Supporting information for

Internal Defects-Oriented Dissolution: Controllable Evolution to Hollow ZSM-5 Nano-Structures

Yingrui Xu,[a] Weikun Lai,[a] Yunyun Dong ,[a] Zhou Chen, [a] Weiping Fang[a] and Xiaodong Yi,[a*]

a. National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China.

*Corresponding author: xdyi@xmu.edu.cn.

Table S1 Bulk and surface compositions of the samples

Samples	Si/Al ratio		
	XRF(Bulk)	EDX(Bulk)	XPS(Surface)
ZSM	81.8	90.2	16.9
ZSM-T	51.9	38.0	43.4
ZSM-N-D	37.4	25.8	59.3

Table S2 Assignment and relative intensities of the peaks in the ^{29}Si MAS NMR spectra of samples.

δ/ppm	Si site	Relative Peak Area/%		
		ZSM-5-A	ZSM-5-T	ZSM-5-N
~-104	$Si(OSi_{)3}OH$	11.4	7.4	9.1
~-108	$Si(OSi)_3Al$	2.6	0.9	2.8
~-111	$T_1Si(OSi)_4$	6.8	10.7	8.4
~-113	$T_2Si(OSi)_4$	31.5	47.4	30.8
~-115	$T_3Si(OSi)_4$	28.5	16.2	38.8
~-116	$T_4Si(OSi)_4$	19.2	17.5	10.2

Table S3 Notation of the samples and reacting conditions

Samples	Etching Media	Temp./ K	C[a]	LSR[b]	Time/min	Conditions
ZSM	-	453	-	-	1440	c
ZSM-T	TPAOH (a.q.)	443	0.5	7.5	4320	e
ZSM-N-S	NH_3 (a.q.)	353	1	100	480	d
ZSM-N-D	NH_3 (a.q.)	353	1	100	40	e
Silicalite-1	-	453	-	-	4320	c
Silicalite-1-H	NH_3 (a.q.)	353	1	100	40	e

a. Concentrations of the etching media (mol/L).
b. Liquid to solid ratio (mL/g).
c. Synthesized in sealed autoclaves.
d. Etched under static condition in open reactors.
e. Etched under vigorous stirring in open reactors.

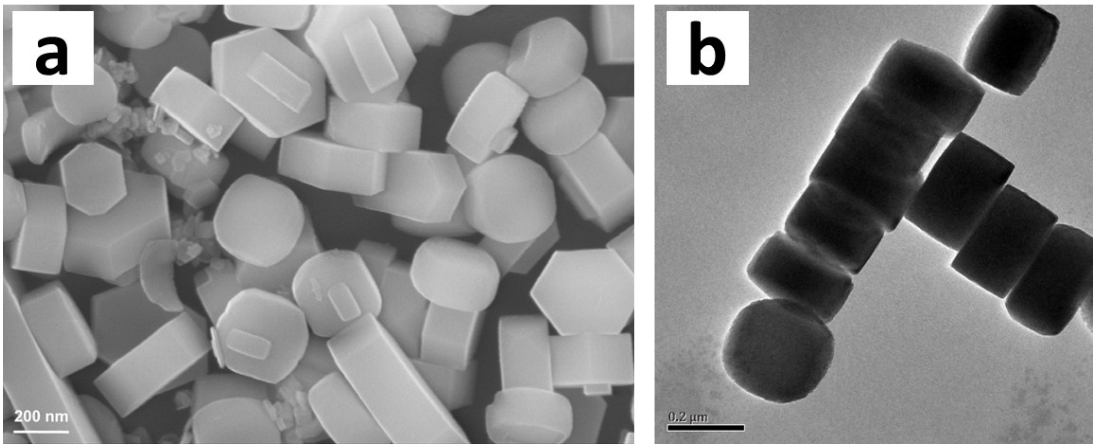

Fig. S1 SEM (a) and TEM (b) images of pristine ZSM-5 nanocrystal samples.

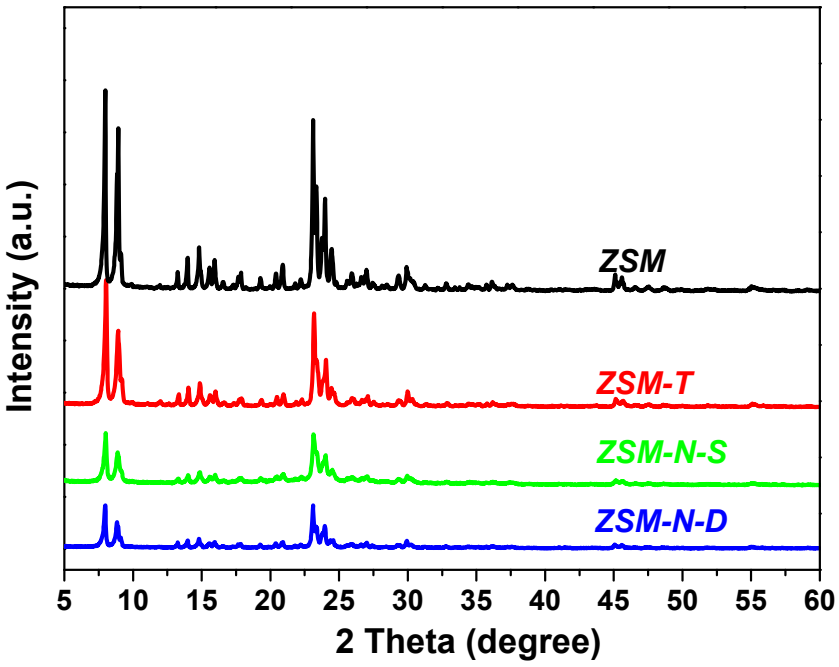

Fig. S2 XRD patterns of the ZSM-5 precursor (ZSM), TPAOH etched ZSM-5 (ZSM-T), static etched ZSM-5 (ZSM-N-S) by ammonia for 8 h and dynamic etched ZSM-5 (ZSM-N-D) by ammonia under stirred condition for 40 min.

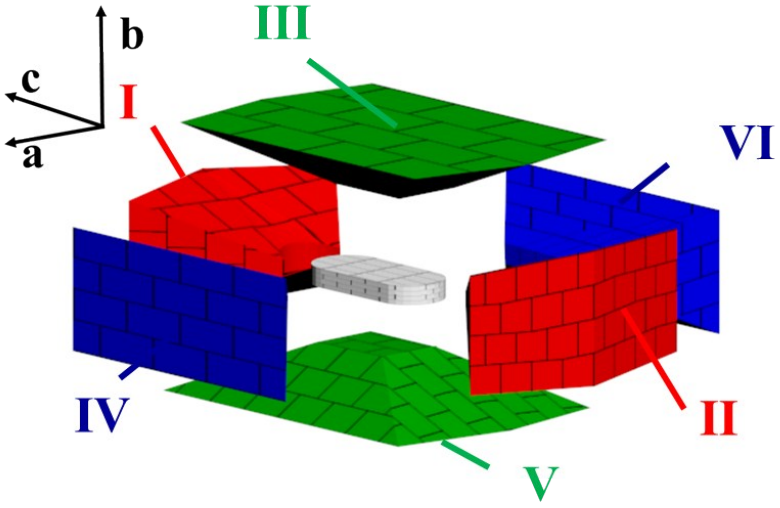

Fig. S3 Exploded representation of the MFI-type crystals with distinct intergrowth structures and diffusion barriers.[1]

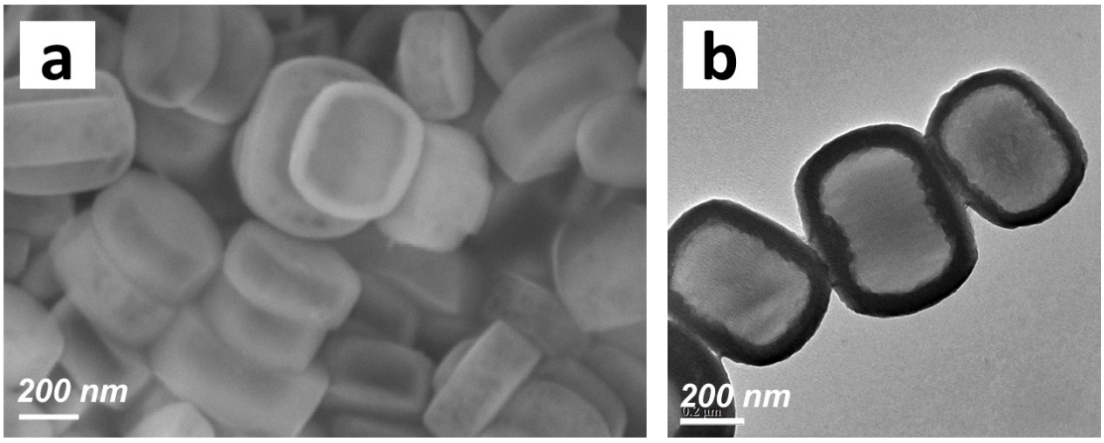

Fig. S4 SEM(a) and TEM (b)images of hollow ZSM-5 (ZSM-T) nanocrystals etched with TPAOH.

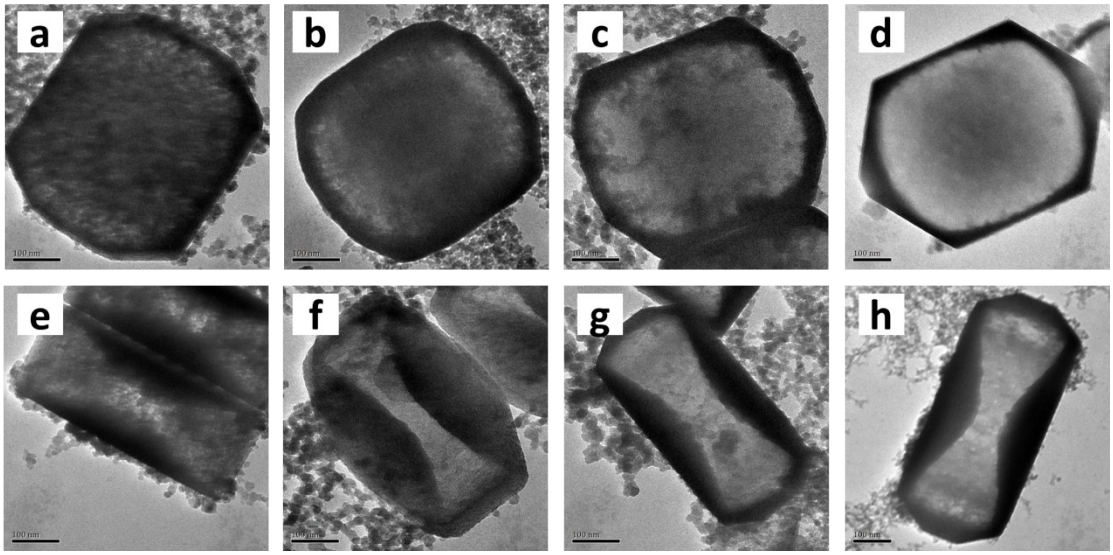

Fig. S5 TEM images of the evolution process of the hollow silicalite-1 nanocrystals (diameter: 300~500 nm) etched by ammonia under static conditions for (a)(e) 10 min, (b)(f) 20 min, (c)(e) 30 min (d)(h) 40 min.

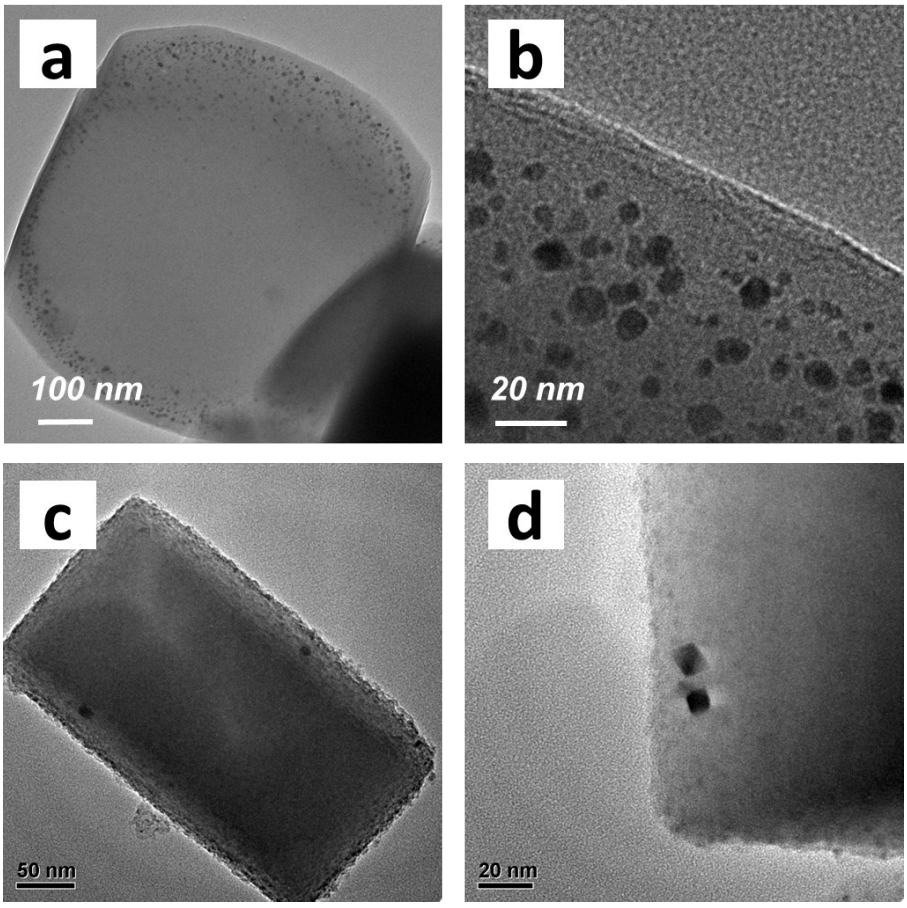

Fig. S6 HRTEM images of the Pt@silicalite-1 (a) (b) and Pt/silicalite-1(c) (d) catalysts.

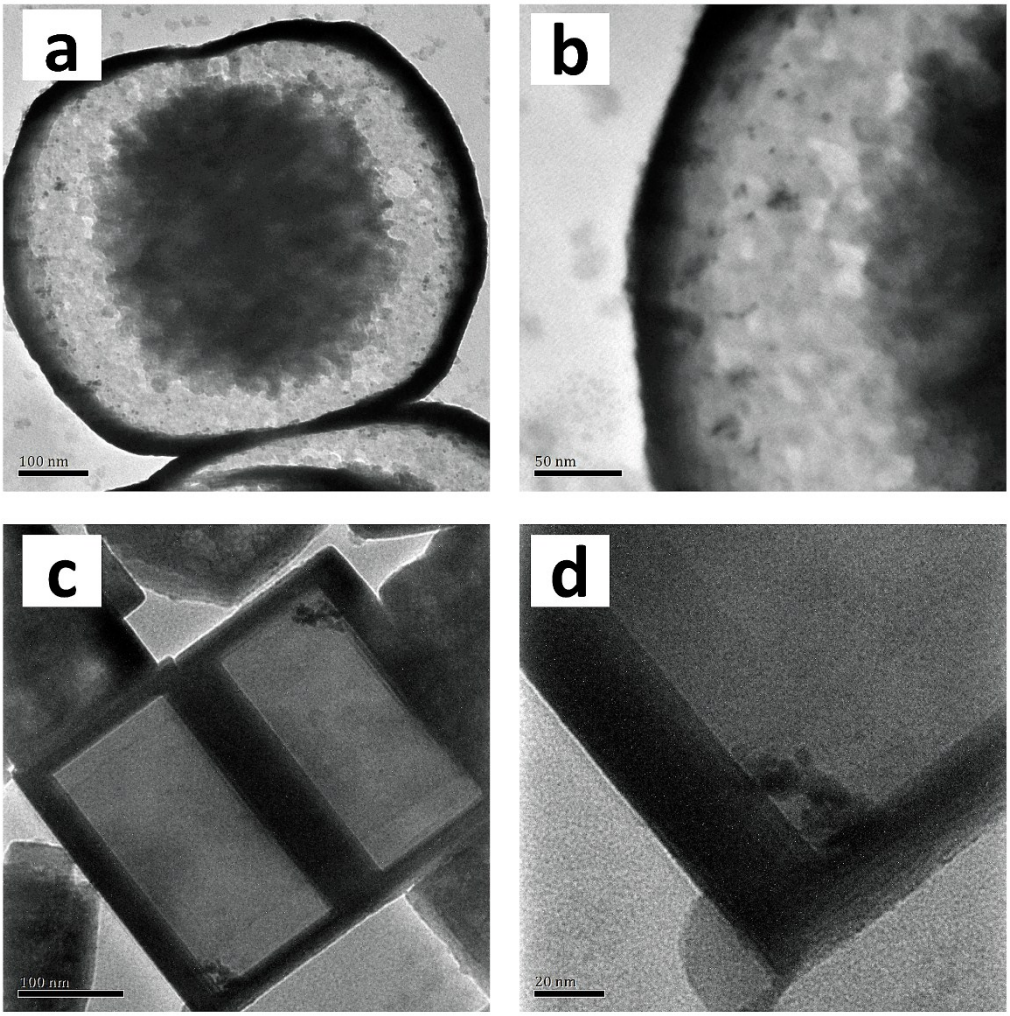

Fig. S7 TEM images of the Pt@silicalite-1 catalysts etched with TPAOH (a) (b) and Pt@silicalite-1 etched with ammonia under static condition (c) (d).

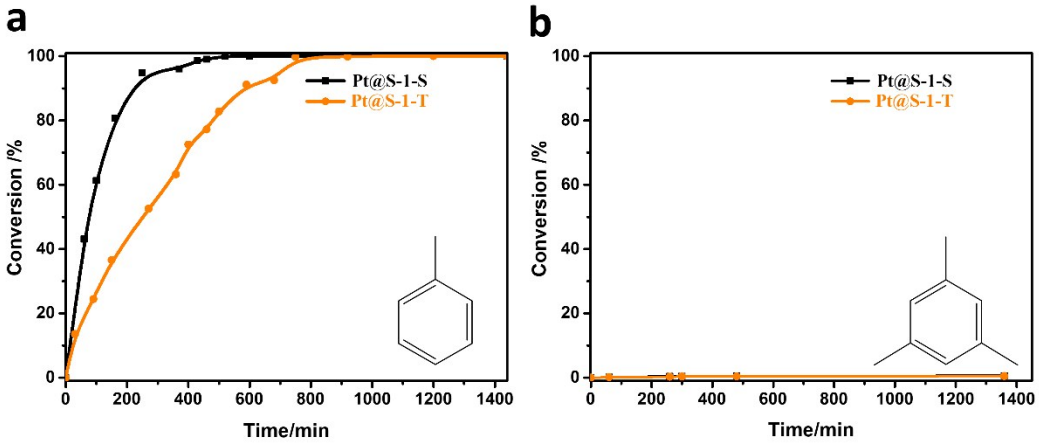

Figure S8 Catalytic performance of the hollow Pt@silicalite-1-H catalysts etched with TPAOH (Pt@S-1-T) and Pt@silicalite-1-H etched with ammonia under static conditions (Pt@S-1-S) for toluene (a) and (b) mesitylene hydrogenation.

References

1. M. B. J. Roeffaers, R. Ameloot, M. Baruah, H. Uji-i, M. Bulut, G. De Cremer, U. Müller, P. A. Jacobs, J. Hofkens, B. F. Sels and D. E. De Vos, *J. Am. Chem. Soc*., 2008, 130, 5763.