Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Selective dealkylation of alkyl polycyclic aromatic hydrocarbons towards innovative upgrading process of practical heavy oil

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Table S1 Physical properties of Al_2O_3

Al_2O_3	Surface area [*1] / $m^2\ g^{-1}$	Pore size [*2] / nm	Mesopore volume [*3] / $cm^3\ g^{-1}$
ALO-6	172	24	0.96
ALO-7	160	33	1.13
ALO-9	189	9.2	0.73
Purchased sample [*4]	210	7.1	0.50

[*1] Calculated by BET equation, [*2] mode value of pore size calculated by BJH method, [*3] calculated by BJH method, [*4] sample purchased from FUJIFILM Wako Pure Chemical Corp.

Table S2 Compositions of each chemical in the original (fed) VGO and the products in the dealkylation on SMA-3.

SMA-3								
		Time on stream						
	Original	2h	3h	4h	5h	6h	7h	8h
Quadric aromatics	0.95	0.05	0.07	0.06	0.05	0.04	0.01	0.06
Tricyclic aromatics + C7+	7.69	0.20	0.30	0.32	0.40	0.36	0.37	0.47
Tricyclic aromatics + C6	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Tricyclic aromatics + C5	0.00	0.07	0.12	0.07	0.06	0.05	0.05	0.08
Tricyclic aromatics + C4	0.29	1.88	1.69	1.64	1.68	1.64	1.47	1.68
Tricyclic aromatics + C3	0.31	1.44	1.36	1.27	1.30	1.20	1.20	1.28
Tricyclic aromatics + C2	0.06	0.87	0.74	0.69	0.62	0.57	0.54	0.60
Tricyclic aromatics + C1	0.00	0.18	0.10	0.01	0.07	0.05	0.02	0.03
Phenanthrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HDN	11.31	0.13	0.34	0.69	0.99	1.17	1.46	1.71
Dibenzothiophene	0.00	0.02	0.03	0.00	0.02	0.02	0.01	0.01
Bicyclic aromatics + C5+	10.97	0.26	0.37	0.25	0.41	0.45	0.30	0.58
Bicyclic aromatics + C4	0.00	0.43	0.37	0.23	0.23	0.18	0.17	0.20
Bicyclic aromatics + C3	0.02	1.00	0.78	0.75	0.69	0.66	0.64	1.20
Bicyclic aromatics + C2	0.00	0.98	0.80	0.67	0.65	0.60	0.52	0.56
Bicyclic aromatics + C1	0.00	0.50	0.42	0.38	0.36	0.31	0.30	0.32
Naphthalene	0.00	7.05	7.18	7.31	7.08	6.67	6.74	6.68
Tetralin	0.00	0.09	0.07	0.07	0.06	0.06	0.05	0.05
Alkylbenzenes	8.84	7.18	7.33	6.60	7.06	6.33	5.75	6.86
>C20 alkanes	55.64	36.95	41.03	43.34	45.98	45.10	44.47	47.23
C17-20 alkanes	3.26	7.97	8.30	9.13	9.72	9.65	9.50	10.10
C16 alkanes	0.30	2.62	3.98	4.98	5.61	5.70	6.11	6.46
C15 alkanes	0.23	2.92	4.63	5.43	5.85	5.52	5.59	5.71
C14 alkanes	0.08	0.85	1.38	1.39	1.49	1.36	1.32	1.41
C13 alkanes	0.04	0.92	1.28	1.30	1.27	1.15	0.94	1.08
C12 alkanes	0.02	1.58	1.65	1.51	1.38	1.24	0.94	1.05
C11 alkanes	0.00	2.14	2.14	1.74	1.63	1.33	1.10	1.08
C10 alkanes	0.00	3.02	2.61	2.20	2.10	1.71	1.62	1.48
C5-9 alkanes	0.00	11.65	8.72	7.79	7.19	6.40	6.03	5.56
Gas	0.00	7.04	2.21	0.20	0.00	0.48	2.76	0.00

Table S3 Compositions of each chemical in the original (fed) VGO and the products in the dealkylation on N631-L.

N631-L								
		Time on stream						
	Original	2h	3h	4h	5h	6h	7h	8h
Quadric aromatics	0.95	0.41	0.31	0.19	0.14	0.06	0.11	0.03
Tricyclic aromatics + C7+	7.69	0.00	0.04	0.07	0.14	0.11	0.18	0.18
Tricyclic aromatics + C6	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Tricyclic aromatics + C5	0.00	0.15	0.18	0.13	0.09	0.11	0.10	0.05
Tricyclic aromatics + C4	0.29	2.57	2.65	2.13	2.12	1.68	1.87	1.68
Tricyclic aromatics + C3	0.31	2.12	2.08	1.74	1.61	1.37	1.51	1.33
Tricyclic aromatics + C2	0.06	1.97	1.74	1.28	1.16	0.80	0.98	0.88
Tricyclic aromatics + C1	0.00	1.01	0.66	0.45	0.32	0.17	0.13	0.17
Phenanthrene	0.00	0.05	0.01	0.00	0.00	0.00	0.00	0.00
HDN	11.31	0.04	0.00	0.00	0.03	0.17	0.46	0.61
Dibenzothiophene	0.00	0.06	0.06	0.06	0.03	0.03	0.00	0.02
Bicyclic aromatics + C5+	10.97	0.88	0.81	0.46	0.39	0.31	0.25	0.28
Bicyclic aromatics + C4	0.00	1.24	0.90	0.70	0.53	0.37	0.42	0.37
Bicyclic aromatics + C3	0.02	1.67	1.60	1.34	1.12	0.86	0.95	0.98
Bicyclic aromatics + C2	0.00	1.95	1.49	1.27	1.12	0.88	0.94	0.80
Bicyclic aromatics + C1	0.00	0.98	0.74	0.65	0.56	0.47	0.49	0.44
Naphthalene	0.00	5.77	6.33	6.64	6.41	5.93	6.67	6.21
Tetralin	0.00	0.22	0.21	0.18	0.15	0.13	0.13	0.12
Alkylbenzenes	8.84	11.19	10.22	9.06	8.32	6.71	7.48	6.69
>C20 alkanes	55.64	21.57	30.03	33.85	35.56	34.01	39.25	37.64
C17-20 alkanes	3.26	6.98	7.98	8.42	8.93	8.35	9.50	9.18
C16 alkanes	0.30	2.29	2.70	3.47	4.05	4.04	5.23	5.25
C15 alkanes	0.23	1.62	2.16	3.28	3.94	3.91	4.93	4.75
C14 alkanes	0.08	0.71	0.89	1.28	1.45	1.30	1.58	1.53
C13 alkanes	0.04	0.72	1.08	1.38	1.52	1.40	1.51	1.50
C12 alkanes	0.02	0.83	1.47	1.95	1.98	1.78	1.88	1.60
C11 alkanes	0.00	1.31	2.15	2.49	2.35	2.04	2.20	1.96
C10 alkanes	0.00	2.38	3.30	3.51	3.25	2.76	2.92	2.44
C5-9 alkanes	0.00	15.40	14.50	13.04	11.06	9.52	10.01	8.23
Gas	0.00	13.90	3.71	0.98	1.67	10.71	0.00	5.07

Table S4 Compositions of each chemical in the original (fed) VGO and the products in the dealkylation on USY.

USY								
		Time on stream						
	Original	2h	3h	4h	5h	6h	7h	8h
Quadric aromatics	0.95	0.50	0.14	0.09	0.03	0.02	0.00	0.04
Tricyclic aromatics + C7+	7.69	0.00	0.08	0.12	0.30	0.46	0.44	0.52
Tricyclic aromatics + C6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tricyclic aromatics + C5	0.00	0.05	0.03	0.02	0.01	0.01	0.00	0.04
Tricyclic aromatics + C4	0.29	1.56	1.42	1.22	1.36	1.22	1.12	1.19
Tricyclic aromatics + C3	0.31	2.20	1.65	1.32	1.39	1.34	1.18	1.13
Tricyclic aromatics + C2	0.06	2.03	1.44	1.05	0.90	0.79	0.75	0.70
Tricyclic aromatics + C1	0.00	0.95	0.63	0.45	0.42	0.27	0.22	0.17
Phenanthrene	0.00	0.23	0.10	0.07	0.06	0.05	0.03	0.02
HDN	11.31	0.06	0.19	0.34	1.24	1.98	2.59	2.93
Dibenzothiophene	0.00	0.20	0.14	0.11	0.11	0.10	0.09	0.09
Bicyclic aromatics + C5+	10.97	0.24	0.12	0.12	0.22	0.37	0.39	0.89
Bicyclic aromatics + C4	0.00	1.01	0.53	0.35	0.24	0.22	0.11	0.14
Bicyclic aromatics + C3	0.02	2.12	1.37	1.44	1.41	1.28	1.05	0.99
Bicyclic aromatics + C2	0.00	4.23	2.51	1.82	1.64	1.40	1.15	1.04
Bicyclic aromatics + C1	0.00	3.62	1.92	1.27	1.14	1.00	0.82	0.70
Naphthalene	0.00	6.51	6.44	5.83	6.68	6.74	6.09	5.80
Tetralin	0.00	0.05	0.10	0.10	0.12	0.13	0.11	0.10
Alkylbenzenes	8.84	19.35	14.77	9.92	10.48	9.26	8.50	7.94
>C20 alkanes	55.64	10.72	29.15	26.50	36.83	41.78	41.89	42.40
C17-20 alkanes	3.26	4.76	7.29	6.68	8.14	8.73	8.59	8.35
C16 alkanes	0.30	1.63	2.49	2.59	3.74	4.40	4.55	4.60
C15 alkanes	0.23	1.20	1.98	2.12	2.74	2.97	2.81	2.56
C14 alkanes	0.08	0.64	0.71	0.70	0.75	0.74	0.62	0.61
C13 alkanes	0.04	0.62	0.79	0.68	0.67	0.65	0.51	0.46
C12 alkanes	0.02	0.69	0.91	0.77	0.74	0.67	0.56	0.43
C11 alkanes	0.00	0.99	1.36	1.06	1.11	0.99	0.71	0.65
C10 alkanes	0.00	1.36	1.92	1.41	1.46	1.27	1.07	0.86
C5-9 alkanes	0.00	9.26	10.66	6.65	7.95	6.82	5.88	4.84
Gas	0.00	23.20	9.17	25.19	8.10	4.36	8.18	9.81

Table S5 Compositions of each chemical in the original (fed) VGO and the products in the dealkylation on ZSM-5.

ZSM-5								
		Time on stream						
	Original	2h	3h	4h	5h	6h	7h	8h
Quadric aromatics	0.95	0.52	0.34	0.28	0.23	0.60	1.94	2.65
Tricyclic aromatics + C7+	7.69	0.50	0.87	1.46	2.25	4.00	5.77	6.67
Tricyclic aromatics + C6	0.00	0.01	0.02	0.06	0.08	0.09	0.10	0.06
Tricyclic aromatics + C5	0.00	0.20	0.15	0.15	0.14	0.13	0.11	0.09
Tricyclic aromatics + C4	0.29	1.98	1.63	1.60	1.51	1.30	1.19	0.96
Tricyclic aromatics + C3	0.31	1.43	1.08	0.97	0.91	0.89	0.67	0.59
Tricyclic aromatics + C2	0.06	1.00	0.59	0.44	0.44	0.38	0.31	0.25
Tricyclic aromatics + C1	0.00	0.28	0.07	0.03	0.02	0.01	0.01	0.00
Phenanthrene	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
HDN	11.31	0.62	1.67	3.46	5.58	7.46	7.70	8.35
Dibenzothiophene	0.00	0.09	0.05	0.04	0.03	0.03	0.02	0.01
Bicyclic aromatics + C5+	10.97	0.58	1.25	2.65	4.20	6.39	7.98	8.65
Bicyclic aromatics + C4	0.00	0.33	0.16	0.08	0.07	0.05	0.04	0.01
Bicyclic aromatics + C3	0.02	0.97	0.54	0.42	0.29	0.21	0.16	0.08
Bicyclic aromatics + C2	0.00	2.85	1.98	1.38	1.13	0.88	0.64	0.45
Bicyclic aromatics + C1	0.00	4.93	3.52	2.68	2.32	1.93	1.35	1.04
Naphthalene	0.00	8.60	8.00	7.14	6.34	5.64	4.28	3.58
Tetralin	0.00	0.10	0.12	0.10	0.09	0.07	0.05	0.05
Alkylbenzenes	8.84	54.72	49.79	44.52	40.82	39.13	30.30	27.68
>C20 alkanes	55.64	5.95	7.23	10.43	13.22	16.33	17.63	18.40
C17-20 alkanes	3.26	0.40	0.24	0.30	0.42	0.38	0.42	0.31
C16 alkanes	0.30	0.01	0.00	0.00	0.00	0.00	0.00	0.00
C15 alkanes	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C14 alkanes	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13 alkanes	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12 alkanes	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C11 alkanes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10 alkanes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5-9 alkanes	0.00	0.32	0.30	0.29	0.25	0.31	0.21	0.16
Gas	0.00	13.60	20.40	21.53	19.66	13.78	19.12	19.95

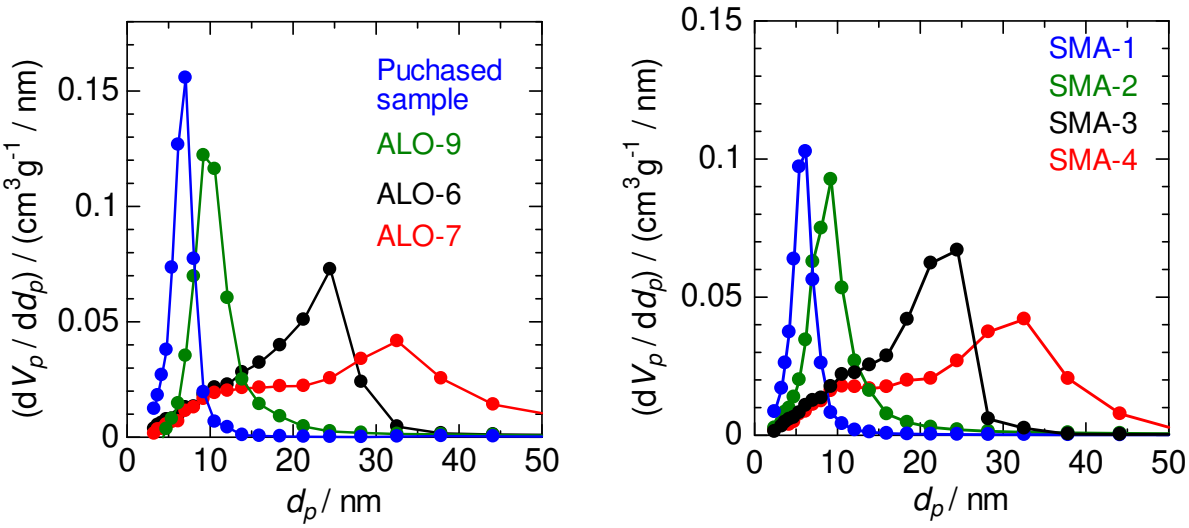


Figure S1 Mesopore size distributions of Al_2O_3 and SMAs determined by BJH method

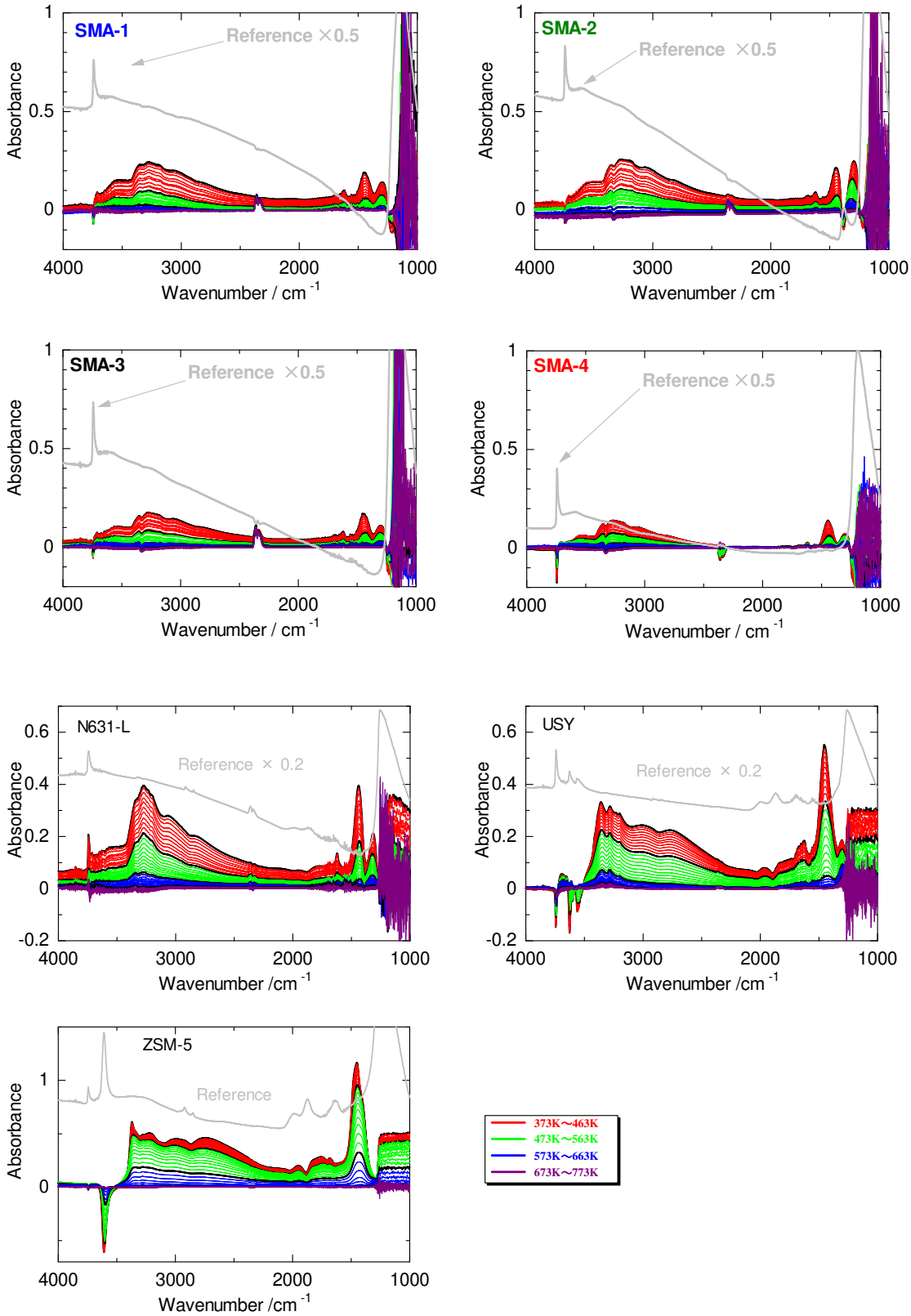


Figure S2 Difference spectra of IR $A(T)$-$N(T)$ [(spectrum after ammonia adsorption) – (spectrum before ammonia adsorption)] and spectrum at 373 K before ammonia adsorption as a reference.

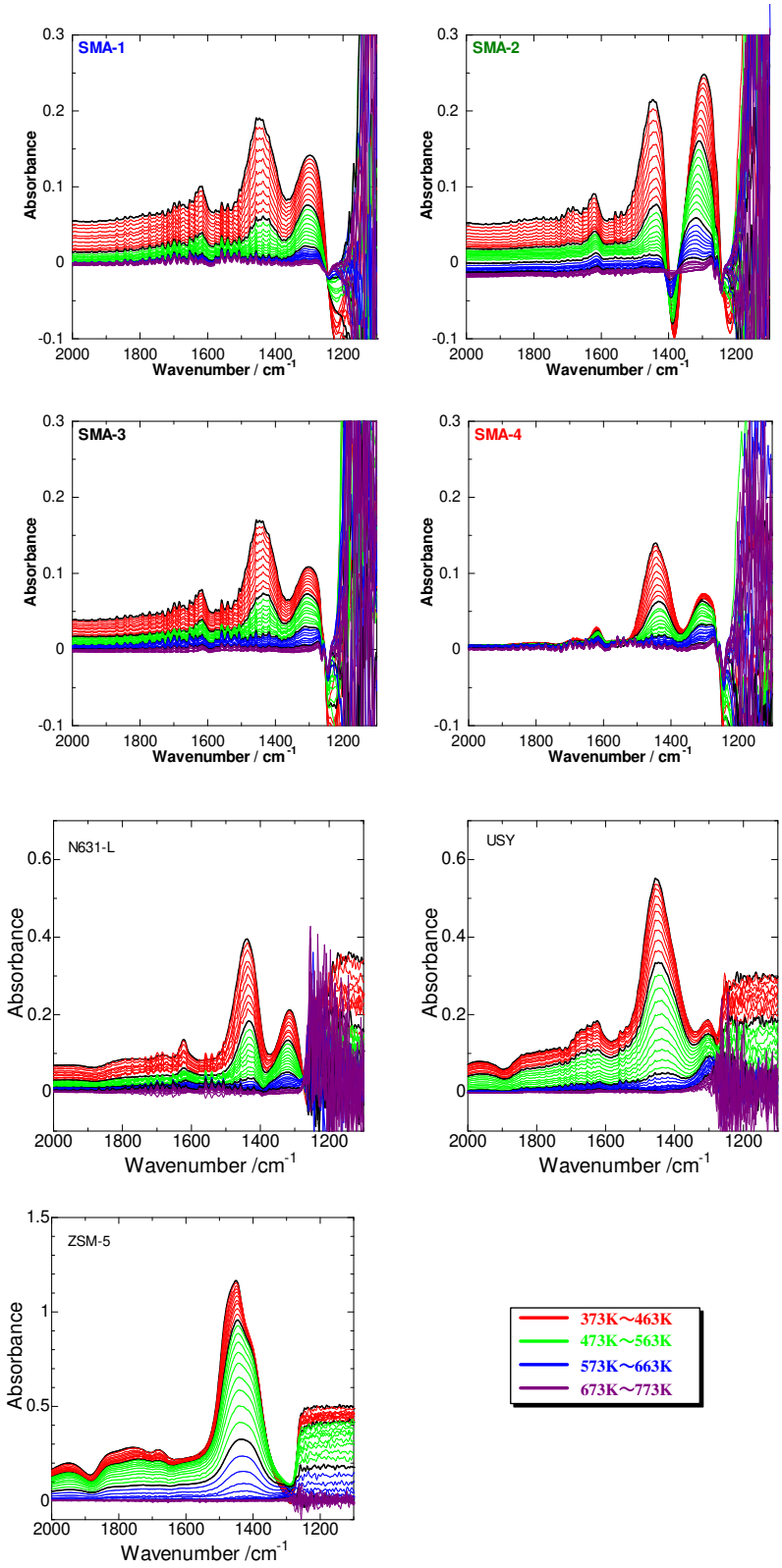


Figure S3 Difference spectra of IR $A(T)$-$N(T)$ [(spectrum after ammonia adsorption) – (spectrum before ammonia adsorption)] in region of bending vibration of ammonia adsorbed on zeolites (1100 – 2000 cm^{-1}).

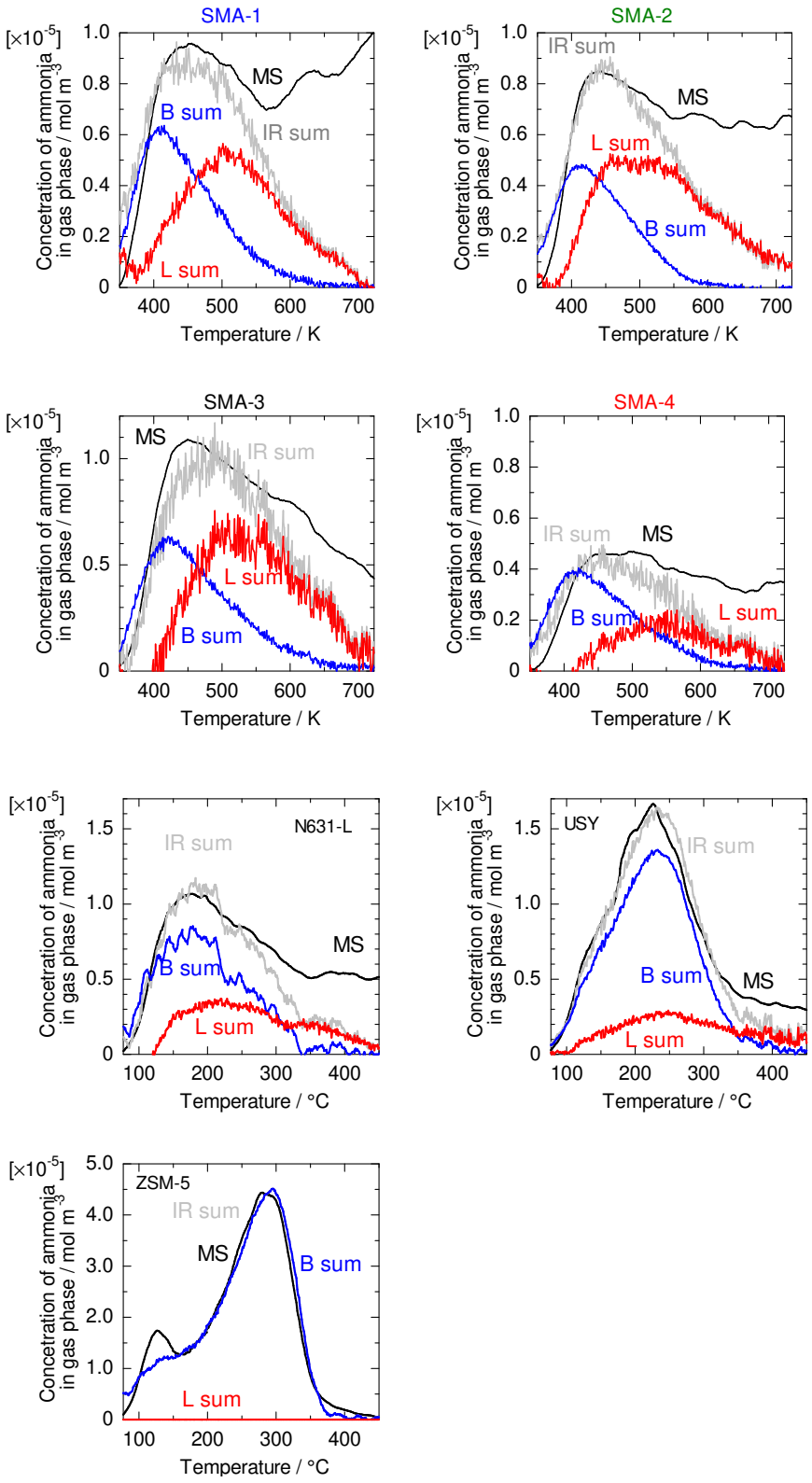


Figure S4 Fitting of IR- and MS-TPD calculating TPD spectrum of Brønsted and Lewis acid sites on zeolites. Black line: MS-TPD, blue line: IR-TPD of Brønsted acid sites (NH_4^+ (BAS)), red line: IR-TPD of Lewis acid sites (NH_3 (LAS)), grey line: the sum of NH_4^+ (BAS) and NH_3 (LAS).

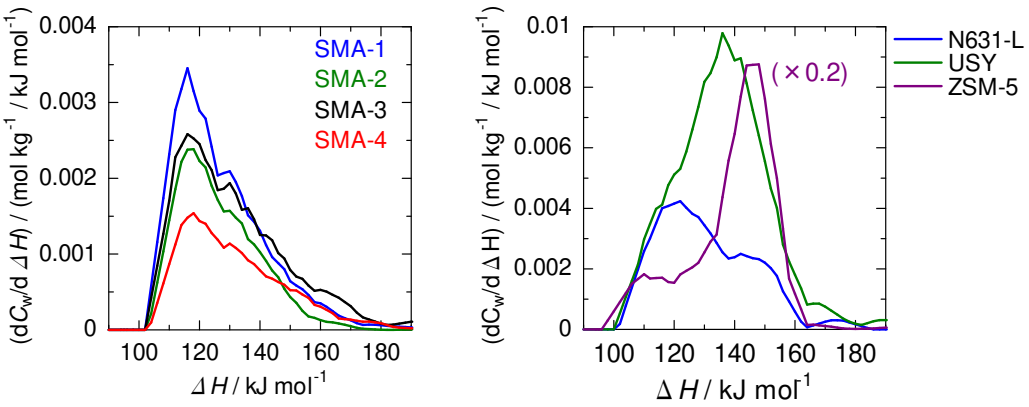


Figure S5 Distribution of Brønsted acid strength (enthalpy of ammonia desorption) of various solid acids estimated from shape of ammonia desorption profile of Brønsted acid sites in Figure S4.

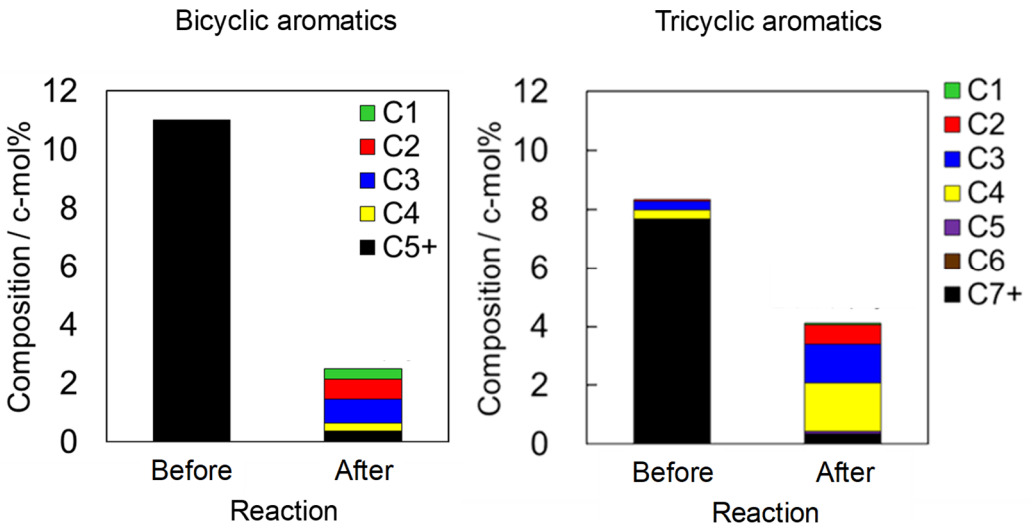


Figure S6 Composition averaged over 2-8 h of various carbon numbers of side chains in alkyl bicyclic and tricyclic aromatic hydrocarbons after the dealkylation over SMA-3.

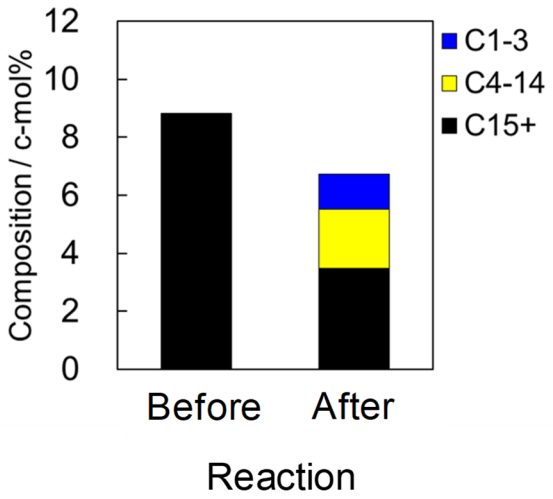


Figure S7 Composition averaged over 2-8 h of various carbon numbers of side chains in alkylbenzenes after the dealkylation over SMA-3.

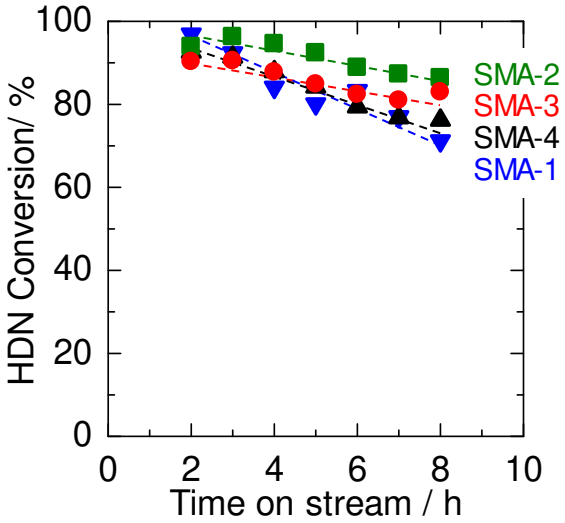


Figure S8 Time courses of HDN (hexadecylnaphthalene) conversion on SMAs in the dealkylation of APAHs in fed VGO at 723 K and LHSV = 5.7 $g_{VGO}\ g_{cat}^{-1}\ h^{-1}$.

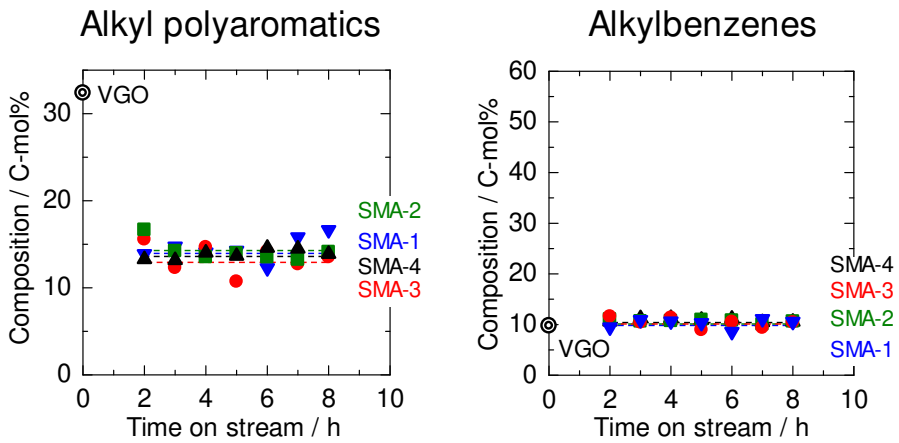


Figure S9 Time courses of composition of APAHs and alkylbenzenes in the dealkylation on SMAs in the dealkylation of APAHs in fed VGO at 723 K and LHSV = 5.7 $g_{VGO}\ g_{cat}^{-1}\ h^{-1}$.

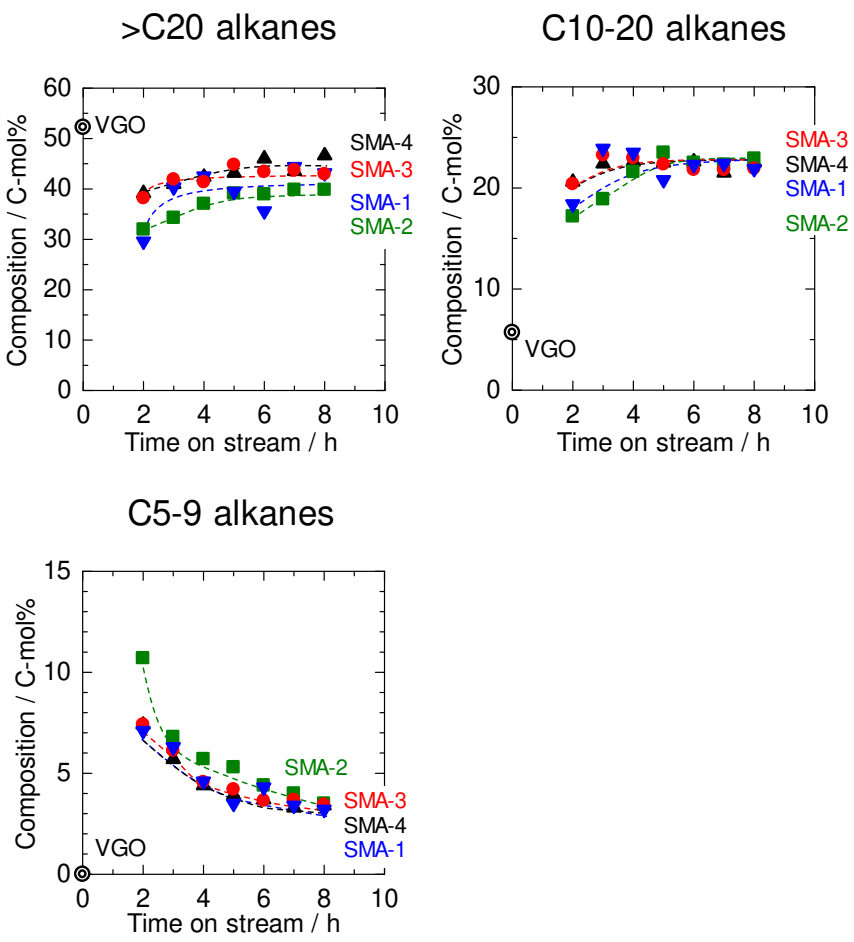
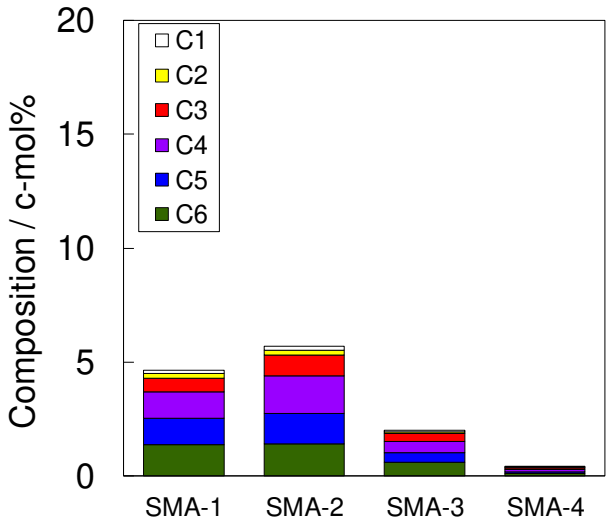


Figure S10 Time courses of composition of alkanes (>C20, C10-20, and C5-9) in the dealkylation on SMAs in the dealkylation of APAHs in fed VGO at 723 K and LHSV = 5.7 $g_{VGO}\ g_{cat}^{-1}\ h^{-1}$.



	SMA-1	SMA-2	SMA-3	SMA-4
C1-3 (%)	21	23	24	25
C4-6 (%)	82	80	79	78

Figure S11 Composition of light hydrocarbons averaged between 2-8h in the dealkylation on SMAs in the dealkylation of APAHs in fed VGO at 723 K and LHSV = 5.7 g_{VGO} g_{cat}^{-1} h^{-1}.

Figure S12 Total images of the reactions on SMA-3, N631-L, USY, and ZSM-5. The bracketed values are composition of the components (C(carbon)-mol %) in original VGO (left side) and in the products averaged over 5-8 h (right side). These images include presumption as stated below. APAHs and HDN were dealkylated into PAHs and alkanes (C10-20, C5-9, and light hydrocarbons), excluding alkanes (>C20). Alkyl groups in alkylbenzenes were cracked into alkanes (C10-20, C5-9, and light hydrocarbons). It is difficult to distinguish between alkanes (C10-20, C5-9, and light hydrocarbons) produced by the cracking of alkanes and alkyl groups in APAHs, HDN, and alkylbenzenes.