Supporting Information

Hierarchical ZSM-5 materials for an enhanced formation of gasoline-range hydrocarbons and light olefins in catalytic cracking of triglyceride-rich biomass

Hoan X. Vu [†,‡,], Matthias Schneider [†], Ursula Bentrup [†], Tung T. Dang [‡], Binh M. Q. Phan [‡], Duc A. Nguyen [‡], Udo Armbruster [†], Andreas Martin [†,*]*

[†]Leibniz Institute for Catalysis e.V. at the University of Rostock, Albert-Einstein-Str.29a, 18059 Rostock, Germany

[‡]Vietnam Petroleum Institute, 173 Trung Kinh ,Yen Hoa, Cau Giay, Hanoi, Vietnam

***Corresponding author:**

H. X. Vu; Tel.: +84 4 3784 3061. Fax: +84 4 3629 0107. E-mail: hoan.vu@catalysis.de or hoanvx.ctat@vpi.pvn.vn

A. Martin; Tel.: +49 381 1281246. Fax: +49 381 128151246. E-mail: andreas.martin@catalysis.de

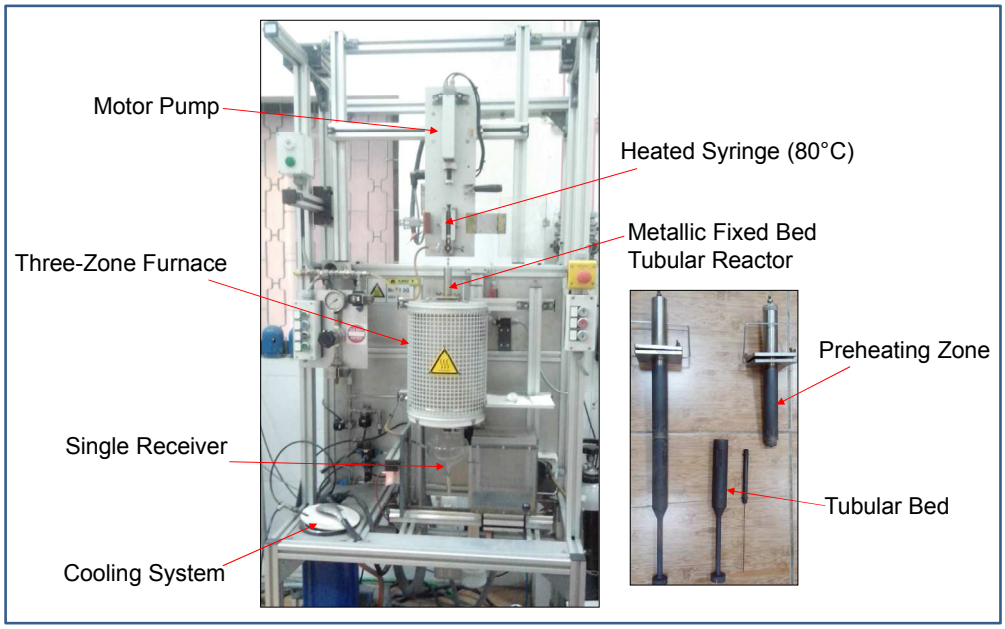

Figure S.1. Experimental set-up of SR-SCT-MAT unit.

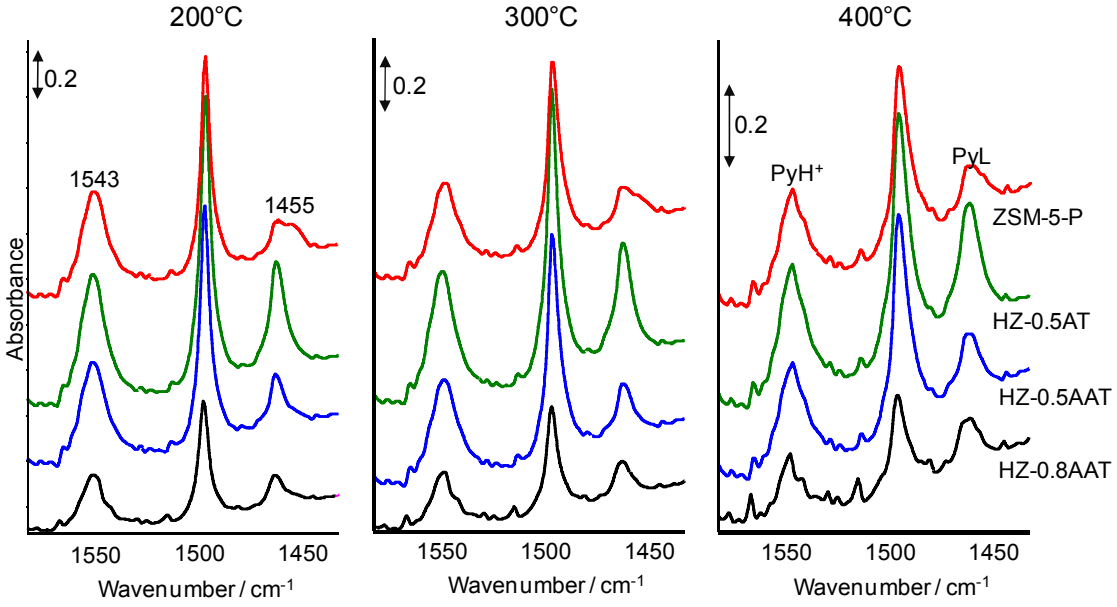

Figure S.2. py-IR spectra of ZSM-5-P, HZ-0.5AT, HZ-0.5AAT and HZ-0.8AAT samples after evacuation at 200, 300 and 400 °C.

Table S.1. Treatment parameters and physico-chemical properties of ZSM-5-P, HZ-xAT and HZ-xAAT materials.

Sample	NaOH (M)	HCl (M)	Yield[a] (%)	Si/Al[b]	S^{c}_{meso} (m^2/g)	S_{BET} (m^2/g)	V^{c}_{micro} (cm^3/g)	V_t (cm^3/g)	Total acidity[d] (mmol NH_3/g)
ZSM-5-P	-	-	100	11	110	373	0.113	0.22	1.24
HZ-0.1AT	0.1	-	90	10	103	363	0.107	0.29	1.31
HZ-0.1AAT	0.1	0.5	81	13	116	412	0.130	0.39	0.98
HZ-0.3AT	0.3	-	79	9	89	367	0.117	0.38	1.39
HZ-0.3AAT	0.3	0.5	67	16	124	445	0.144	0.49	0.85
HZ-0.5AT	0.5	-	74	7	131	411	0.110	0.52	1.26
HZ-0.5AAT	0.5	0.5	62	20	297	456	0.130	0.71	0.71
HZ-0.7AT	0.7	-	56	5	160	342	0.096	0.61	1.13
HZ-0.7AAT	0.7	0.5	45	32	252	462	0.121	0.79	0.50
HZ-0.8AT	0.8	-	48	4	104	224	0.063	0.41	1.22
HZ-0.8AAT	0.8	0.5	33	38	253	436	0.116	0.82	0.42

[a] recovery yield (defined as grams of solid received after treatment per gram of parent sample; [b]Si/Al molar ratios analyzed by AAS and ICP; [c] t-plot method; [d] NH_3-TPD. The specific BET surface area (S_{BET}) was calculated using adsorption data at a relative pressure (p/p_0) up to 0.012; the total pore volume (V_t) was estimated from the amount adsorbed at a p/p_0 of 0.976.

Table S.2. Fatty acid and elemental compositions of technical grade triolein and WCO.

Feedstock	Triolein	WCO
Fatty acid composition as wt% methyl esters		
Dodecanoic acid [C12:0]	-	1.2
Palmitic acid [C16:0]	1.1	37.2
Stearic acid [C18:0]	1.9	4.9
Oleic acid [C18:1]	75.6	48.8
Linoleic acid [C18:2]	21.4	7.9
Elemental composition, wt%		
Carbon	79.4	79.4
Hydrogen	12.0	12.6
Oxygen	8.6	7.8
Nitrogen	0	0.2

[Cx:y] where x is the number of carbon atoms and y is the number of double bonds.

Table S.3. Effect of reaction temperature on the composition of gaseous products in the catalytic cracking of triolein over ZSM-5-P and HZ-0.5AAT at a CTO ratio of 0.4 (g/g).

Sample	ZSM-5-P				HZ-0.5AAT			
Reaction temperature (°C)	400	450	500	550	400	450	500	550
Hydrogen	0.10	0.09	0.15	0.23	0.05	0.06	0.10	0.16
Methane	0.24	0.27	0.43	0.93	0.25	0.30	0.47	0.89
Ethane	0.55	0.50	0.88	1.65	0.40	0.44	0.78	1.43
Ethene	7.00	8.28	11.89	15.15	6.52	8.02	11.73	14.87
Propane	6.37	5.47	11.21	14.62	3.83	4.21	8.70	11.71
Propene	28.34	31.05	28.30	27.52	30.16	32.56	30.65	29.21
i-Butane	4.33	4.08	6.13	5.76	4.16	4.02	5.60	5.40
n-Butane	2.30	2.49	5.22	4.53	1.56	2.01	4.14	3.93
t-2-Butene	10.72	9.27	5.88	4.29	11.66	9.34	6.45	4.81
1-Butene	5.65	5.74	4.22	3.49	6.05	5.81	4.63	3.92
i-Butene	13.58	15.41	10.14	7.13	15.99	16.50	11.12	7.93
c-2-Butene	7.08	6.43	4.22	3.13	7.72	6.50	4.64	3.53
CO_2	6.27	3.92	3.37	3.28	4.60	3.15	3.10	3.64
CO	7.46	7.01	7.98	8.30	7.06	7.09	7.87	8.55

Table S.4. Effect of CTO ratios on the composition of gaseous products in the catalytic cracking of triolein over ZSM-5-P and HZ-0.5AAT at 450 °C.

Sample	ZSM-5-P				HZ-0.5AAT			
CTO ratio (g/g)	0.2	0.4	0.8	1.2	0.2	0.4	0.8	1.2
Hydrogen	0.13	0.09	0.13	0.20	0.08	0.06	0.10	0.17
Methane	0.62	0.27	0.33	0.53	0.61	0.30	0.42	0.66
Ethane	0.67	0.50	0.74	1.18	0.71	0.44	0.80	1.34
Ethene	6.71	8.28	8.55	7.45	5.94	8.02	8.72	7.17
Propane	2.65	5.47	14.66	22.20	1.74	4.21	12.60	21.92
Propene	29.49	31.05	23.45	17.74	30.39	32.56	25.00	16.95
i-Butane	1.16	4.08	12.37	16.87	0.97	4.02	12.60	19.36
n-Butane	1.55	2.49	6.13	8.22	1.23	2.01	5.41	8.30
t-2-Butene	10.02	9.27	6.10	4.12	10.32	9.34	6.29	3.98
1-Butene	6.38	5.74	3.83	2.60	6.41	5.81	3.98	2.47
i-Butene	13.01	15.41	10.97	7.35	13.44	16.50	11.28	7.00
c-2-Butene	6.96	6.43	4.25	2.89	7.15	6.50	4.42	2.80
CO_2	9.11	3.92	2.57	2.84	9.25	3.15	2.35	2.29
CO	11.54	7.01	5.91	5.82	11.77	7.09	6.03	5.60