (12)	38 (34)	0
	4	26	26	11 (11)	38 (31)	0
	1	25	25	12 (11)	38 (33)	0
	1	14	14	28 (27)	38 (34)	5
	1	17	17	24 (24)	38 (36)	4
	1	18	18	23 (22)	38 (35)	4
	1	19	19	20 (19)	38 (32)	4
	1	20	20	20 (19)	37 (34)	4
Y15Ca	8	14	14	26 (24)	42 (40)	3
	8	17	17	23 (22)	40 (36)	3
	8	17	17	22 (22)	40 (33)	4
	8	17	17	23 (22)	39 (34)	3
	7	19	19	20 (19)	39 (34)	3
	5	19	19	20 (19)	39 (34)	3
	3	13	13	26 (25)	45 (39)	2
	2	17	17	21 (21)	43 (37)	2
	2	18	18	19 (18)	42 (36)	1
	2	18	18	20 (19)	42 (37)	1
	2	19	19	18 (17)	42 (36)	1
	2	19	19	19 (18)	42 (37)	1

(B) Isooctane cracking reaction conditions comparisons with literature

Table S3. Isooctane conversion and reaction conditions of this work and those in the literature.

	This work	Brillis and Manos [20]	Beirnaert et al. [18]	Van Borm et al. [17]
Reaction temperature (K)	673	523-623	698-748	748
Isooctane partial pressure (kPa)	2.7	10-20	6.8 – 15 kPa	7
Isooctane conversion (%)	0.5-10	>90	10-55	15
Coke deposited (wt%)	-	10	1.5-3.5	-

(C) Isobutane Cracking

Table S4. Product selectivity (mol%) and conversion of isobutane cracking over zeolite Y with varying Si/Al. Reaction conditions: 400ºC, 50 mg, 3mL/min of reactant injected, 100 mL/min of N_2 inert flow. 1 atm. Pretreatment under N2 at 300 ºC for 2 hours.

	Product Selectivity		
	Y2.6	Y15	Y30
C_1	26%	14%	19%
$C_{3=}$	20%	14%	19%
$C_{4=}$	43%	64%	58%
C_5	10%	8%	5%
Conversion	0.033%	0.040%	0.020%
DH rate/PC rate	1.9	4.6	3.0

(D) 2-methylhexane Cracking

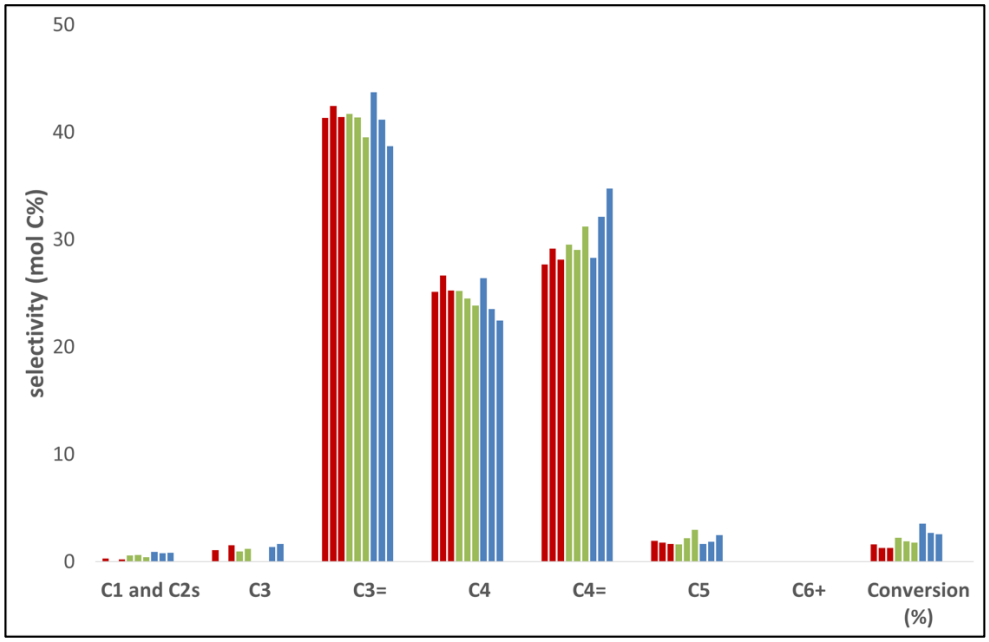

Figure S4. Products distribution and conversion of 2-methylhexane cracking over Y15 zeolite in flow mode. Red bars: 400 ºC, green bars: 410 ºC, blue bars: 420 ºC. Subsequent bar of a given color represents various iC8 feeding rate: 0.4, 0.6 and 0.8 mL/hr. Reaction conditions: 50 mg, 80 mL/min of He flow. Pretreatment under He flow at 300 ºC for 2 hours.

(E) 2,5-dimethylhexane cracking Cracking

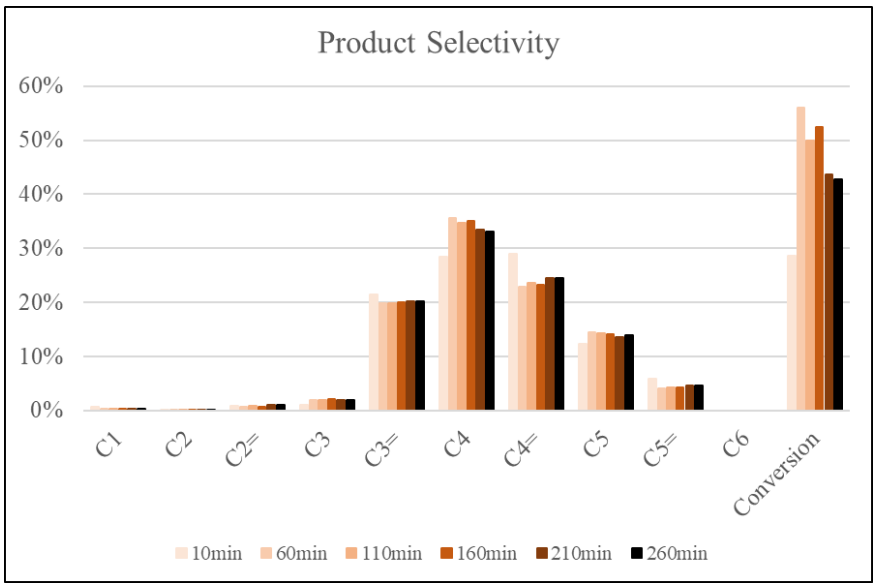

Figure S5. Product distribution (mol%) of 2,5-dimethylhexane catalytic cracking over zeolite Y15 in flow mode. Bar representation is relative to product distribution within progressing reactant time on stream. Reaction conditions: 400 ºC, 50 mg, 0.5 mL of reactant injected per hour, 100 mL/min of N_2 inert flow. Pretreatment under N_2 at 300 ºC for 2 hours.

(F) Isooctane cracking at different partial pressures as a function of time on stream

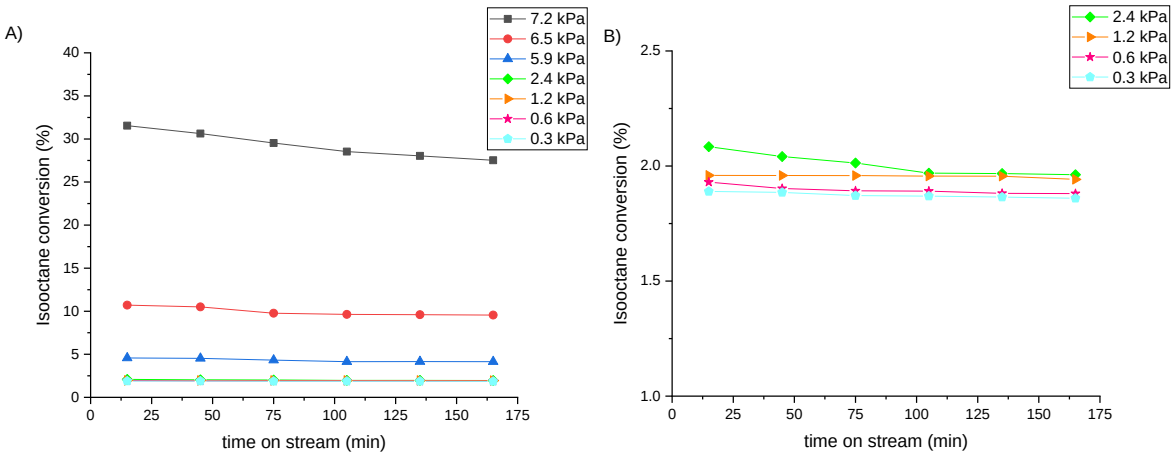

Figure S6. Isooctane conversion as a function of time on stream over LaY2.6 at A) varying isooctane partial pressure and B) first order partial pressure region. Reaction conditions: continuous flow reactor, 80 mL/min of carrier gas flow, 400ºC, 1 atm, 50mg.

S.3. Spent Catalysts Characterization

(A) TGA curves.

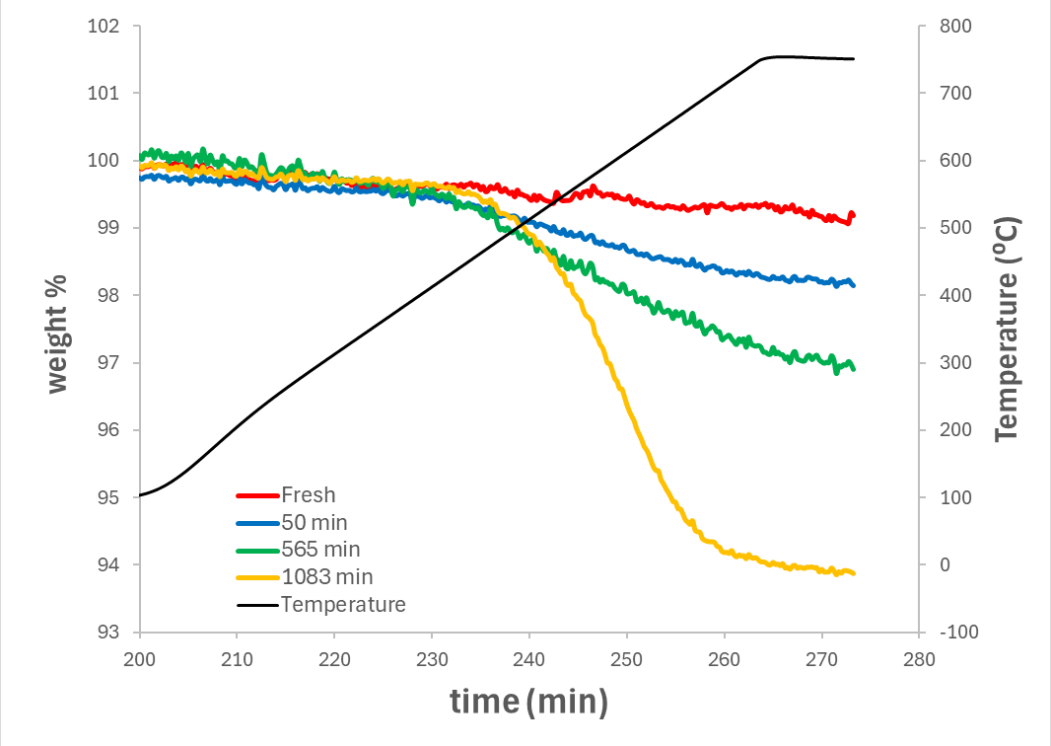

Figure S7. TGA curves of spent Y15Na at various time on stream. Reaction conditions: 5.5 mg catalyst, 400 ºC, 0.87 kPa isooctane partial pressure, continuous flow mode.