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SUPPORTING INFORMATION

Effects of location of Al-species in hierarchical ZSM-11 on its catalytic performances in methanol to propylene



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Table S1 Proportion of integrated peaks obtained by curve fitting of the ²⁹Si MAS NMR for various ZSM-11-*x* zeolites

Samples	SiO ₂ /Al ₂ O ₃ ratio ^a	Si(3Si, 1Al) sites (%) - (-106.0 ppm)	Si(4Si, 0Al) sites (%)			
			-110.4	-112.3	-113.7	-115.7
			ppm	ppm	ppm	ppm
ZSM-11-60	49.01	16.32	13.13	32.94	24.63	12.97
ZSM-11-90	76.92	10.40	18.76	32.43	25.67	12.74
ZSM-11-120	98.40	8.13	14.60	38.02	24.28	14.97
ZSM-11-160	132.89	6.02	14.32	43.82	22.36	13.48

^aThe framework SiO₂/Al₂O₃ ratio is obtained from the ²⁹Si MAS NMR deconvolution results, according to the equation of Si/Al = $(I_{Q4} + I_{Q3})/0.25I_{Q3}$, where I_{Q4} and I_{Q3} are the intensity of Q₄ (Si(OSi)₄) and Q₃ (Si(OAl)₁(OSi)₃) peaks, respectively. In the ²⁹Si MAS NMR spectra, four Q₄ (Si(OSi)₄) peaks around -115.7, -112.3 and -110.4 ppm appear, while the peak at about-106 ppm is assigned to the Q₃ (Si(OAl)₁(OSi)₃) peaks.

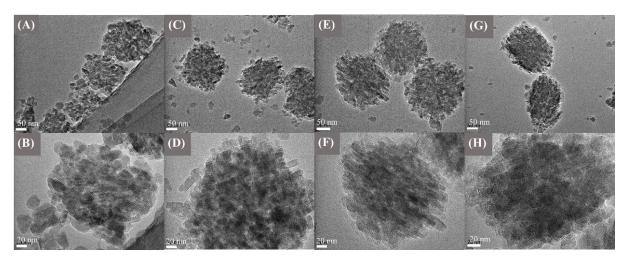


Figure S1 TEM images of the as-synthesized ZSM-11-*x*. (A) and (B): ZSM-11-60; (C) and (D): ZSM-11-90; (E) and (F): ZSM-11-120; (G) and (H): ZSM-11-160

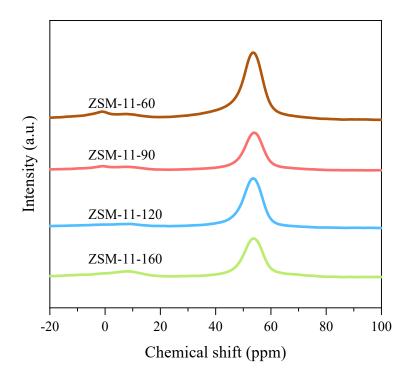


Figure S2 ²⁷Al MAS NMR spectra of the samples ZSM-11-*x*.

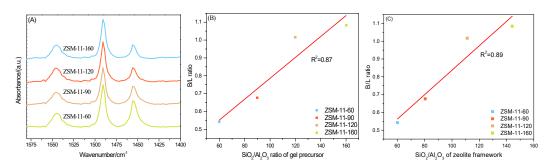


Figure S3 The infrared spectra of pyridine absorbed at 623 k (A); Influence of change in the Si/Al ratio of the gel precursors on the B/L ratio (B); Influence of changed Si/Al ratio of zeolite framework on the B/L ratio (C)

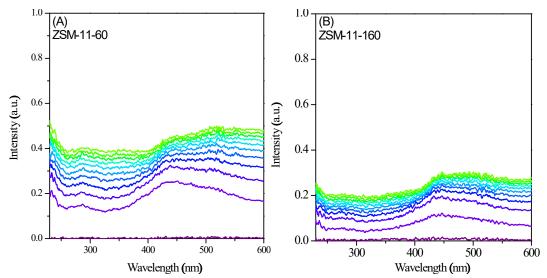


Figure S4 In situ UV/vis spectra recorded during the MTO conversion on ZSM-11-60 and ZSM-11-160 zeolite samples at the reaction temperature of 430 °C. The band at ~250-290 and 400-500 nm is attributed to neutral alkylated benzenes/carbenium ions and the bicyclic species of aromatics with different degrees of methylation[1-3], respectively. Whereas, the band above 500 nm is assigned to highly condensed polycyclic aromatics (e.g., phenanthrenic/anthracenic species)[4]. Clearly, in comparison with the sample ZSM-11-60, the sample ZSM-11-160 shows a much slower increase rate at these band. The results further well explain the superior catalytic performance for highly catalytic stability of ZSM-11-160 in MTP reaction.

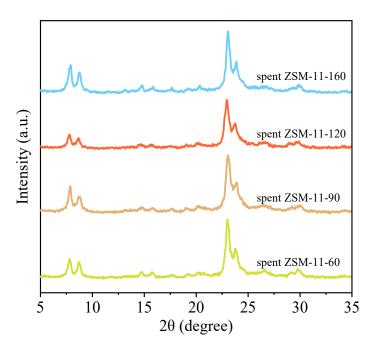


Figure S5 XRD pattern of the spent ZSM-11-x samples.

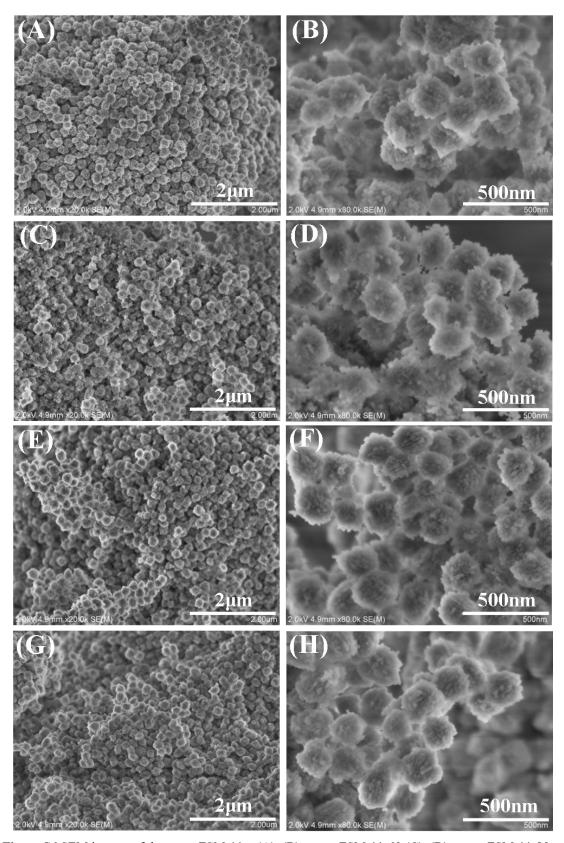


Figure S6 SEM images of the spent ZSM-11-*x*.(A), (B): spent ZSM-11-60;(C), (D): spent ZSM-11-90 (E), (F): spent ZSM-11-120;(G), (H): spent ZSM-11-160

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