Supplementary Materials

Operando dual beam FTIR study of hydroxyl groups and Zn species over defective HZSM-5 zeolite supported zinc catalysts

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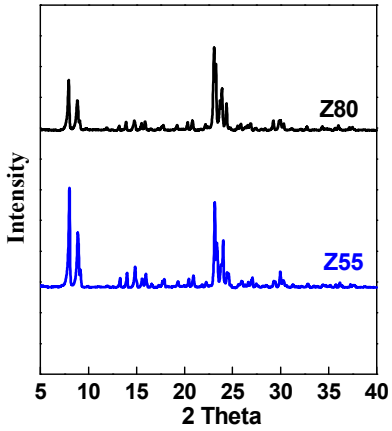


Figure S1. XRD patterns of the commercial ZSM-5 zeolite (CBV8014 coded as Z80) and defective Z55 sample.

Table S1. Textural properties of Z80 and defective Z55 zeolites.

Samples	SiO_2/Al_2O_3	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{toltal} (cm^3/g)	V_{micro} (cm^3/g)	Crystallinity (%)
Z80	80	405	332	0.25	0.13	100
Z55	55	395	362	0.20	0.13	89.84

Note: S_{BET}, BET surface area was calculated by the Brunauer-Emmett-Teller (BET) method; Vmicro, micropore volume was determined by t-plot; Vmeso, mesopore volume was determined by Vtotal-Vmicro. ZSM-5 zeolite with SiO_2/Al_2O_3 ratio of 80 purchased from Zeolyst company (CBV8014) was chosen as reference. The relative crystallinity was estimated by comparing the total XRD peak area of defective ZSM-5 zeolite sample in the range of 2 theta from 22 to 25° with that of the reference ZSM-5.

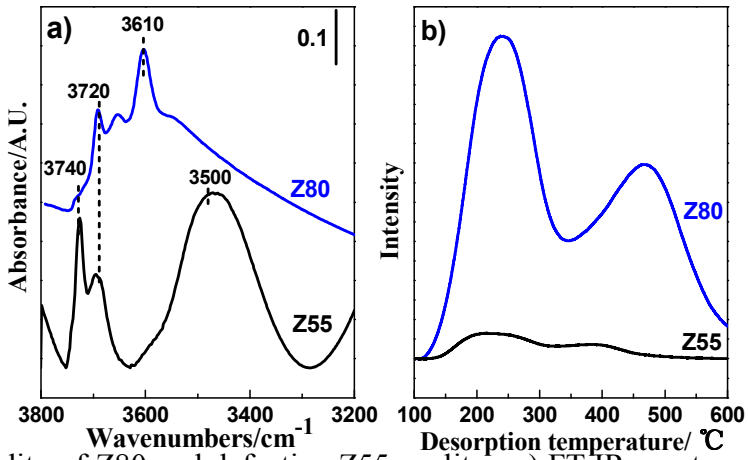
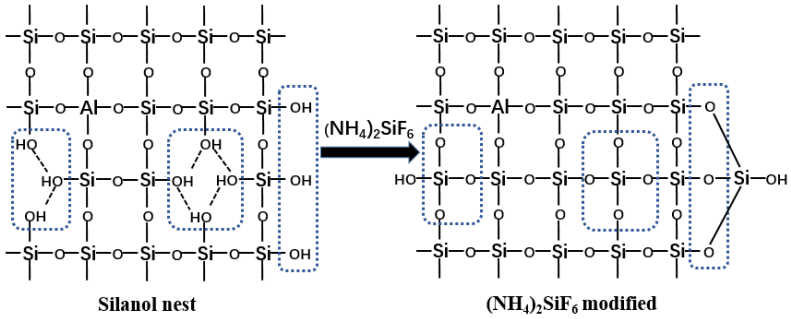


Figure S2. Acidity of Z80 and defective Z55 zeolites. a) FT-IR spectra of hydroxyl groups, b) NH_3-TPD profile.

The strength and total amount of acid sites over Z80 is considerably larger than defective Z55 zeolite. These differences are possibly caused by the synthesis method of zeolites such as template applied, crystallization time, silicon and aluminum source.



Scheme S1. Schematic diagram for repairing lattice defects of ZSM-5 zeolite by $(NH_4)_2SiF_6$.

Table S2. Products distribution of *n*-hexane aromatization on Zn/Z950 and Zn/Z950R catalysts in pulse micro-reactor.

Cat	Con.%	S%-C_1^O+C_2^O	S%-$C_2^=$-$C_4^=$	S%-C_3^O+C_4^O	S%- C_5+	BTX in C_5+ %
Z950	2.09	3.35	28.71	12.44	55.50	21.55
$Zn_{0.09}$/Z950	5.85	2.46	39.15	6.50	51.90	34.45
$Zn_{0.20}$/Z950	5.88	1.87	41.67	6.29	50.17	46.10
$Zn_{0.51}$/Z950	8.48	0.71	39.03	7.31	52.95	58.80
Z950R	2.64	3.41	24.62	17.88	54.09	17.51
$Zn_{0.10}$/Z950	6.19	3.72	31.02	14.38	50.89	20.00
$Zn_{0.20}$/Z950R	5.78	2.94	32.35	14.36	50.35	28.52
$Zn_{0.50}$/Z950R	7.89	2.41	34.98	10.65	51.96	26.34

Reaction conditions: T = 600 °C (Zn/Z950) and 500 °C (Zn/Z950R), P = 101.33 kPa.

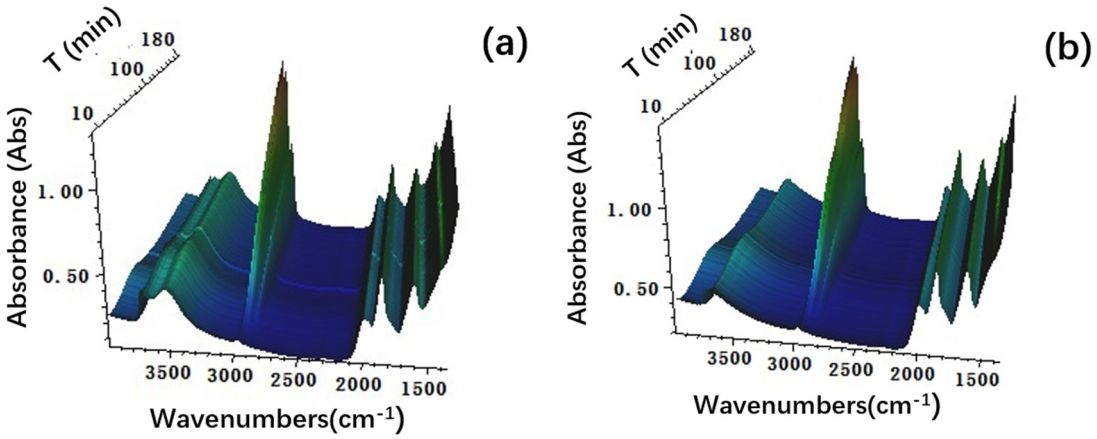


Figure S3. The overall three-dimensional FTIR profiles of *n*-hexane aromatization on Zn/Z950 (a) and Zn/Z950R (b) catalysts in 180 min. Reaction conditions: T = 300 °C, P = 101.33 kPa, *n*-hexane was carried into IR-cell reactor by N_2 (10mL/min), GHSV = 220 h^{-1}.