

Supporting Information

***N*-methyl-2-pyrrolidone-promoted crystallization of MEL zeolite and its acceleration mechanism**

Chuanyu Yang ^{a,b,1}, Dongpu Zhao ^{a,b,1}, Weifeng Chu^a, Yanan Wang ^{a,b}, Xiujie Li ^a, Sujuan Xie ^a, Wenjie Xin

^a, Xiangxue Zhu ^{a,*}, Shenglin Liu ^{a,*} and Longya Xu ^{a,*}

^a *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,*

Dalian 116023, Liaoning, PR China

^b *University of Chinese Academy of Sciences, Beijing 100049, PR China*

* Corresponding author. E-mail address: zhuxx@dicp.ac.cn

* Corresponding author. E-mail address: slliu@dicp.ac.cn

* Corresponding author. E-mail address: lyxu@dicp.ac.cn

¹ Equally contributed to this work.

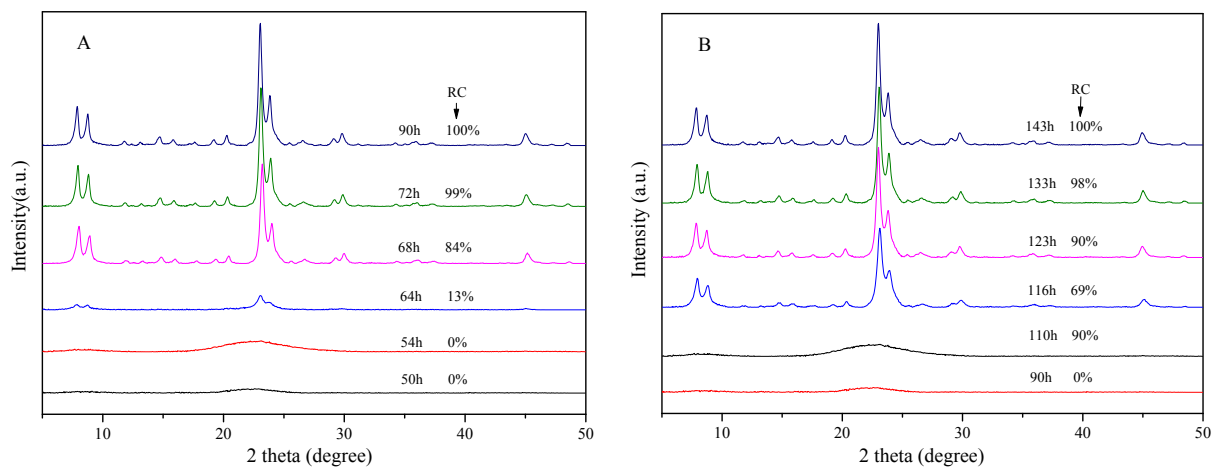


Fig. S1 XRD patterns of the samples synthesized (A) with NMP and (B) without NMP for different time.

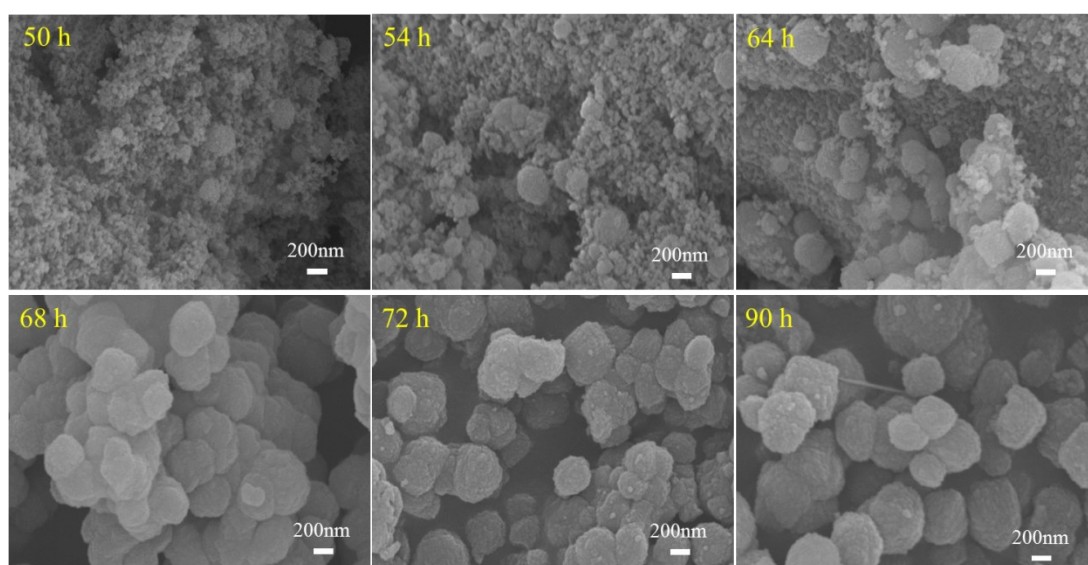


Fig. S2 SEM images of samples crystallized at 130 °C for different periods of time with NMP/SiO₂ molar ratio of 1.5.

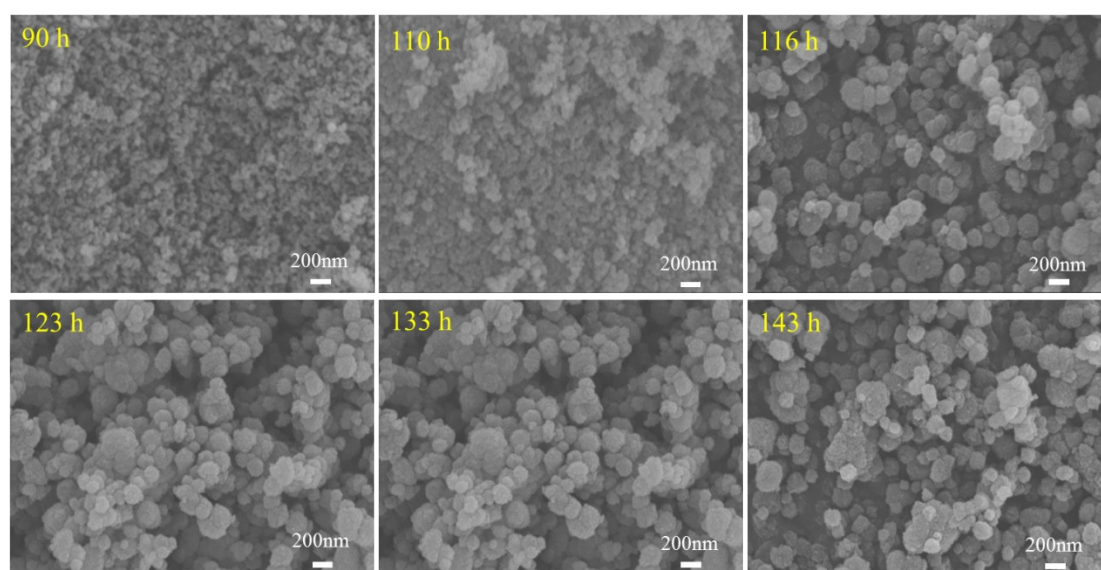


Fig. S3 SEM images of samples crystallized at 130 °C for different periods of time with NMP/SiO₂ molar ratio of 0.0.

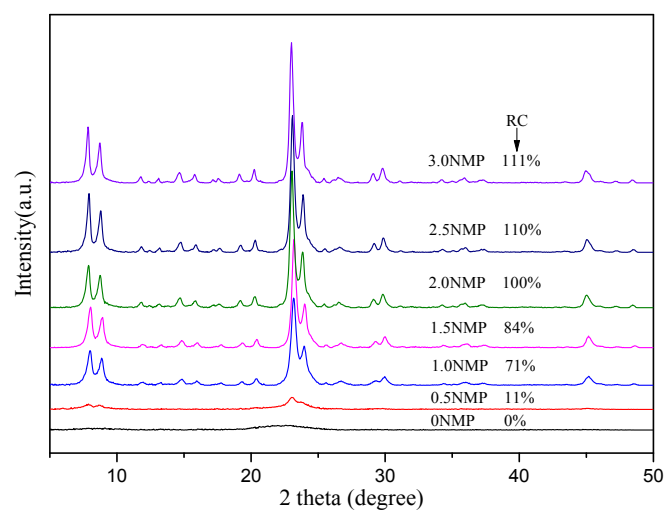


Fig. S4 XRD patterns of samples crystallized at 130 °C for 68 h with different ratios of NMP/SiO₂.

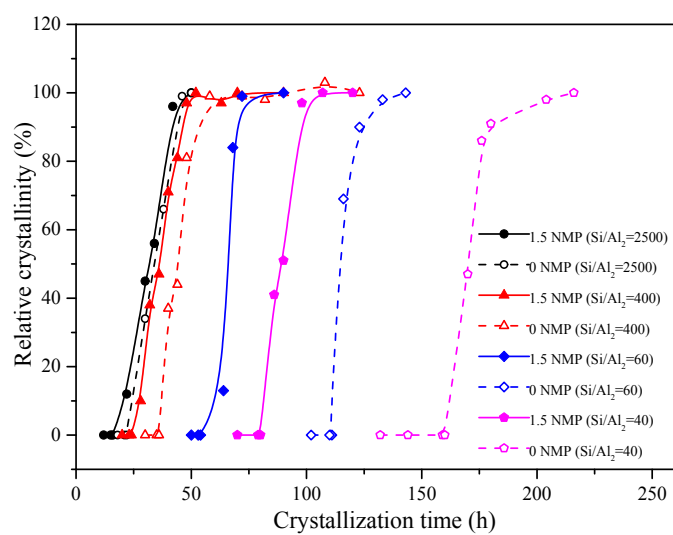


Fig. S5 Crystallization curves of zeolite ZSM-11 synthesized with different Si/Al₂ molar ratios at 130 °C.

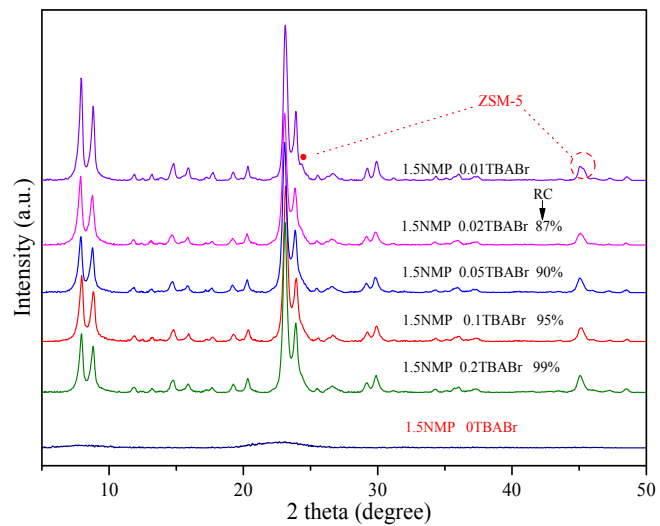


Fig. S6 XRD patterns of samples prepared with different ratios of TBABr/SiO₂.

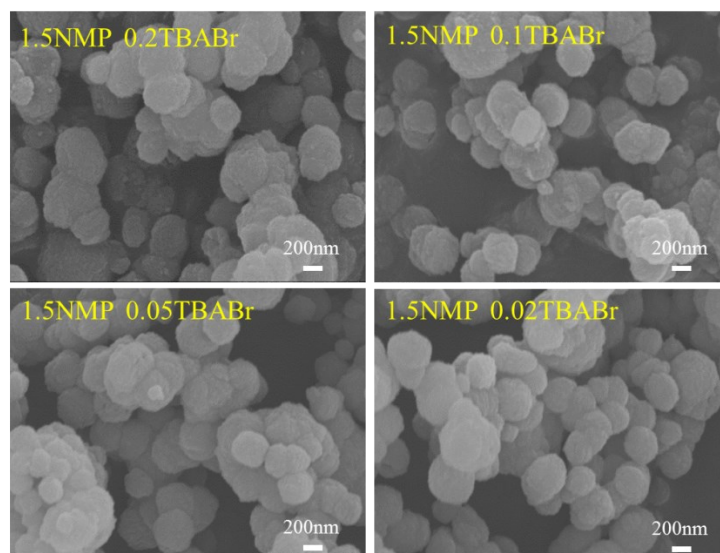


Fig. S7 SEM images of samples prepared with different ratios of TBABr/SiO₂.

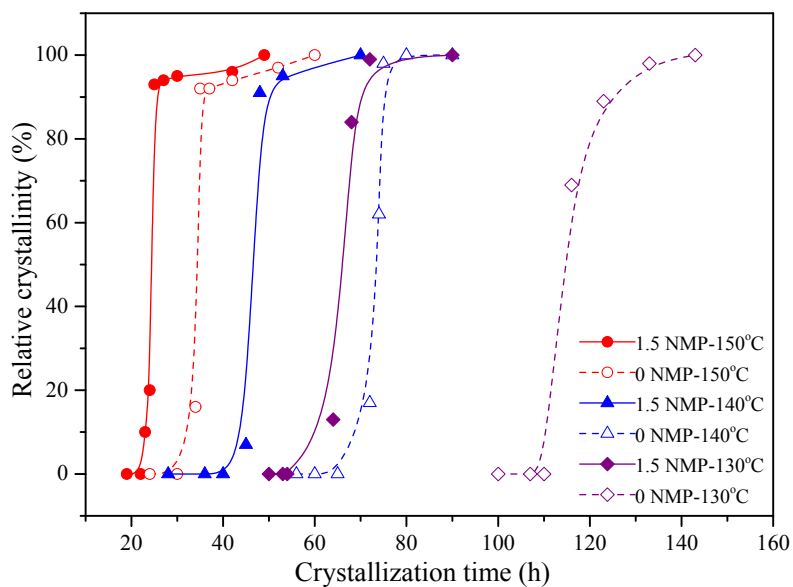


Fig. S8 Crystallization curves of zeolite ZSM-11 synthesized with and without NMP at different temperature.

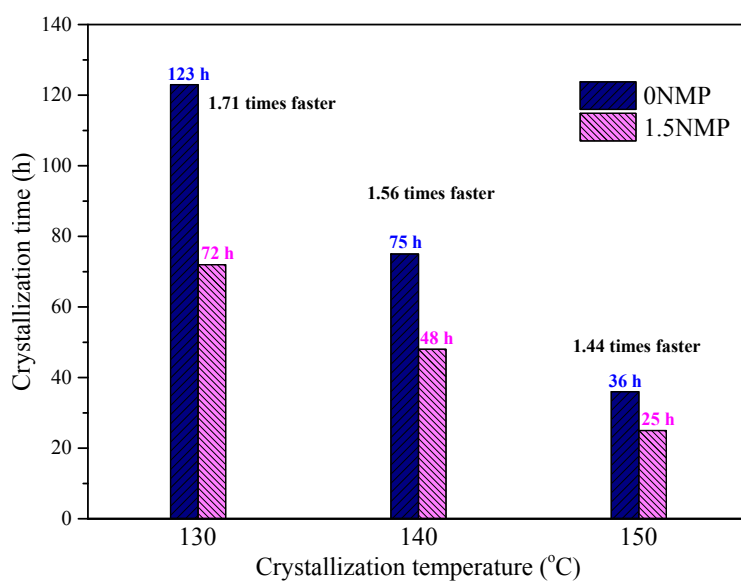


Fig. S9 Crystallization temperature dependence of acceleration effect of NMP.

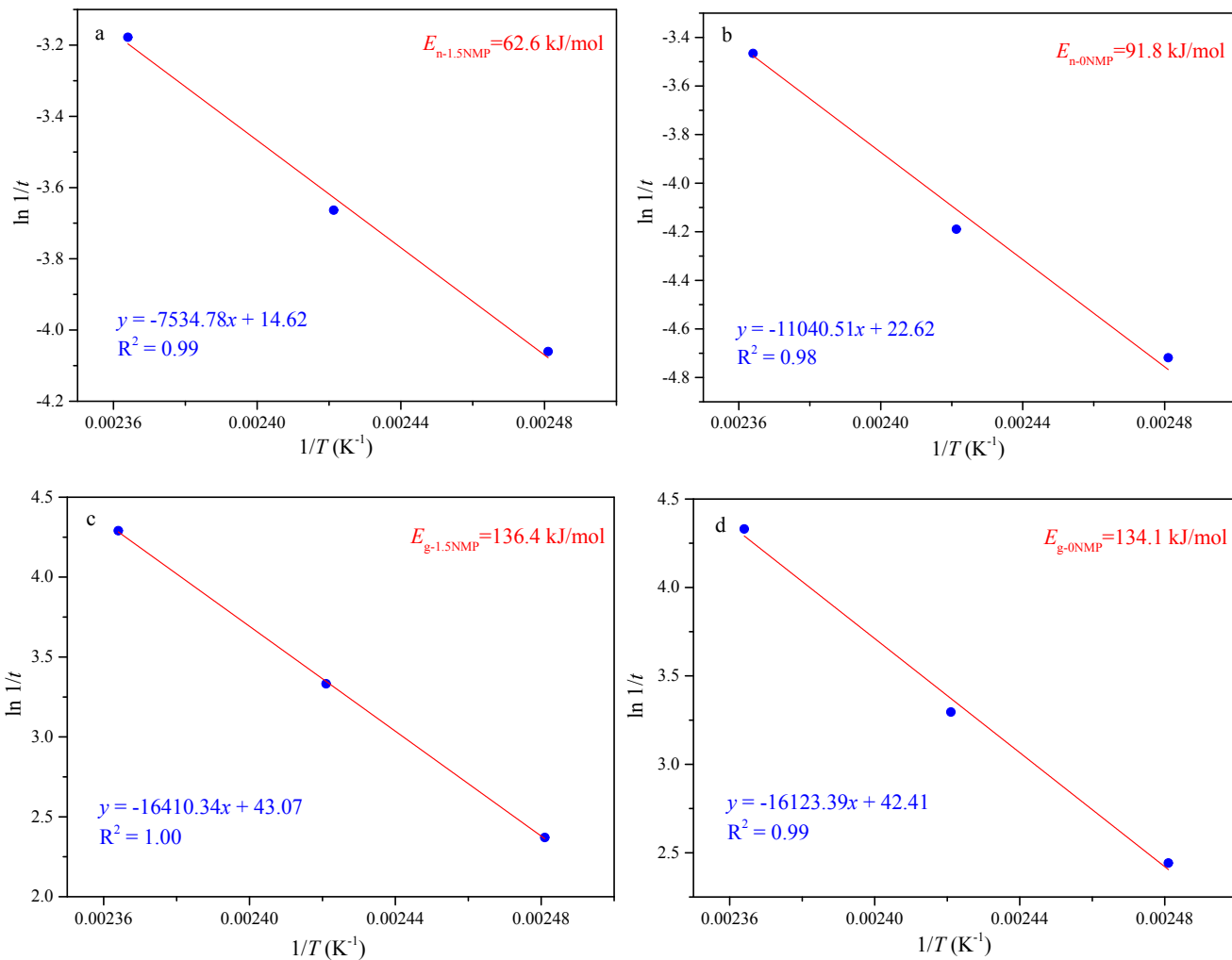


Fig. S10 Arrhenius plot for the synthesis of ZSM-11 zeolite using TBABr as the organic template.

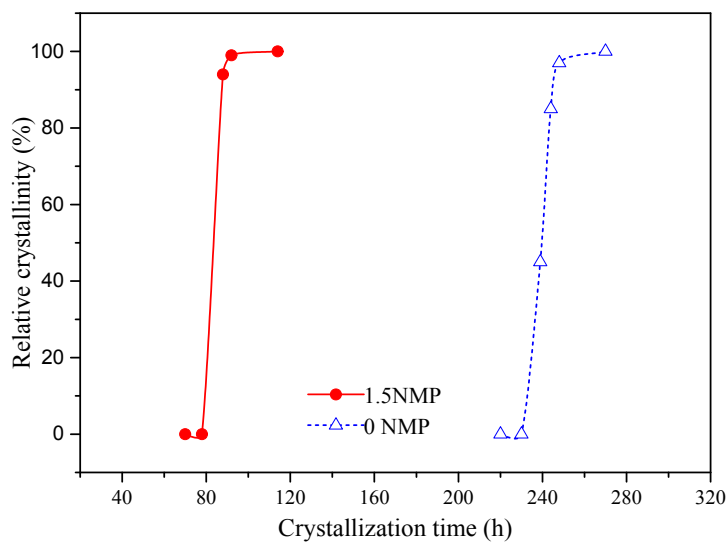


Fig. S11 Crystallization curves of zeolite ZSM-11 synthesized with and without NMP under TBAOH as OSDAs at 130 °C.

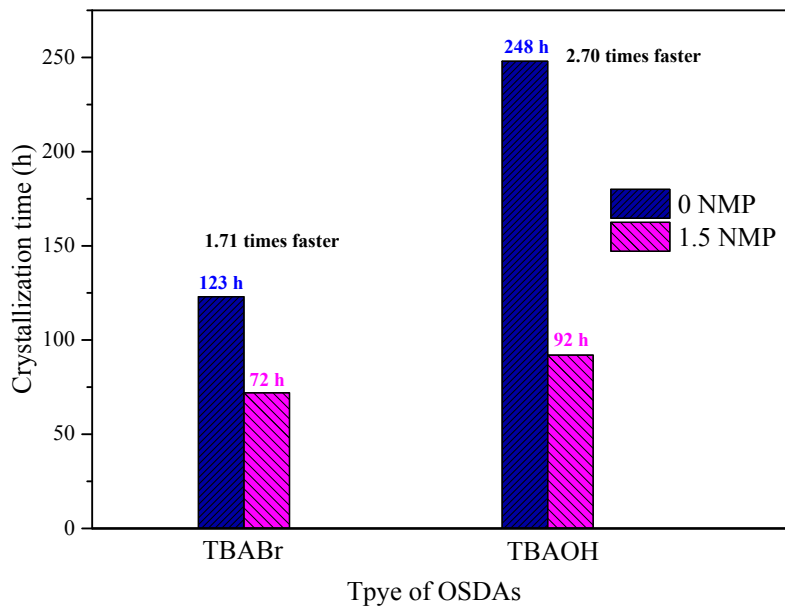


Fig. S12 Type of OSDAs dependence of acceleration effect of NMP.

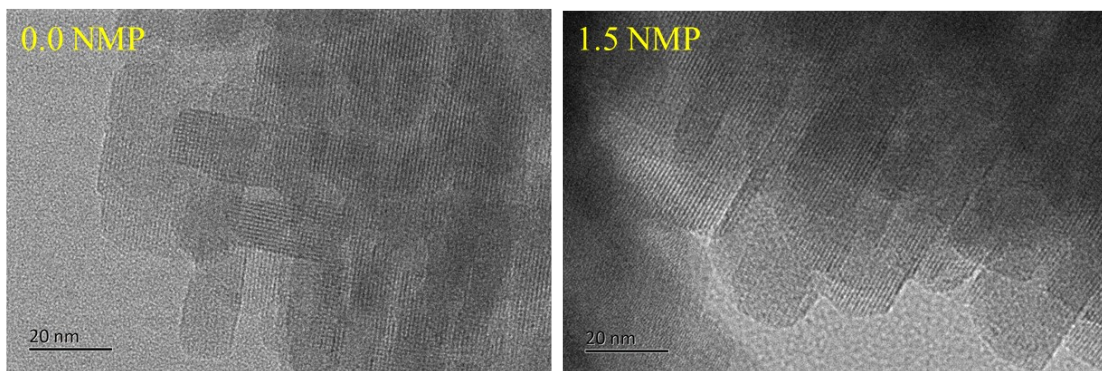


Fig. S13 TEM images of samples crystallized at 130 °C with NMP/SiO₂ molar ratio of 0.0.

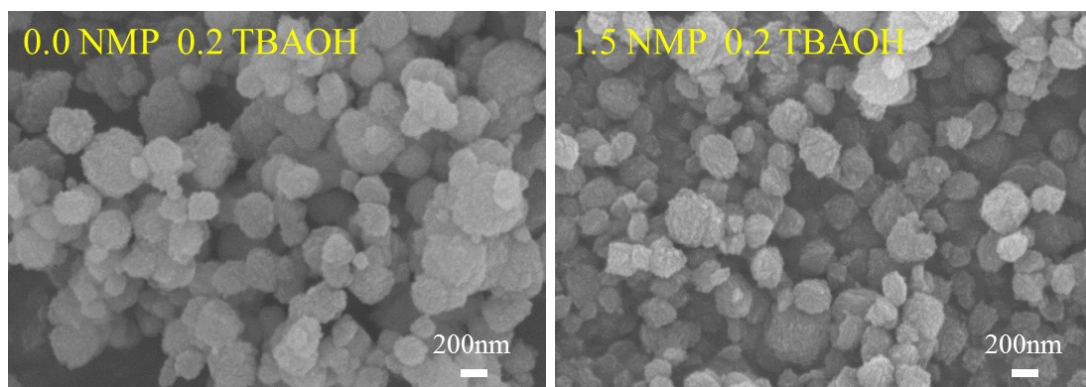


Fig. S14 SEM images of samples crystallized at 130 °C for with NMP/SiO₂ molar ratio of 0.0 and 1.5.

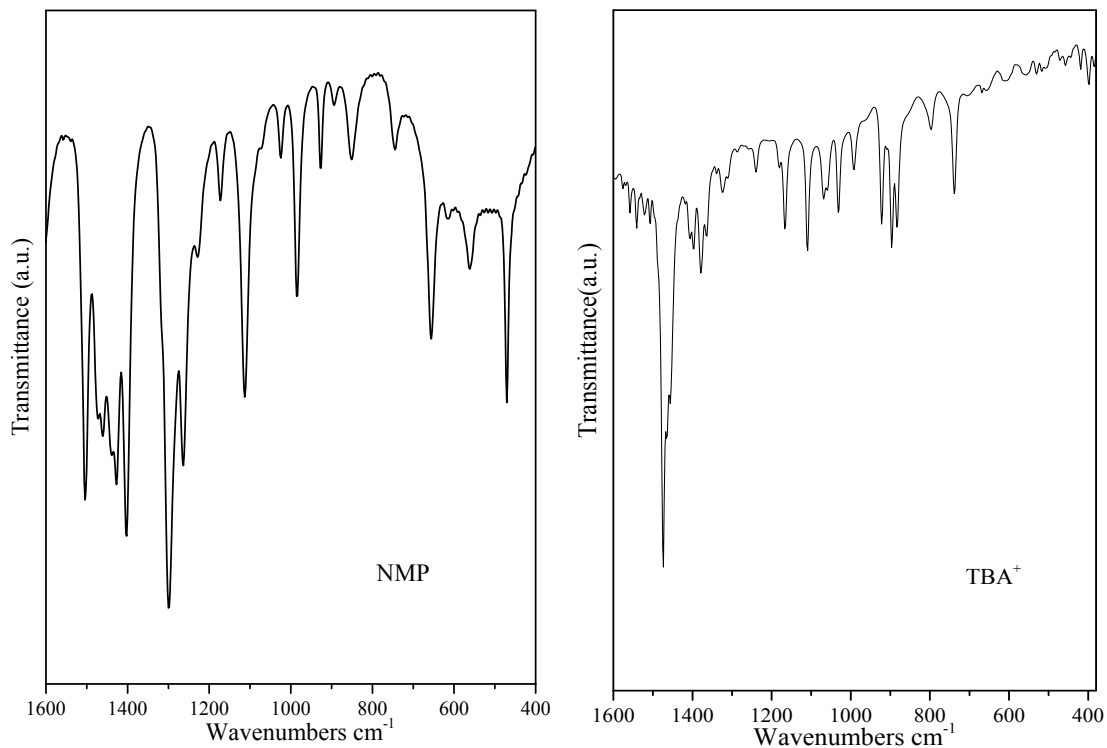


Fig. S15 FT-IR spectra of NMP and TBA^+ .

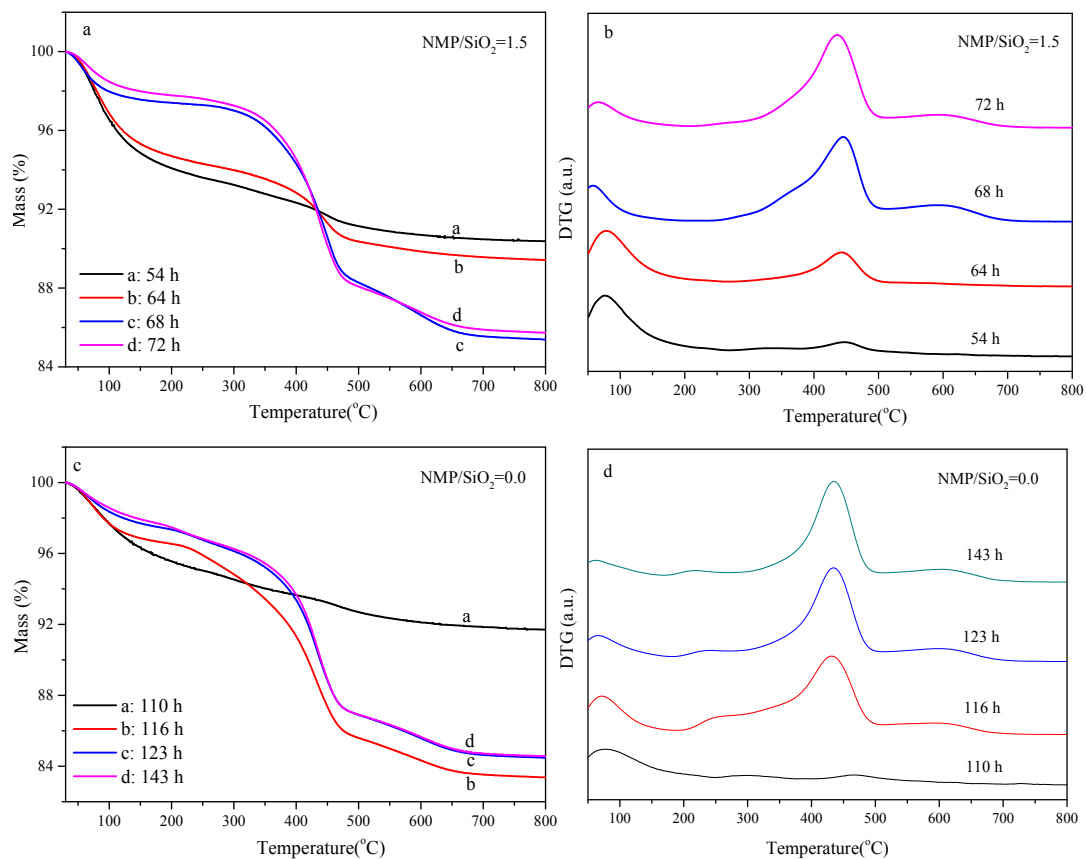


Fig. S16 TG and DTG curves for the samples synthesized with (a, b) and without NMP (c, d).

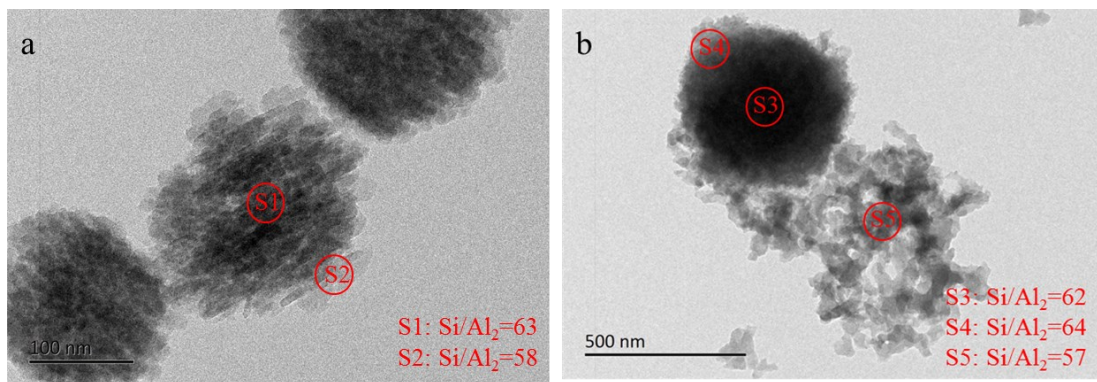


Fig. S17 TEM-EDS analyses of the samples synthesized (a) without NMP for 116h and (b) with NMP (NMP/SiO₂=1.5)

for 64h.

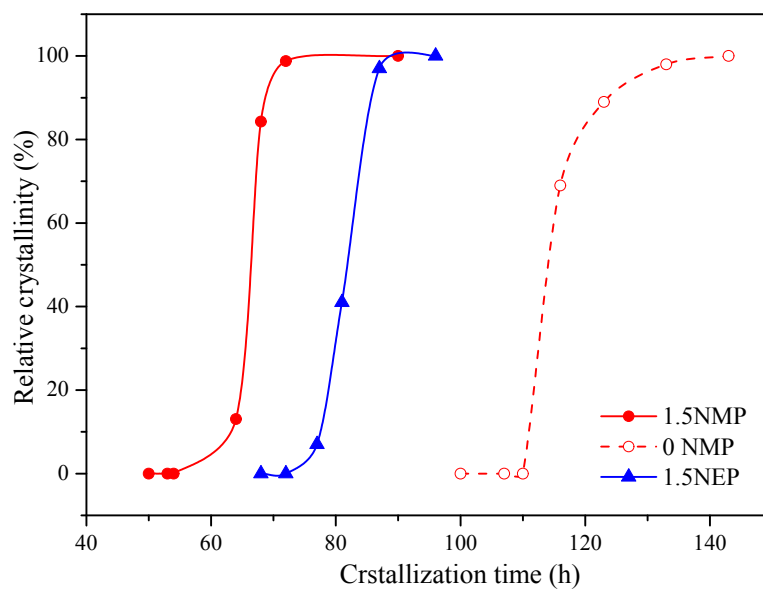


Fig. S18 Crystallization curves of zeolite ZSM-11 synthesized with NMP or NEP and without NMP under TBABr/ SiO₂=

0.2 at 130 °C.

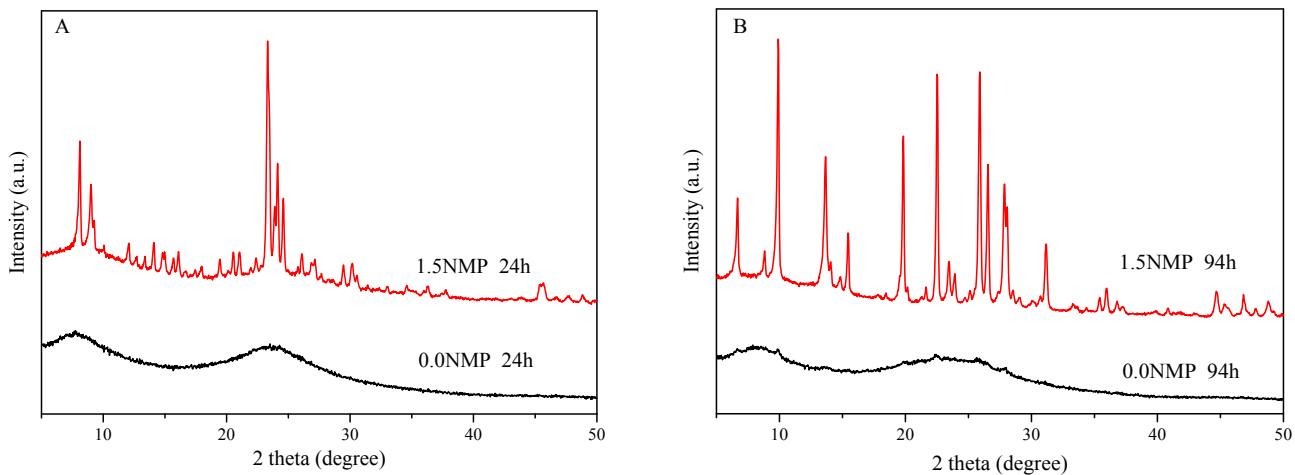


Fig. S19 XRD patterns of MFI (A) and MOR (B) zeolite synthesized with and without NMP.

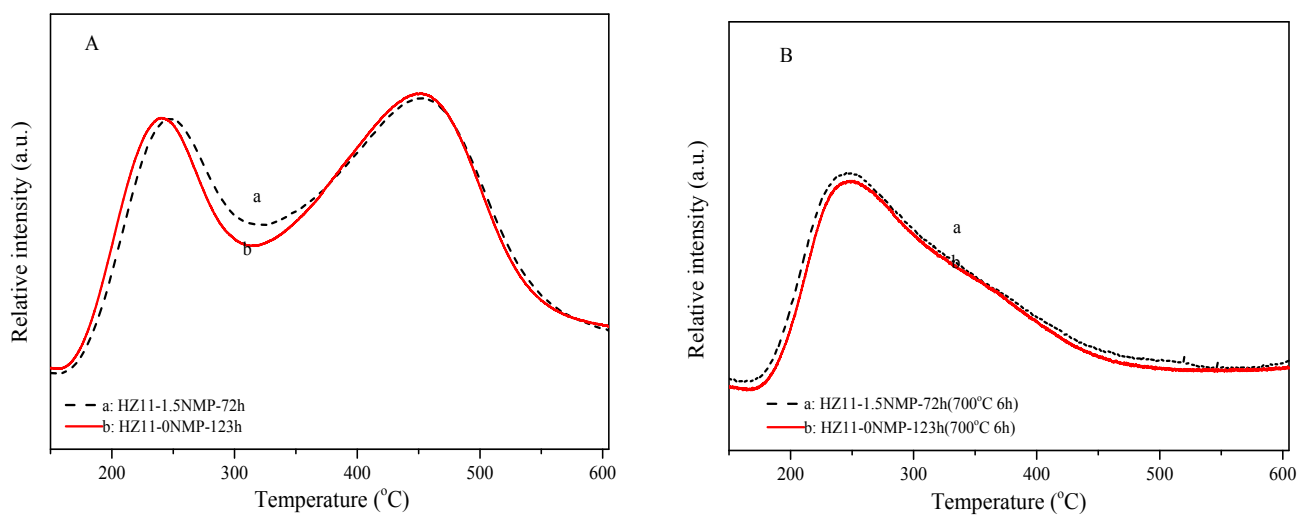


Fig. S20 NH₃-TPD profiles of samples before (A) and after (B) steam treatment at 700°C for 6 h.

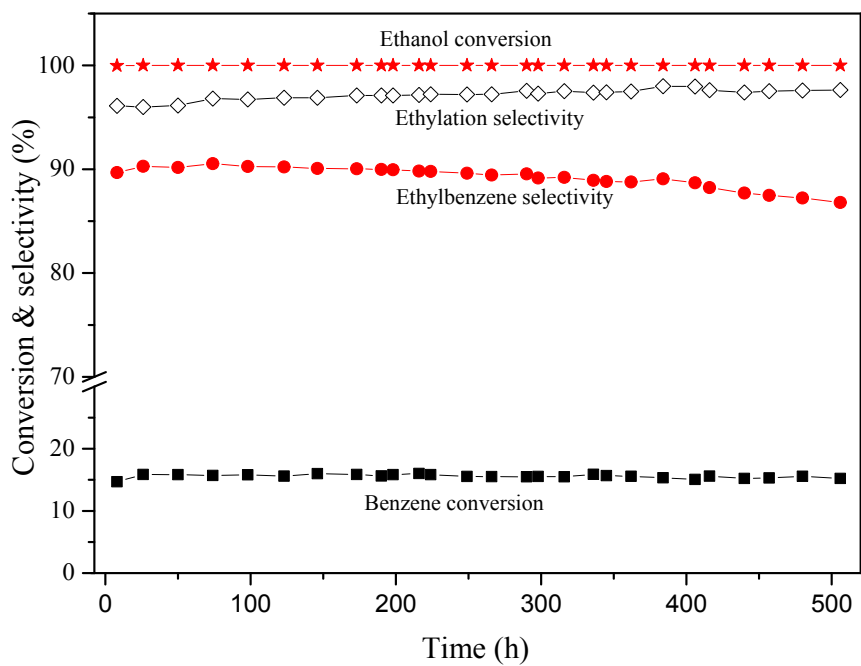


Fig. S21 Conversion and product selectivity of benzene-ethanol alkylation reaction as a function of time over HZ11-1.5NMP-72h.

Reaction condition: $m(\text{catalyst}) = 0.5\text{g}$; $380\text{ }^\circ\text{C}$; 1.5MPa ; $\text{WHSV}(\text{ethanol}) = 1.0\text{h}^{-1}$; $n(\text{benzene})/n(\text{ethanol}) = 6/1$.

Table S1 The raw material, electricity and labor costs.

	Raw material ^a						Electricity & Labor costs (¥/h)
	Silica sol (¥/ton)	TBABr (¥/ton)	NaOH (¥/ton)	Aluminium sulfate (¥/ton)	Deionized water (¥/ton)	NMP (¥/ton)	
Price ^b	4000	30000	4000	1000	10	7000	200

^a: Raw material specifications were same as those used in the experimental section of this paper.

^b: The costs of raw materials, electricity and labor were supplied by Zibo Qichuang Chemical Technology Development Co. Ltd, Chain in 2019.

Table S2 The theoretical production costs of 500kg ZSM-11 zeolites in 12 m³ synthetic reactor.

Products		Raw material						Sum	Crystallization time (h)	Electricity & Labor costs (¥)	Total production cost (¥)
		Silica sol	TBABr	NaOH	Aluminium sulfate	Deionized water	NMP				
Z11-0NMP(0.2TBABr)	Dosages (kg)	1600	525	95	89	4700	0	7009	123	24600	47266
	Price (¥)	6400	15750	380	89	47	0	22666			
Z11-1.5NMP(0.2TBABr)	Dosages (kg)	1600	525	95	89	4700	1223	8232	72	14400	45627
	Price (¥)	6400	15750	380	89	47	8561	31227			
Z11-0NMP(0.02TBABr)	Dosages (kg)	1600	53	95	89	4700	0	6537	145	29000	37506
	Price (¥)	6400	1590	380	89	47	0	8506			
Z11-1.5NMP(0.02TBABr)	Dosages (kg)	1600	53	95	89	4700	1223	7760	75	15000	32067
	Price (¥)	6400	1590	380	89	47	8561	17067			

Table S3 XRF results of samples crystallized for different periods of time with and without NMP.

NMP/SiO ₂ = 1.5		NMP/SiO ₂ = 0.0	
Time /h	Si/Al ₂	Time /h	Si/Al ₂
0	46.4	0	45.6
64	49.5	116	47.3
68	52.0	123	48.8
72	52.3	143	49.2
90	52.1	-	-

Table S4 XRF results of samples crystallized for different periods of time with and without NMP.

The Si/Al ₂ ratio of the initial gel	The Si/Al ₂ ratio of the ZSM-11	
	With NMP	Without NMP
40	34.1	33.3
60	52.1	49.2
400	288.3	255.4
2600	1841.6	1241.8

Table S5 Kinetics parameters of ZSM-11 crystallization with NMP and without NMP.

T(°C)	NMP/SiO ₂ = 1.5					NMP/SiO ₂ = 0.0				
	t ₀ (h)	V _n (h ⁻¹)	V _g (h ⁻¹)	E _n (kJ/mol)	E _g (kJ/mol)	t ₀ (h)	V _n (h ⁻¹)	V _g (h ⁻¹)	E _n (kJ/mol)	E _g (kJ/mol)
130	58	0.0172	10.70			113	0.0089	11.50		
140	39	0.0256	28.00	62.6	136.4	66	0.0152	27.00	91.8	134.1
150	23	0.0435	73.00			31	0.0323	76.00		

Table S6 Textural data of samples before and after steam treatment.

Samples	Si/Al ₂ molar ratio	Textural data			
		S _{BET} /m ² g ⁻¹	S _{ext} /m ² g ⁻¹	V _{micro} /cm ³ g ⁻¹	V _{meso} /cm ³ g ⁻¹
HZ11-0NMP-123h-130	49.2	468	168	0.121	0.442
HZ11-0NMP-123h-130(700°C 6h)	-	385	135	0.101	0.439
HZ11-1.5NMP-72h-130	52.1	472	130	0.136	0.167
HZ11-1.5NMP-72h-130(700°C 6h)	-	367	103	0.106	0.223