Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Evolution of confined species and its effects on catalyst deactivation and olefin selectivity in SAPO-34 catalyzed MTO process

Mingjian Luo,*[a,b] Hongyan Zang,[a] Bing Hu,[a] Baohui Wang,[a] Guoliang Mao,[a]

a. Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, P.R. China. E-mail: luomingjian@nepu.edu.cn, Tel.: +86 459 6507736

b. QiTaiHe BaoTaiLong Coal Chemical Co., Ltd., QiTaiHe 154000, P.R. China.

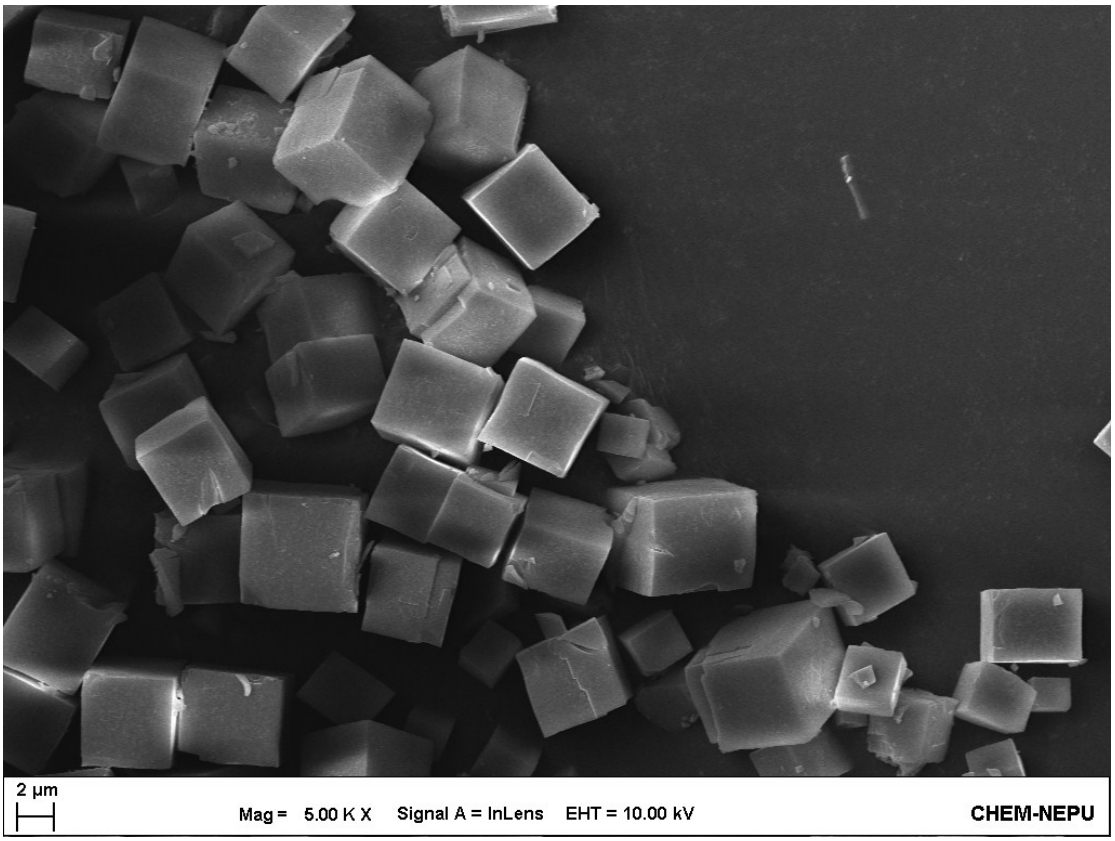

Figure S1. SEM image of SAPO-34 catalyst. SAPO-34 crystals are mainly in 4-5 µm size.

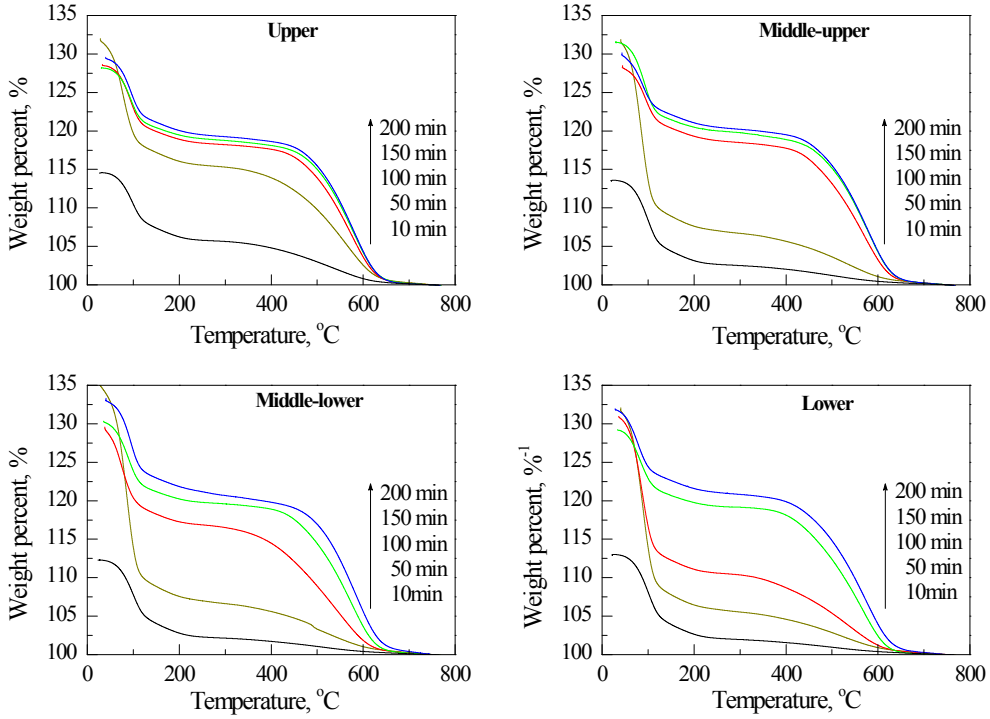

Figure S2. Thermogravimetric (TG) profiles of coked catalyst. The weight lost at low temperature (< 300 °C) can be ascribed to the loss of phisycal and chemical adsorbed water.[33, 34] The weight lost above 300 °C is related to the oxidation of coke confined in catalyst cages. Total weight losts are similar for all catalysts. Thus the diffusion of small molecules, e.g., H_2O, is not hindered by the confined species.

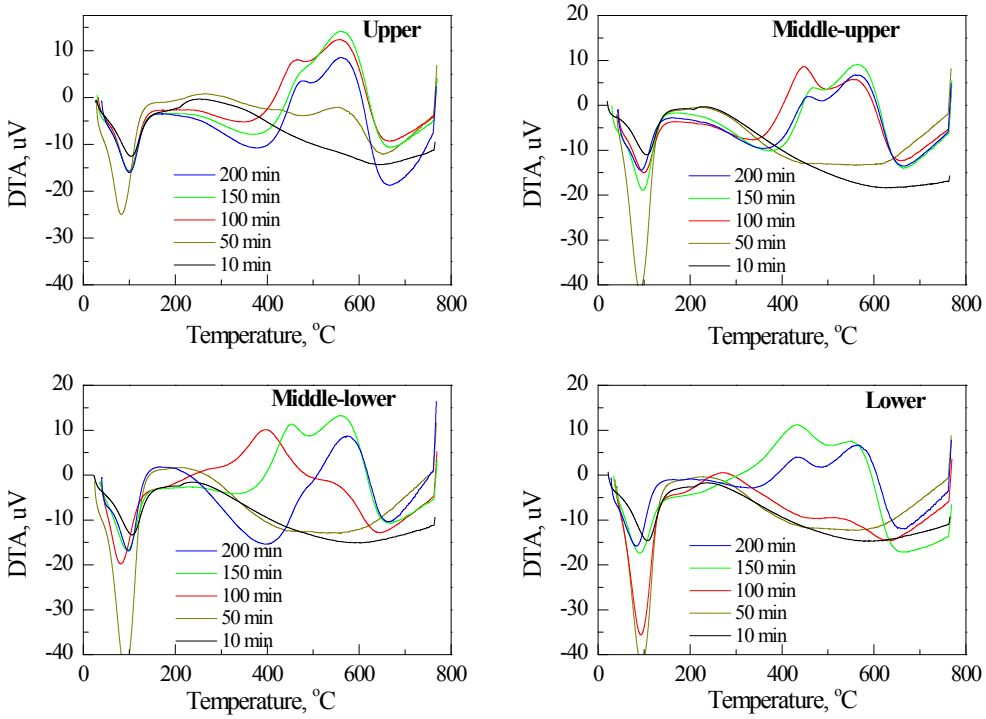

Figure S3. Differential thermal analysis (DTA) profiles of coked catalyst.

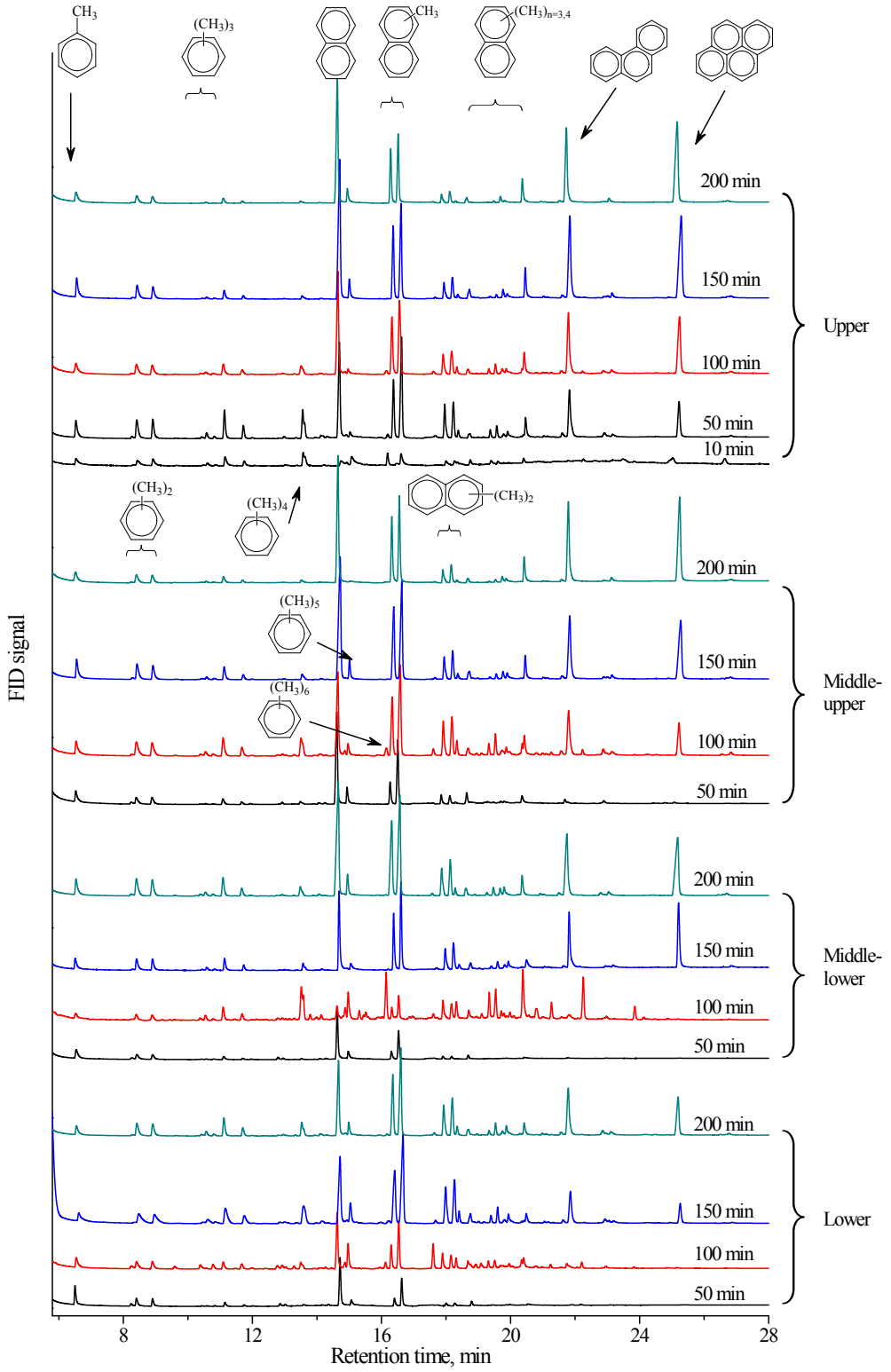

Figure S4. Gas chromatograms of confined species in coked catalyst.

Table S1. Percentage of confined species in coked catalyst, %.

Position	TOS	Methylbenzenes with different methyl number						methylnaphthalenes with different methyl number					Phena-	Methyl-	pyrene	Methyl
	min	1	2	3	4	5	6	0	1	2	3	4	threne	phenathrenes		pyrenes
Upper	10	5.72	9.18	12.16	13.82	12.41	5.06	6.58	7.85	6.01	4.69	0				
	50	2.91	6.94	7.65	6.72	1.85	0.55	13.87	22.45	12.57	3.48	3.85	8.78	1.73	6.11	0.54
	100	2.21	5.00	3.98	2.74	1.07	0.48	16.53	21.00	9.39	4.31	4.31	12.15	2.16	13.86	0.80
	150	4.67	4.47	2.23	0.82	2.56	0.04	19.80	19.41	6.55	2.25	4.49	13.24	1.51	17.21	0.74
	200	2.30	3.71	1.87	0.55	2.44	0.00	22.36	17.70	4.92	1.69	4.29	14.74	1.13	21.56	0.73
Middle-Upper	50	4.23	7.15	4.20	3.23	6.31	0.00	29.66	24.04	10.16	6.63	0.22	1.65	1.98	0.39	0.15
	100	2.42	6.62	6.57	5.53	2.07	1.19	11.41	21.03	13.69	7.42	4.16	7.97	3.72	5.31	0.88
	150	2.81	5.94	3.59	1.59	2.61	0.06	17.97	23.16	8.56	2.82	3.51	11.96	1.48	13.32	0.61
	200	2.08	3.92	2.26	0.88	0.41	0.00	19.94	20.98	6.53	2.24	4.40	14.93	1.13	19.55	0.75
Middle-Lower	50	8.57	11.27	4.94	4.90	5.22	0.00	30.56	21.50	10.38	0.70	1.18	0.59	0.18	0.00	0.00
	100	1.82	3.12	6.67	12.69	7.57	6.27	2.46	8.45	12.73	12.76	13.73	1.41	9.44	0.55	0.33
	150	2.90	5.62	4.60	2.10	1.26	0.14	13.02	23.47	12.37	3.12	3.35	11.51	1.79	13.96	0.79
	200	2.29	5.74	5.00	2.42	2.61	0.11	17.37	23.82	9.83	3.46	3.18	10.20	1.48	11.81	0.66
Lower	50	11.39	13.17	5.56	5.46	4.22	0.00	28.79	20.62	7.51	1.05	1.44	0.58	0.22	0.00	0.00
	100	3.01	5.75	7.67	7.19	7.64	1.38	12.46	15.25	17.28	10.98	6.34	1.82	2.97	0.16	0.09
	150	2.03	6.12	8.01	6.35	3.53	0.53	11.82	24.55	16.48	7.29	1.54	5.74	2.48	3.18	0.34
	200	1.83	5.95	6.38	4.30	2.10	0.29	12.01	23.83	14.22	4.77	3.31	9.66	2.83	7.85	0.68

Table S2. Weight of confined species in coked catalyst, $mg/g_{catalyst}$.

Position	TOS min	Total coke	Methylbenzenes with different methyl number						methylnaphthalenes with different methyl number					Phena-threne	Methyl-phenathrenes	pyrene	Methyl pyrenes
			1	2	3	4	5	6	0	1	2	3	4				
Upper	10	56.4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	50	153.0	4.46	10.61	11.71	10.29	2.82	0.85	21.22	34.34	19.23	5.33	5.88	13.44	2.64	9.34	0.82
	100	182.1	4.03	9.10	7.25	4.99	1.96	0.87	30.11	38.24	17.10	7.84	7.84	22.13	3.94	25.24	1.46
	150	187.6	8.77	8.39	4.18	1.55	4.81	0.07	37.15	36.42	12.28	4.22	8.42	24.83	2.83	32.29	1.38
	200	192.5	4.43	7.14	3.60	1.07	4.70	0.00	43.05	34.07	9.47	3.25	8.25	28.37	2.17	41.51	1.41
Middle-Upper	10	25	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	50	66.9	2.83	4.78	2.81	2.16	4.22	0.00	19.84	16.08	6.79	4.44	0.15	1.10	1.33	0.26	0.10
	100	184.9	4.48	12.24	12.15	10.22	3.83	2.20	21.10	38.89	25.32	13.71	7.69	14.74	6.87	9.82	1.63
	150	197.7	5.56	11.75	7.09	3.15	5.16	0.12	35.53	45.79	16.92	5.57	6.95	23.64	2.93	26.33	1.20
	200	202.2	4.20	7.92	4.57	1.79	0.83	0.00	40.32	42.42	13.20	4.52	8.90	30.20	2.29	39.52	1.52
Middle-Lower	10	21.5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	50	66.4	5.69	7.49	3.28	3.25	3.47	0.00	20.29	14.27	6.89	0.47	0.78	0.39	0.12	0.00	0.00
	100	165.1	3.01	5.15	11.01	20.95	12.50	10.35	4.07	13.95	21.01	21.06	22.67	2.33	15.58	0.90	0.55
	150	195.8	5.67	11.00	9.01	4.11	2.47	0.27	25.50	45.96	24.22	6.10	6.55	22.55	3.51	27.34	1.54
	200	206.7	4.73	11.86	10.35	5.01	5.39	0.24	35.91	49.23	20.31	7.16	6.58	21.09	3.06	24.41	1.37
Lower	10	19.6	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	50	55.4	6.31	7.30	3.08	3.02	2.34	0.00	15.95	11.42	4.16	0.58	0.80	0.32	0.12	0.00	0.00
	100	103.6	3.12	5.96	7.95	7.45	7.92	1.43	12.91	15.80	17.91	11.37	6.57	1.89	3.07	0.17	0.09
	150	195.1	3.96	11.95	15.63	12.39	6.89	1.04	23.07	47.90	32.15	14.22	3.01	11.20	4.83	6.20	0.67
	200	208.2	3.82	12.38	13.28	8.95	4.38	0.60	24.99	49.61	29.60	9.94	6.88	20.10	5.89	16.35	1.42

Table S3. Methanol conversion and product selectivity, %.

	0.8 g catalyst						0.4 g catalyst				0.2 g catalyst		
TOS,min	10	50	100	150	200	200[a]	10	50	100	100[a]	10	50	50[a]
Methanol conversion	99.97	99.95	99.95	99.91	97.01		99.95	99.96	60.02		99.98	99.96	
Methane	1.47	1.63	1.72	1.61	0.53	1.49	1.22	1.28	0.32	3.61	0.90	0.36	1.93
Ethylene	15.68	19.89	26.95	33.16	11.26	31.62	19.58	26.78	2.12	24.14	24.20	4.52	24.37
Ethane	2.67	2.82	2.94	2.55	0.64	1.80	2.17	2.49	0.52	5.94	1.85	0.64	3.43
Propene	24.75	33.91	34.45	36.38	14.99	42.07	29.82	37.42	3.45	39.34	35.76	7.54	40.62
Propane	28.89	16.40	12.18	8.30	1.47	4.12	22.24	10.24	0.47	5.33	14.02	1.25	6.75
C_4 olefins	18.31	18.71	16.30	13.65	5.52	15.50	18.22	17.07	1.52	17.39	18.39	3.39	18.26
C_{5+}	8.20	6.60	5.41	3.99	1.22	3.41	6.71	4.66	0.38	4.29	3.56	0.87	4.67
Dimethyl ether	0.00	0.00	0.00	0.26	61.38		0.00	0.02	51.26		0.00	46.30	

a: Selectivity in hydrocarbons.