Towards the Preparation of Binderless ZSM-5 Zeolite Catalyst: The Crucial Role of Silanol Nest

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Supporting information:

Table S1 Influence of different concentration of TPAOH on physical properties of the defective ZSM-5 zeolites

Sample[a]	C_{TPAOH} (%)	Temperature (℃)	V_{tol}^{b} ($cm^3\ g^{-1}$)	V_{micro}^{c} ($cm^3\ g^{-1}$)	S_{BET}^{d} ($m^2\ g^{-1}$)	S_{micro}^{c} ($m^2\ g^{-1}$)	S_{meso}^{c} ($m^2\ g^{-1}$)
P-D	—	—	0.22	0.11	386	261	125
E-D	—	—	0.26	0.09	357	207	150
E-D-T24	0.2	170	0.23	0.09	327	197	130
E-D-T24	0.6	170	0.19	0.09	349	216	133
E-D-T24	1.2	170	0.21	0.09	380	216	164
E-D-T24	2.1	170	0.21	0.10	400	236	164
E-D-T24	2.5	170	0.22	0.10	403	228	175

Table S2 Influence of different alkali treatment temperature on physical properties of the defective ZSM-5 zeolites

Sample[a]	C_{TPAOH} (%)	Temperature (℃)	V_{tol}^{b} ($cm^3\ g^{-1}$)	V_{micro}^{c} ($cm^3\ g^{-1}$)	S_{BET}^{d} ($m^2\ g^{-1}$)	S_{micro}^{c} ($m^2\ g^{-1}$)	S_{meso}^{c} ($m^2\ g^{-1}$)
P-D	—	—	0.22	0.11	386	261	125
E-D	—	—	0.26	0.09	357	207	150
E-D-T24	2.1	150	0.24	0.10	400	230	170
E-D-T24	2.1	170	0.21	0.10	400	236	164
E-D-T24	2.1	200	0.24	0.10	403	226	177

Table S3 Influence of different alkali treatment time on physical properties of the defective ZSM-5 zeolites

Sample[a]	C_{TPAOH} (%)	Temperature (℃)	V_{tol}[b] (cm^3 g^{-1})	V_{micro}[c] (cm^3 g^{-1})	S_{BET}[d] (m^2 g^{-1})	S_{micro}[c] (m^2 g^{-1})	S_{meso}[c] (m^2 g^{-1})
P-D	—	—	0.22	0.11	386	261	125
E-D	—	—	0.26	0.09	357	207	150
E-D-T22	2.1	200	0.23	0.10	396	223	173
E-D-T24	2.1	200	0.24	0.10	403	226	177
E-D-T26	2.1	200	0.23	0.10	395	221	174
E-D-T28	2.1	200	0.25	0.10	400	223	177
E-D-T30	2.1	200	0.25	0.10	403	225	178

[a]Sample codes: E-D-TXX (TXX-TPAOH treat time)
[b] V_{total} was determined from the amount of N_2 adsorbed at $p/p_0 = 0.99$
[c] *t*-plot method applied to the N_2 isotherm
[d] BET method applied to the N_2 isotherm

Table S4 SiO_2/Al_2O_3 molar ratio of the different commercial ZSM-5 zeolites

Sample[a]	SiO_2/Al_2O_3
P-C	24
E-C	31
E-C-2.1%T	30
E-C-2.1%T-Al	30

[a] Determined by XRF

Table S5 roperties of the different defective ZSM-5 zeolites.

Samples	Particle Size (nm)	Acidic by strength (mmol/g) [a]			
		Weak/Total	Medium/Total	Strong/Total	Total
P-D	211	0.056 (42.9%)	0.030 (22.9%)	0.044 (34.2%)	0.130
P-D-T	—	0.030 (32.2%)	0.032 (33.9%)	0.032 (33.9%)	0.094
P-D-T-E	—	0.028 (48.7%)	0.017 (30.4%)	0.012 (24.4%)	0.057
E-D	209	0.047 (51.0%)	0.022 (24.5%)	0.022 (24.5%)	0.091
E-D-2.1%T	168	0.042 (45.6%)	0.023 (24.4%)	0.028 (30.0%)	0.093
E-D-2.1%T-Al	205	0.058 (45.1%)	0.031 (23.7%)	0.039 (31.2%)	0.128

[a] Density of the acid sites, assorted according to the acid strength, determined by NH_3-TPD.
Weak: NH_3 desorbed at 120-250℃;
Medium: NH_3 desorbed at 250-350℃;
Strong: NH_3 desorbed at 350-550℃.

Table S6 physical and chemistry properties of the different defective ZSM-5 zeolites

Sample	P-D-T	E-D-2.1%T-Al
$\boldsymbol{V}_{tol}$ (cm^3 g^{-1})	0.25	0.23
$\boldsymbol{S}_{BET}$ (m^2 g^{-1})	396	407
Relative crystallinity (%)	99%	100%
n-hexane conversation -650℃ (%)	85.9%	62.5%
$S_{Ethylene+Propylene}$ -650℃ (%)	54.6%	49.6%

Table S7 SiO_2/Al_2O_3 molar ratio of the different defective ZSM-5 zeolites

Samples	SiO_2/Al_2O_3	
	Bulk[a]	Surface[b]
P-D	107	78
E-D	136	101
E-D-2.1%T	137	102
E-D-2.1%T-Al	102	65

[a] Determined by XRF
[b] Determined by XPS

Table S8 Al content in filtrate after alkaline treatment of defective ZSM-5 zeolites.

Sample[a]	Al content in filtrate (mg L^{-1})
E-D-2.1%T	0.02
E-D-2.1%T-Al	0.60

[a] Determined by ICP-OES

Table S9 Physical properties of the defective ZSM-5 zeolites

Sample[a]	$\boldsymbol{V}_{\mathrm{tol}}{}^{b}$ (cm^3 g^{-1})	$\boldsymbol{V}_{\mathrm{micro}}{}^{c}$ (cm^3 g^{-1})	$\boldsymbol{S}_{\mathrm{BET}}{}^{d}$ (m^2 g^{-1})	$\boldsymbol{S}_{\mathrm{micro}}{}^{c}$ (m^2 g^{-1})	$\boldsymbol{S}_{\mathrm{meso}}{}^{c}$ (m^2 g^{-1})
E-D-T2	0.25	0.13	404	300	104
E-D-T6	0.25	0.13	402	296	106
E-D-T12	0.25	0.12	408	289	119
E-D-T18	0.24	0.12	415	266	149
E-D-T24	0.24	0.10	403	226	177
E-D-T30	0.25	0.10	403	225	178

[a]Sample codes: E-D-TXX (TXX-TPAOH treat time)

[b] V_{total} was determined from the amount of N_2 adsorbed at $p/p_0 = 0.99$

[c] *t*-plot method applied to the N_2 isotherm

[d] BET method applied to the N_2 isotherm

Table S10 Conversion and products distribution of n-hexane catalytic cracking over different defective ZSM-5 zeolites[a]

Samples	**Conversion (%)**	**Selectivity (%)**								
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5^+	BTX
P-D-500℃	24.5	0.9	6.6	6.7	25.3	12.1	17.7	7.3	15.4	8.0
P-D-550℃	44.7	2.0	10.9	8.4	25.5	19.2	6.4	14.2	8.0	5.4
P-D-600℃	63.9	2.4	14.1	10.4	34.5	13.2	4.1	12.9	5.1	3.3
P-D-650℃	85.1	3.4	19.8	10.6	34.7	11.3	3.9	8.1	3.3	4.9
E-D-500℃	8.9	1.1	5.7	6.5	30.2	9.9	4.0	11.3	26.1	5.2
E-D-550℃	16.3	1.9	8.6	9.7	35.0	12.3	1.1	15.2	11.9	4.3
E-D-600℃	30.1	2.8	11.7	10.2	32.7	12.4	4.1	14.2	7.2	4.7
E-D-650℃	48.2	4.3	16.2	10.1	31.3	11.1	3.7	11.6	6.0	5.7
E-D-2.1%T-500℃	9.3	1.4	7.1	7.9	38.0	11.2	3.0	15.0	14.3	2.1
E-D-2.1%T-550℃	18.9	2.1	9.1	10.0	34.9	13.7	4.3	16.3	7.6	2.0
E-D-2.1%T-600℃	36.9	2.9	12.2	10.6	33.6	13.6	4.1	15.5	5.2	2.3
E-D-2.1%T-650℃	55.2	4.5	17.4	11.3	31.6	11.4	4.4	11.1	3.8	4.5
E-D-2.1%T-Al-500℃	11.2	1.2	6.7	7.6	36.4	11.1	2.9	13.8	16.1	4.2
E-D-2.1%T-Al-550℃	22.0	1.8	8.7	9.8	34.8	13.0	4.1	15.8	8.3	3.7
E-D-2.1%T-Al-600℃	40.2	2.7	12.2	11.1	34.1	11.8	4.9	13.5	5.3	4.4
E-D-2.1%T-Al-650℃	62.5	4.0	16.4	10.4	33.2	11.3	3.9	11.8	4.4	4.6

[a] Reaction conditions: T = 500°C, 550°C, 600 °C, and 650 °C, P = 101.33 kPa.

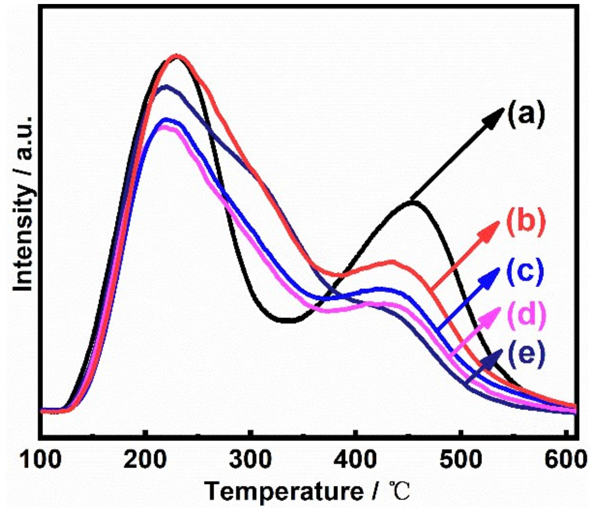

***Fig. S1** NH_3-TPD profiles of the effect over different types of aluminum source on the acidity of different defective ZSM-5 zeolites during alumination process.*

(a) P-D (defective ZSM-5 zeolite powder), (b) E-D-2.1%T-Al (E-D-2.1%T + 0.03 g Al_2O_3), (c) E-D-2.1%T-Al-1 (E-D-2.1%T + 0.03 g $C_9H_{21}AlO_3$), (d) E-D-2.1%T-Al-2 (E-D-2.1%T + 0.03 g $Al(NO_3)_3·9H_2O$), (e) E-D-2.1%T-Al-3 (E-D-2.1%T + 0.03 g $NaAlO_2$).

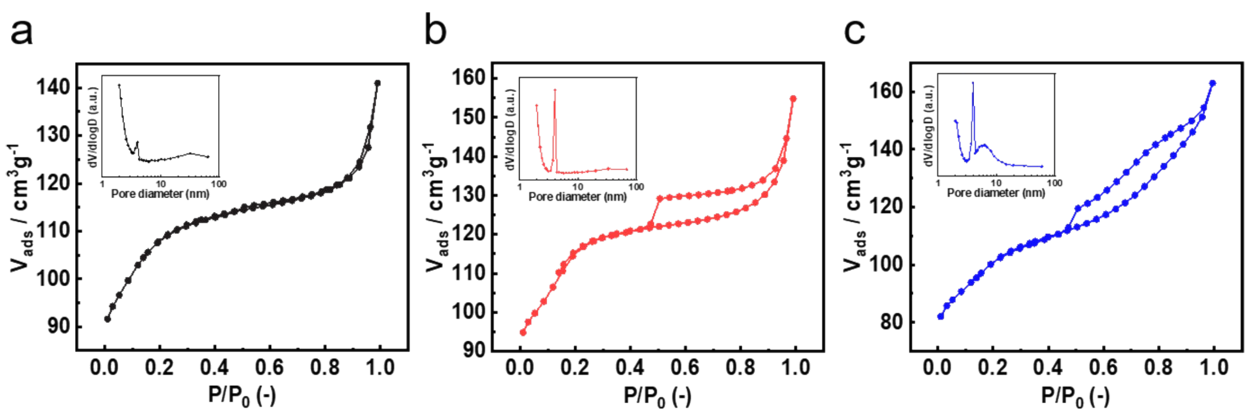

***Fig. S2** N_2-adsorption and desorption isotherms of the different defective ZSM-5 zeolites.*

(a) P-D (defective ZSM-5 zeolite powder), (b) P-D-T (alkali treatment of P-D), (c) P-D-T-E (Extrudate: P-D-T + 20% SiO_2 binder).

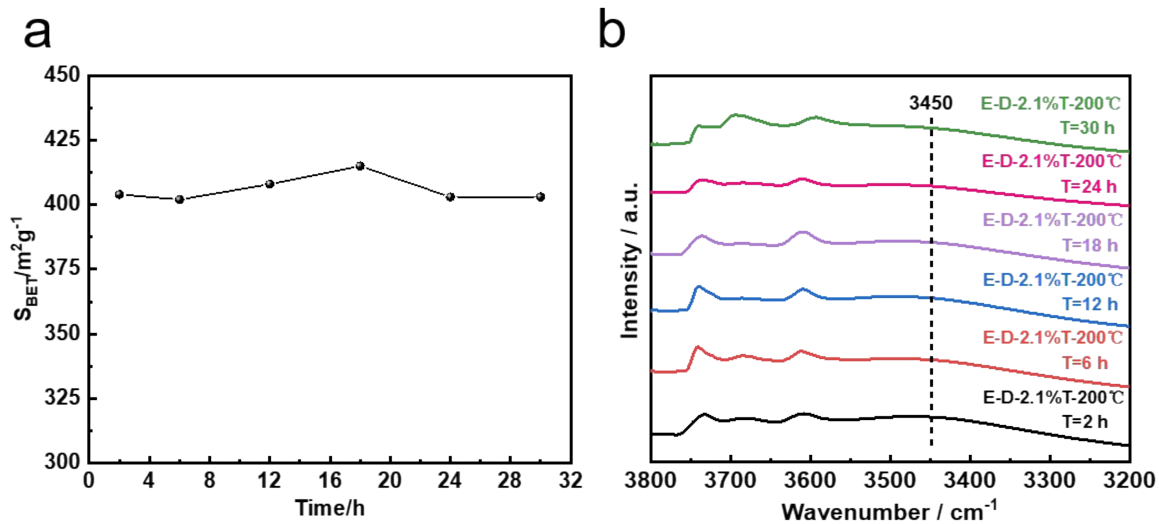

Fig. S3 (a) The time of TPAOH treatment versus the detailed changes of pore structure. (b) The time of TPAOH treatment versus the detailed changes of hydroxyl-nest and acidity.

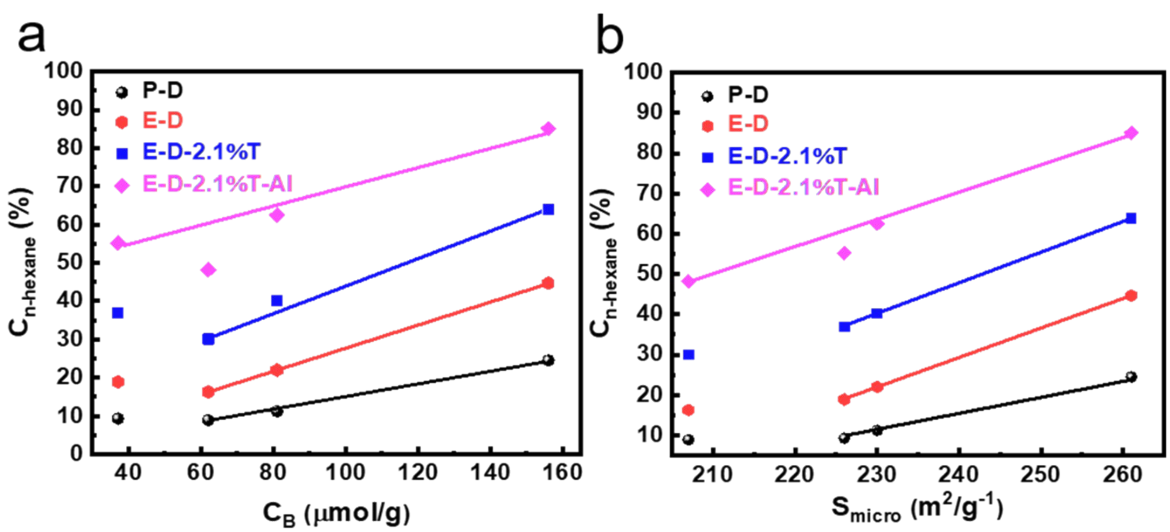

Fig. S4 Catalytic performance of the different defective ZSM-5 zeolites in the n-hexane catalytic cracking reaction.

P-D (defective ZSM-5 zeolite powder), E-D (Extrudate: P-D + 20% SiO_2 binder), E-D-2.1%T (2.1%TPAOH treatment of E-D), E-D-2.1%T-Al (E-D-2.1%T + 0.03 g Al_2O_3).

(a) Conversion of n-hexane ($C_{n\text{-hexane}}$) versus C_B derived from pyridine, (b) Conversion of n-hexane ($C_{n\text{-hexane}}$) versus the micropore surface area.