Electronic Supplementary Information for

Nonionic polymer and amino acid-assisted synthesis of ZSM-5 nanocrystals and their catalytic application in alkylation of 2-methylnaphthalene

Jun-Ling Zhan,[a,b] Ying Wang,[b] Teng-Fei He,[b] Lu-Yang Sheng,[b] Bang-Hao Wu,[b] Qun Liu,[b] Ming-Jun Jia,[a*] Yu Zhang,[b*]

[a] Key Laboratory of Surface and Interface Chemistry of Jilin Province, College of Chemistry, Jilin University, Changchun, 130012, P. R. China

[b] College of Petrochemical Technology, Jilin Institute of Chemical Technology, Jilin, 132022, P. R. China

*Email: jiamj@jlu.edu.cn; zhang99yu@hotmail.com

Samples	SiO_2	Al_2O_3	$_L$-lysine	PVP ($*10^{-3}$)	H_2O/ SiO_2	Temperature /°C(time/d)	RCs (%)
Z5-20_Con	1	0.05	/	/	30	175(3)	71
Z5-20_Ref	1	0.05	/	/	8	90(2)/175(1)	67
Z5-20_$P_{0.06}$	1	0.05	/	0.06	8	90(2)/175(1)	100

Z5-20_$P_{0.12}$	1	0.05	/	0.12	8	90(2)/175(1)	82
Z5-20_$P_{0.24}$	1	0.05	/	0.24	8	90(2)/175(1)	81
Z5-20_$L_{0.05}$	1	0.05	0.05	/	8	90(2)/175(1)	56
Z5-20_$L_{0.10}$	1	0.05	0.10	/	8	90(2)/175(1)	94
Z5-20_$L_{0.15}$	1	0.05	0.15	/	8	90(2)/175(1)	77

Z5-20_$L_{0.30}$	1	0.05	0.30	/	8	90(2)/175(1)	28
Z5-20_$L_{0.10}P_{0.06}$	1	0.05	0.10	0.06	8	90(2)/175(1)	96
Z5-20_$L_{0.10}P_{0.12}$	1	0.05	0.10	0.12	8	90(2)/175(1)	85
Z5-20_$L_{0.10}P_{0.24}$	1	0.05	0.10	0.24	8	90(2)/175(1)	90
Z5-10_$L_{0.10}P_{0.12}$	1	0.10	0.10	0.12	8	90(2)/175(1)	54

Z5-30_$L_{0.10}P_{0.12}$	1	0.03	0.10	0.12	8	90(2)/175(1)	80

Table S1. Molar composition and crystallization conditions of various ZSM-5 initial mixture.

Table S2. The 2-MN conversion, 2,6-DMN selectivity and yield, and 2,6-/2,7-DMN ratio and product distribution in this experiment were calculated by the equation (1)-(5).

	Equation
(1)	2-MN conversion = $(M_{MN0}\text{-}M_{MN1})/M_{MN0} \times 100\%$ [a]
(2)	2,6-DMN selectivity = $(M_{2,6\text{-}DMN})/ (M_{MN0}\text{-}M_{MN1}) \times 100\%$ [b]
(3)	2,6-DMN yield = (2-MN Conversion ×2,6-DMN selectivity)×100%
(4)	2,6-DMN/2,7-DMN ratio = $n_{2,6\text{-}DMN}/n_{2,7\text{-}DMN}$ [c]
(5)	Product distribution = $M_1/M_t \times 100\%$ [d]

[a] M_{MN0} is the mole percentage of 2-MN before the reaction and M_{MN1} is the mole percentage of 2-MN after the reaction.

[b] $M_{2,6\text{-}DMN}$ is the molar percentages of 2,6-DMN.

[c] $n_{2,6\text{-}DMN}$ and $n_{2,7\text{-}DMN}$ are molar ratio of 2,6-DMN to 2,7-DMN.

[d] the product distribution is the concentration of naphthalene (NA), 1-methylnaphthalene (1-MN), dimethylnaphthalene (DMNs), or poly-methylnaphthalene (poly-MN) in the product mixture, M_1 is the molar percentage of NA,1-MN, DMNs, or poly-MN, and M_t is the sum of the molar percentages of the above four products.

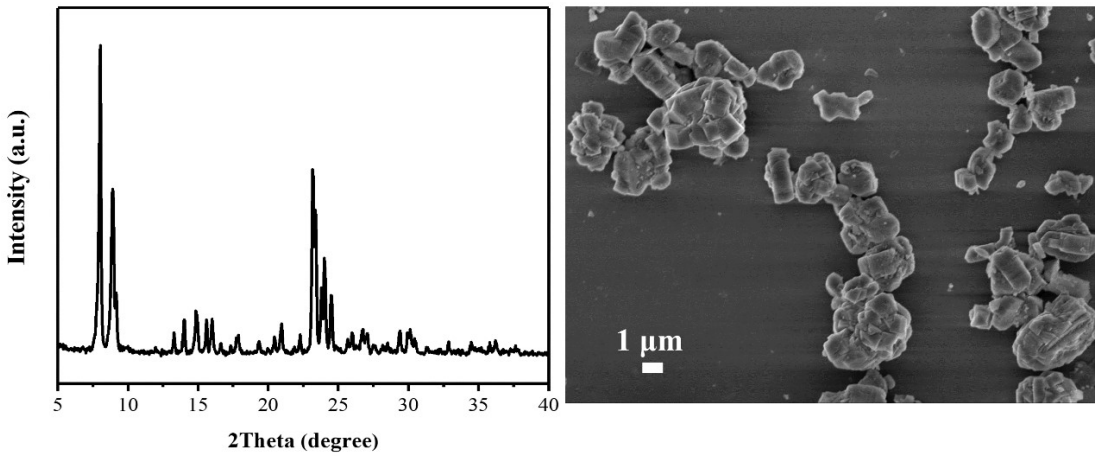

Fig. S1 XRD patterns (left) and SEM images (right) of Z5-20_Con sample.

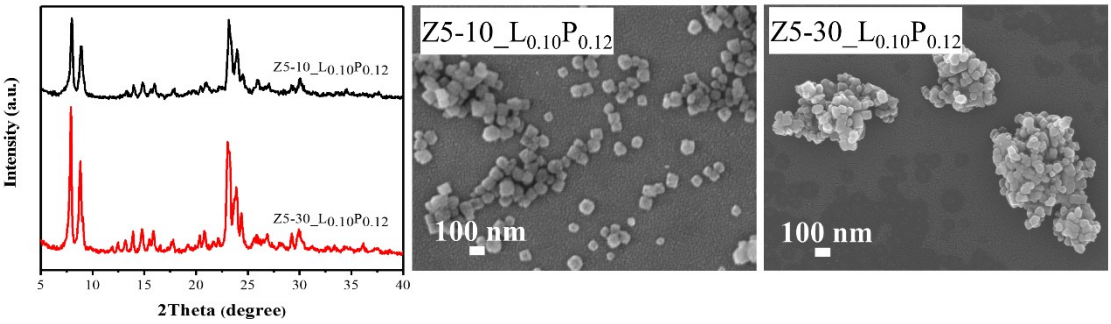

Fig. S2 XRD patterns and SEM images of Z5-10_$L_{0.10}P_{0.12}$ and Z5-30_$L_{0.10}P_{0.12}$ samples.

Table S3. The results of elemental analysis and acidity properties.

Samples	SiO_2/Al_2O_3[a]	Acidity (NH_3)/(mmol/g)[b]		
		Weak[b]	Medium[b]	Strong[b]

		(100~250 °C)	(250~350 °C)	(350~550 °C)
Z5-20_Con	16.6	0.455(205)	0.228(295)	0.388(423)
Z5-20_Ref	17.4	0.471 (203)	0.173(284)	0.441(418)
Z5-20_$L_{0.30}$	19.1	0.345(197)	0.165(288)	0.298(417)
Z5-20_$P_{0.24}$	17.3	0.470(216)	0.195(288)	0.521(420)
Z5-20_$L_{0.10}P_{0.12}$	17.8	0.530(209)	0.238(288)	0.495(419)
Z5-20_$L_{0.10}P_{0.24}$	17.6	0.545(210)	0.265(286)	0.464(423)
Z5-10_$L_{0.10}P_{0.12}$	9.2	0.786(210)	0.278(303)	0.690(436)
Z5-30_$L_{0.10}P_{0.12}$	26.4	0.218(204)	0.210(283)	0.256(410)

[a] Measured by ICP-OES. Typically, 0.2 g of H-form ZSM-5 was dissolved in 800 μL of hydrofluoric acid (40%) and 5 mL deionized water via microwave digestion. Then, the digestion solution was transferred to a volumetric flask and made up to 50 mL with water. The Si and Al contents were then analyzed by ICP-OES, where the standard samples of Si and Al were purchased directly from commercial companies.

[b] Acid amounts of the weak/ medium/strong acid site were calculated by Gaussian fitting.

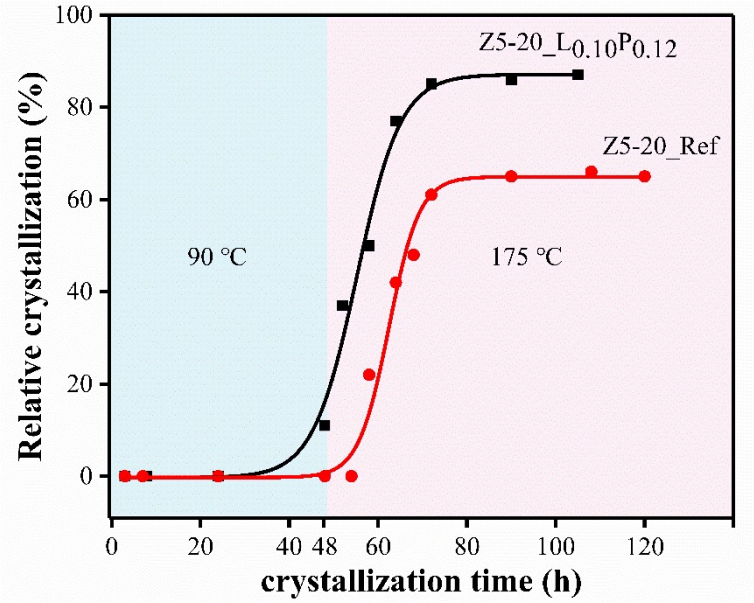

Fig. S3 Crystallization curves of Z5-20_$L_{0.10}P_{0.12}$ and Z5-20_Ref samples.

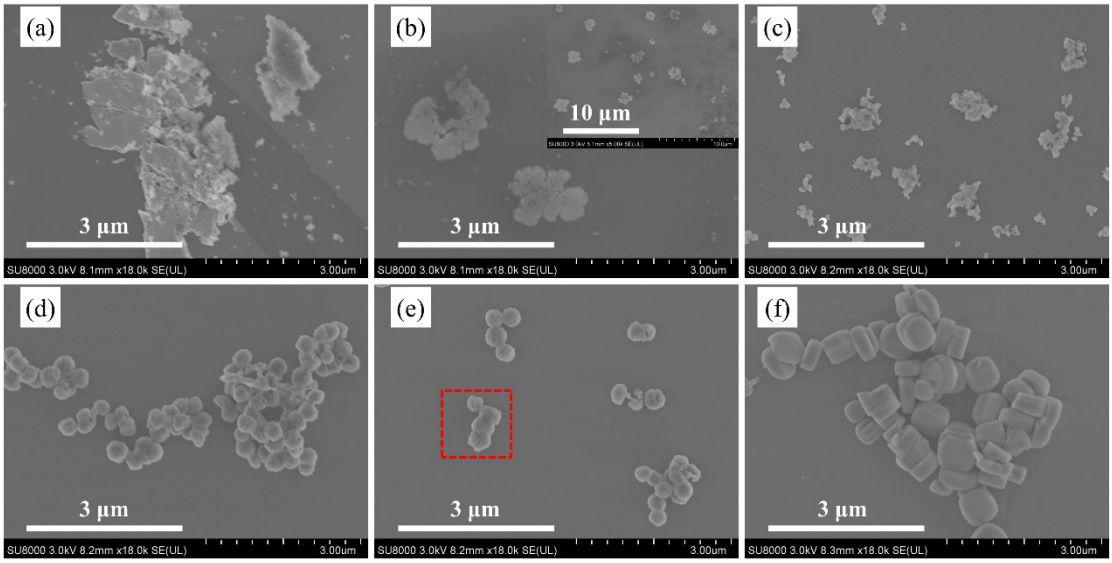

Fig. S4 SEM images of Z5-20_Ref samples at different crystallization stages. (a) 90 °C for 3 h; (b) 90 °C for 7 h; (c) 90 °C for 24 h; (d) 90 °C for 48 h; (e) 175 °C for 6 h; (f) 175 °C for 24 h;

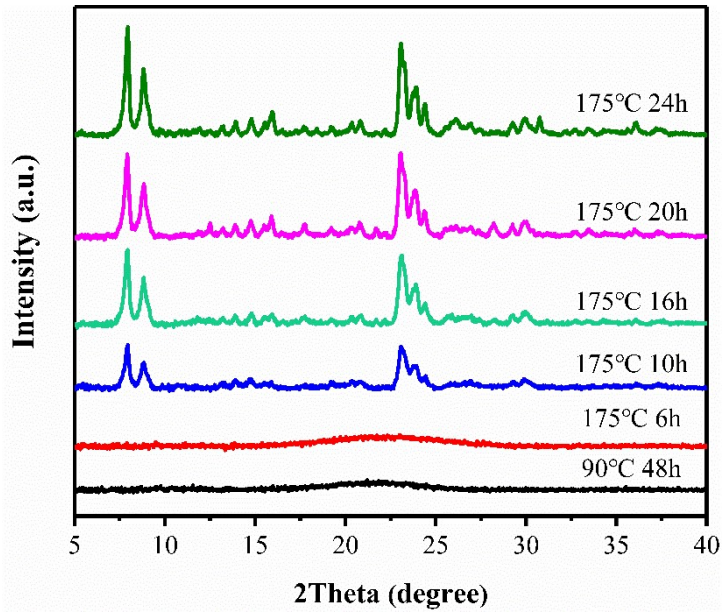

Fig. S5 XRD patterns of Z5-20_Ref samples with different crystallization temperature and time.

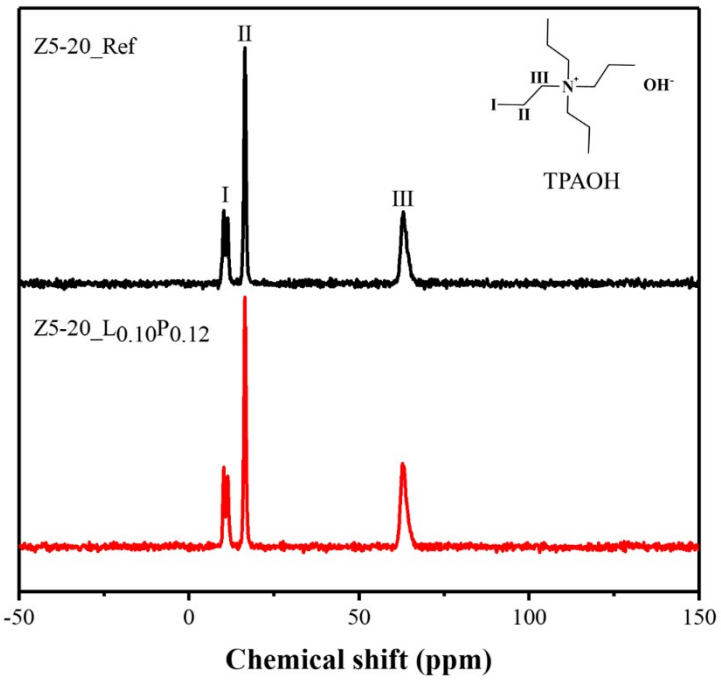

Fig. S6 Solid-state ^{13}C NMR spectra of the as-synthesized zeolites Z5-20_Ref and Z5-20_$L_{0.10}P_{0.12}$ (without calcination).

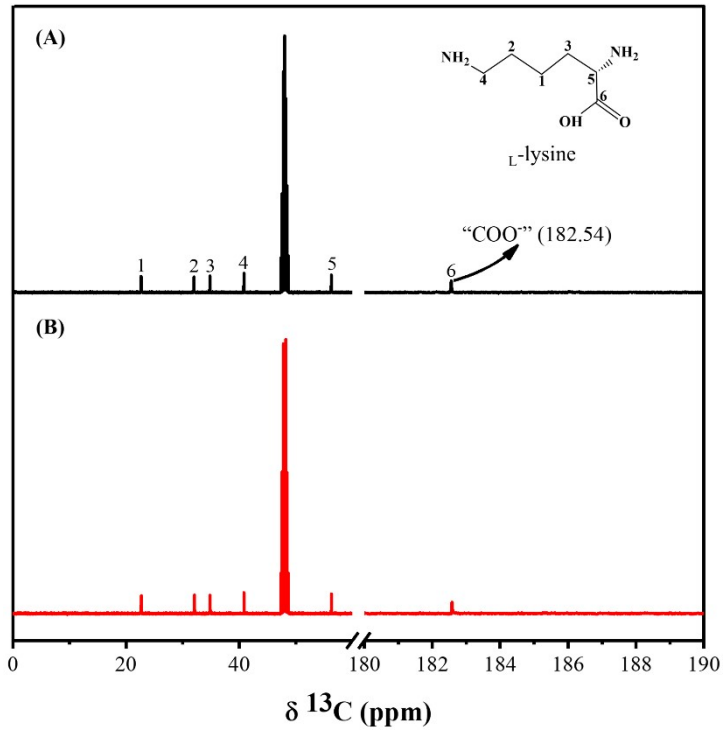

Fig. S7 Liquid-state ^{13}C NMR spectra of $_L$-lysine dissolved in NaOH solution with or without thermal treatment. (A) ambient temperature; (B) high temperature treatment (first 90 °C for 2 days and then175 °C for 1 day)

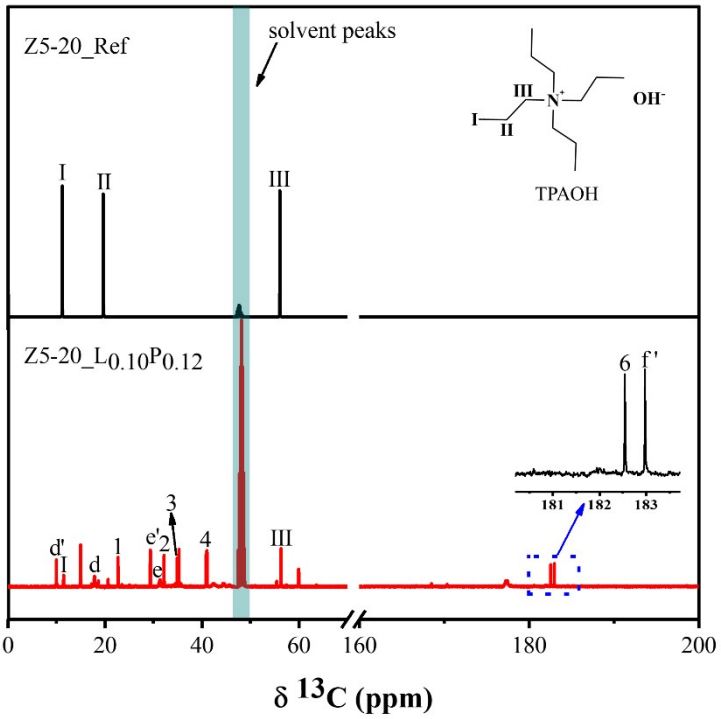

Fig. S8 Liquid-state ^{13}C NMR spectra of the supernatants derived from the synthesis system of Z5-20_Ref and Z5-20_$L_{0.10}P_{0.12}$.

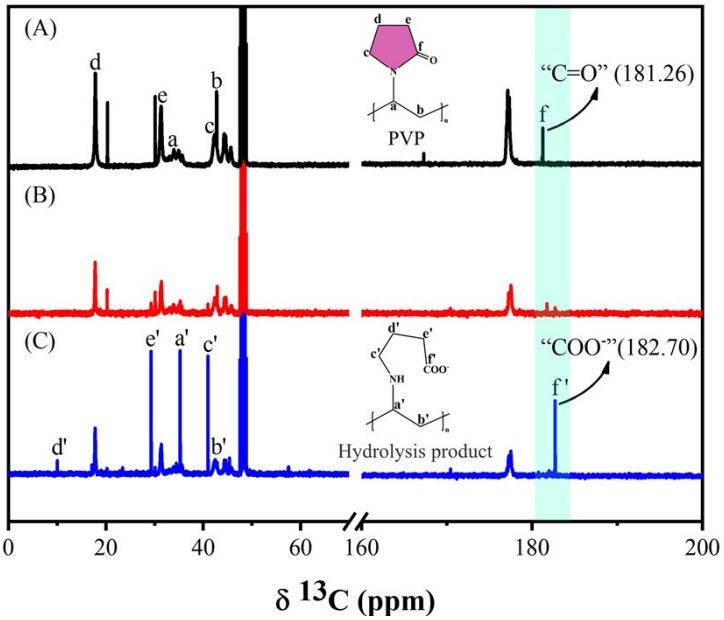

Fig. S9 Liquid-state ^{13}C NMR spectra of PVP solutions. (A) PVP aqueous solution; (B) PVP alkaline solution (NaOH); (C) thermally treated PVP alkaline solution (first 90 °C for 2 days and then175 °C for 1 day)

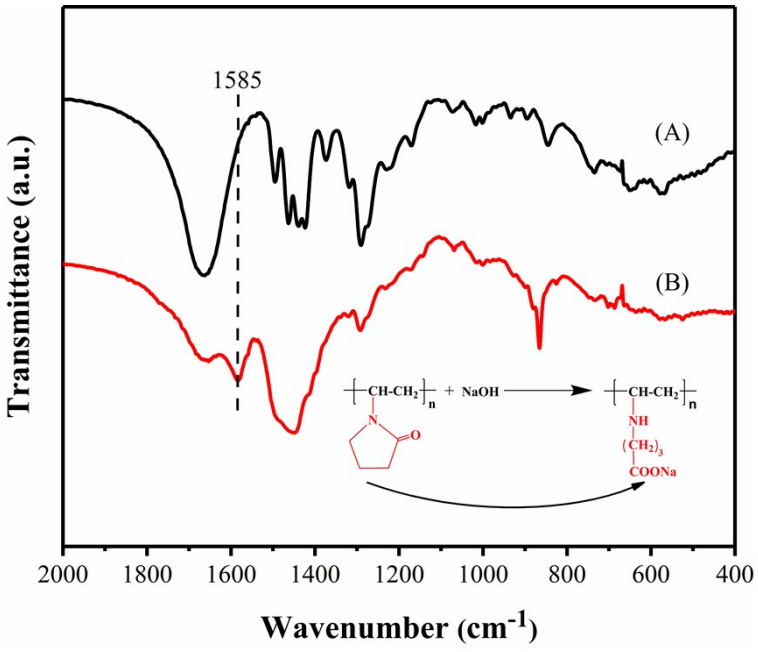

Fig. S10 FT-IR spectra of PVP solutions. (A) PVP aqueous solution; (B) thermally treated PVP alkaline solution (first 90 °C for 2 days and then175 °C for 1 day)

Table S4. Catalytic results of methylation of 2-MN over different H-form ZSM-5 catalysts [a].

Sample	Reaction time	2-MN Conversion /%	Product distribution				Selectivity of 2,6-DMN/%	2,6-DMN/ 2,7-DMN	2,6-DMN Yield/%
			NA	1-MN	DMNs	Poly-MN			
Z5-20_	1	31.0	3.2	66.4	30.0	0.4	6.0	0.7	1.9
Ref	6	22.8	2.2	16.3	71.6	9.9	22.4	1.5	5.1
Z5-20_	1	37.9	2.1	40.6	52.2	5.1	14.5	1.5	5.5
$P_{0.24}$	6	32.7	1.2	15.2	74.2	9.4	24.6	1.6	8.0
Z5-20_	1	26.3	1.4	23.4	69.2	6.0	15.2	1.6	4.0
$L_{0.30}$	6	20.7	1.1	-	91.2	7.7	27.7	1.5	5.8
Z5-20_	1	35.7	1.2	36.6	56.8	5.4	13.3	1.5	4.8
$L_{0.10}P_{0.12}$	6	29.4	0.8	6.8	85.9	6.5	30.4	1.7	8.9
Z5-20_	1	38.0	2.4	46.7	47.0	4.0	12.5	1.6	4.6
$L_{0.10}P_{0.24}$	6	30.0	0.4	22.3	70.3	7.0	25.4	1.6	7.6
Z5-20_	1	33.0	3.0	66.8	28.5	1.7	4.6	0.7	1.5
Con	6	18.7	1.4	21.7	63.0	13.9	19.2	0.8	3.6

[a] Reaction conditions: n(2-MN): n(CH_3OH): n(1,3,5-TMB) = 1:4:4, T = 400 °C, $WHSV_{2\text{-}MN}$ = 1.0

h^{-1}, catalysts weight = 0.5 g, t =1 h, 6 h and 10 h.

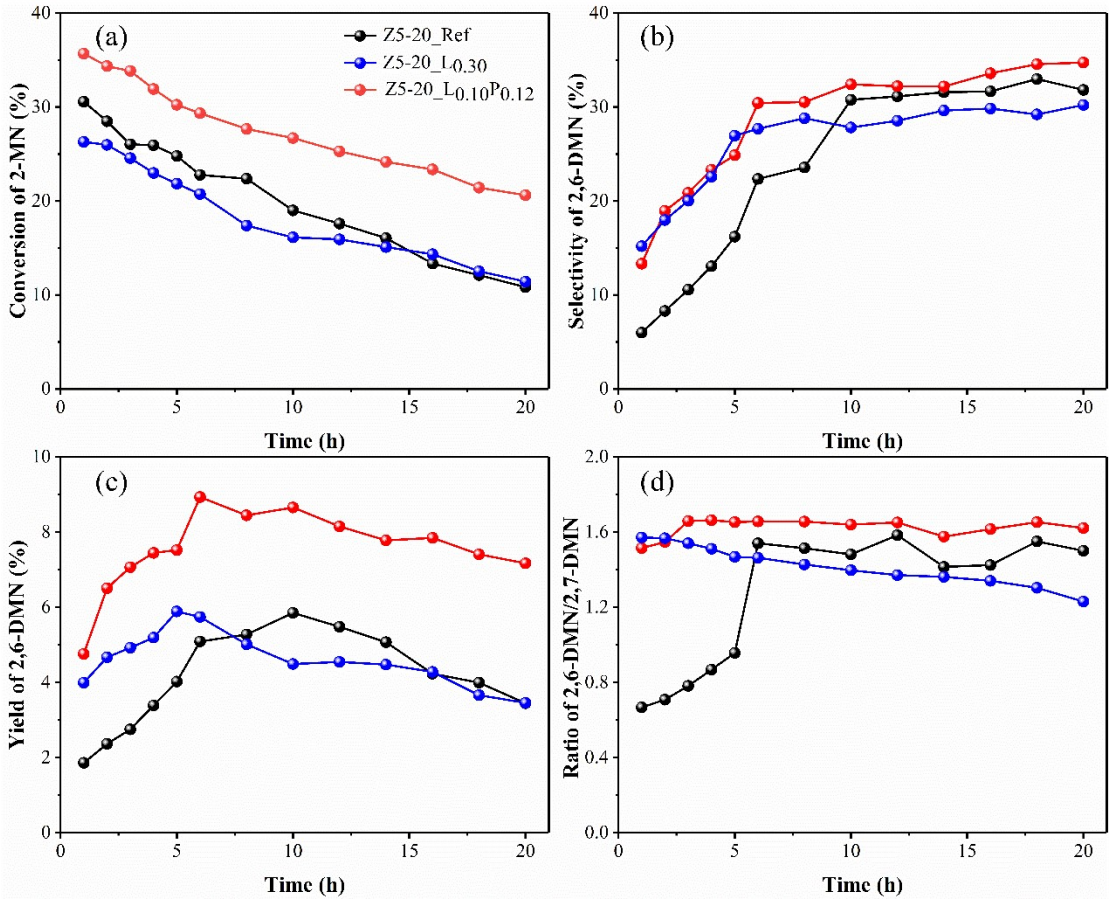

Fig. S11 The catalytic stability of the Z5-20_Ref, Z5-20_$L_{0.30}$ and Z5-20_$L_{0.10}P_{0.12}$ catalysts in the alkylation of 2-MN with methanol. Reaction conditions: n(2-MN): n(CH_3OH): n(1,3,5-TMB) = 1:4:4, T = 400 °C, $WHSV_{2\text{-}MN}$ = 1.0 h^{-1}, catalysts weight = 0.5 g, time-on-stream = 20 h. (a) conversion of 2-MN; (b) the selectivity of 2,6-DMN; (c) yield of 2,6-DMN; (d) ratio of 2,6-/2,7-DMN.

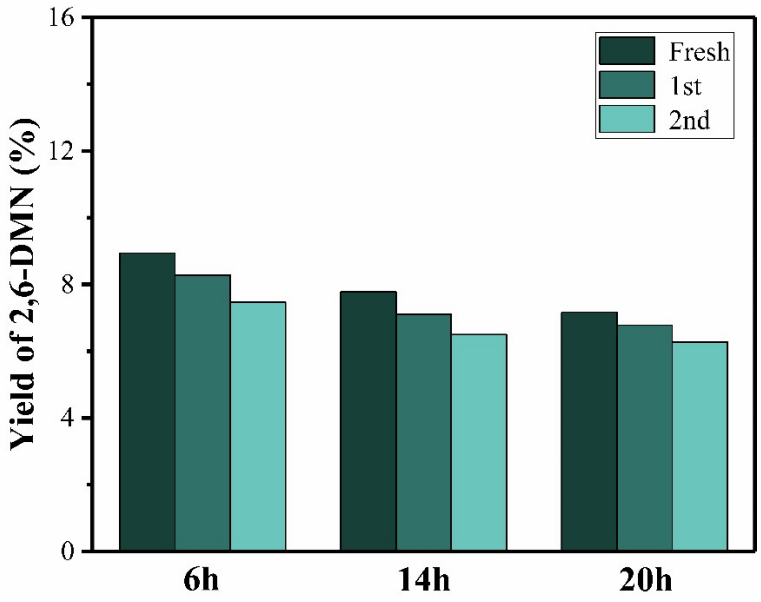

Fig. S12 Recyclability of Z5-20_$L_{0.10}P_{0.12}$ for methylation of 2-MN. Rection condition: n(2-MN): n(CH3OH): n(1,3,5-TMB) = 1:4:4, T = 400 °C, $WHSV_{2\text{-}MN}$ = 1.0 h^{-1}, catalysts weight = 0.5 g.

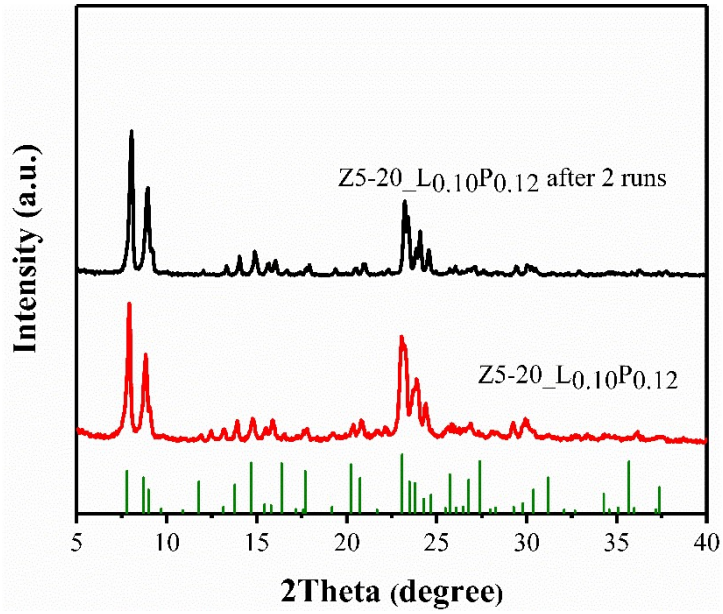

Fig. S13 XRD patterns of Z5-20_$L_{0.10}P_{0.12}$ before and after catalytic durability experiment.

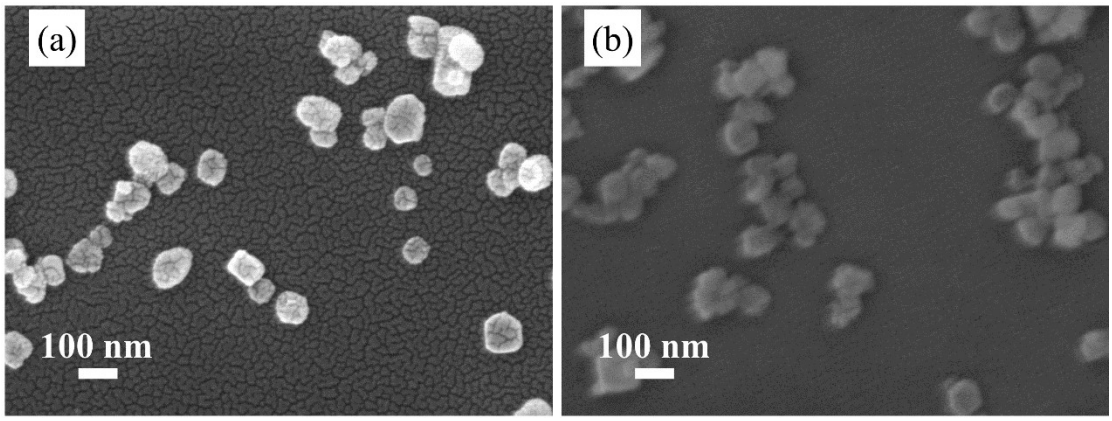

Fig. S14 SEM images of Z5-20_$L_{0.10}P_{0.12}$ before (a) and after (b) catalytic durability experiment.

Table S5. The distributions product and DMNs over different HZSM-5 catalysts with time.

Sample	Reaction Time (h)	1-MN (%)	DMNs (%)	DMNs distribution (%)							
				2,6-DMN	2,7-DMN	2,3-DMN	1,6-DMN	1,7-DMN	1,4-DMN	1,8-DMN	1,2-DMN
Z5-20_Ref	1	66.4	30.0	18.1	26.9	-	21.6	20.0	3.3	1.6	6.1
	6	16.5	72.4	38.4	25.1	-	17.1	11.1	-	3.8	-
	10	11.3	84.5	45.1	30.4	-	-	13.6	-	3.2	-
Z5-20_$P_{0.24}$	1	40.6	52.2	45.8	27.2	2.4	-	7.6	4.1	3.0	4.5
	6	15.2	74.2	51.5	31.8	1.4	-	2.9	9.0	-	1.6
	10	-	86.9	52.4	33.9	-	-	2.3	9.6	-	-
Z5-20_$L_{0.30}$	1	23.4	69.2	35.8	22.8	3.7	2.4	18.0	2.9	4.1	4.9
	6	-	91.2	42.7	29.2	4.4	-	9.8	8.1	3.7	2.0
	10	-	87.4	40.2	29.0	5.7	-	9.8	10.2	3.6	1.6
Z5-20_$L_{0.10}P_{0.12}$	1	36.6	56.8	44.5	29.4	2.2	-	7.4	4.1	2.3	3.8
	6	6.8	85.9	53.9	32.6	-	-	2.4	7.2	-	1.2
	10	-	89.3	55.4	33.8	-	-	2.0	7.4	-	-
Z5-20_$L_{0.10}P_{0.24}$	1	46.7	47.0	38.5	24.4	6.5	-	14.2	1.5	4.0	8.0
	6	22.3	70.3	46.1	29.2	3.5	-	6.5	5.7	2.7	6.3
	10	-	90.9	46.7	31.5	3.3	-	5.0	9.2	2.2	2.2
Z5-20_Con	1	66.8	28.5	11.8	17.2	-	25.0	23.1	1.6	9.4	8.1
	6	21.6	63.0	22.5	27.5	-	19.2	16.4	-	4.7	5.5
	10	17.3	79.2	24.8	28.5	-	20.8	16.3	-	3.8	6.1

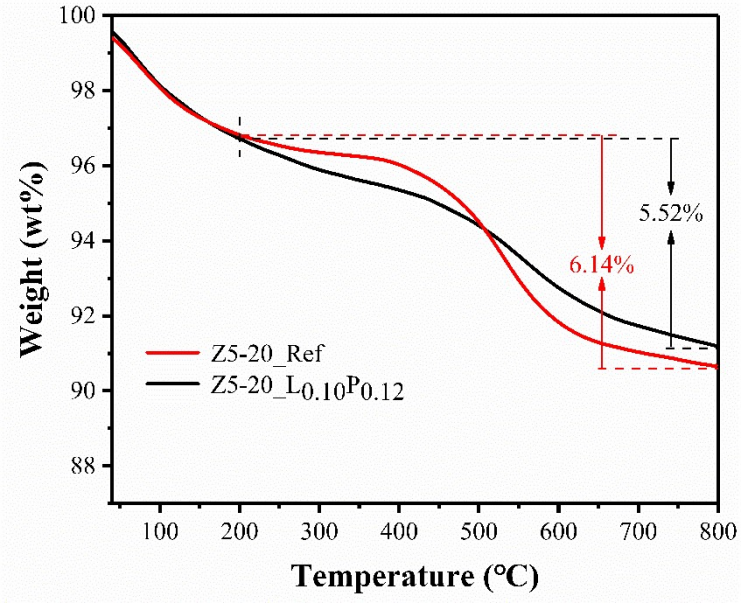

Fig. S15 TG profiles of Z5-20_Ref and Z5-20_$L_{0.10}P_{0.12}$ catalysts after 20 h of the alkylation reaction.

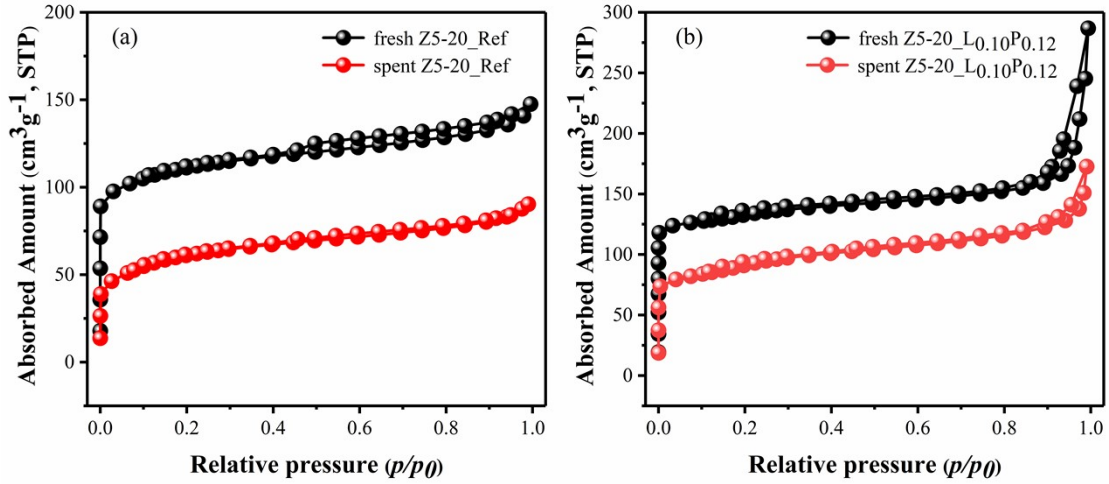

Fig. S16 N_2 adsorption-desorption isotherms of fresh and spent catalysts. (a) Z5-20_Ref, (b)Z5-20_$L_{0.10}P_{0.12}$

Table S6. Textural properties of Z5-20_Ref and Z5-20_$L_{0.10}P_{0.12}$ samples before and after catalytic durability experiment.

Samples	S_{BET} ($m^2 \cdot g^{-1}$)	S_{micro} ($m^2 \cdot g^{-1}$) [a]	V_{mic} ($cm^3 \cdot g^{-1}$) [a]
Z5-20_Ref	344	293	0.14
spent Z5-20_Ref	104	71 (24%)[c]	0.04 (29%)[c]
Z5-20_$L_{0.10}P_{0.12}$	391	319	0.16
spent Z5-20_$L_{0.10}P_{0.12}$	187	104(33%)[c]	0.07(44%)[c]

[a] S_{Micro} (micropore area), and V_{micro} (micropore volume) calculated using the t-plot method. [b] The percentage of S_{micro} and V_{mic} remaining of spent catalysts compared to fresh catalysts.

Table S7. Catalytic performances of the Z5-20_$L_{0.10}P_{0.12}$ catalyst and some representative ZSM-5 zeolites reported in literatures for the alkylation of 2-MN with methanol.

Catalyst [a]	Reaction conditions			Reaction results			Ref
	Time (h)	Temp. (°C)	WHSV (h^{-1})	Sele. (%)	Yield (%)	2,6-DMN /2,7-DMN	
MZSM-5(1.0)	10.25	400	0.5	~29	~6.8	-	1
AT8	10.25	400	0.5	~22	~3.7	~1.1	2
Nano-sized ZSM-5	10.25	400	0.5	~31	~4.7	~1.1	2
AT8-Zr1	3.25	400	0.5	~39	8.6	2.0	2
AT8-Zr1	10.25	400	0.5	~39	~6.6	~2.0	2
MZ(0.05)	14	400	0.5	~37	7.8	-	3
Zr/(Al)ZSM-5	10.25	400	0.5	~45	~4.1	~2.0	4
Zr-Si/(Al)ZSM-5	3	400	0.5	~52	9.0	~2.1	4
0.5Zr/(Al)ZSM-5	3.25	400	0.5	~53	-	3.0	5
SrO/HZSM-5	3	360	6.0	54.6	6.0	1.7	6
La_2O_3-HZSM-5	-	400	1.0	26.6	5.4	1.7	7
Composite ZSM-5/Beta	-	400	1.0	21.2	6.8	1.3	7
Composite ZSM-5/Beta[b]	-	400	1.0	20.8	11.01	1.4	7
HZSM-5(550)	5	360	2.0	54.9	5.3	1.5	8
HZSM-5(550A)	5	360	2.0	57.5	7.1	1.7	8
HT-HZSM-5	2	360	6.0	48.2	4.9	1.6	9
ZrBZ(Zr/Beta)	-	400	1.0	~10	~5.2	~1.6	10
Z5-20_$L_{0.10}P_{0.12}$	6	400	1.0	30.3	8.9	1.7	M
	10	400	1.0	32.6	8.7	1.6	M
	20	400	1.0	35.0	7.2	1.6	M

[a] Based on 1,3,5-TMB as solvent. [b] Based on C_{10} aromatics as solvent and transmethylation-agentia. [M] This work.

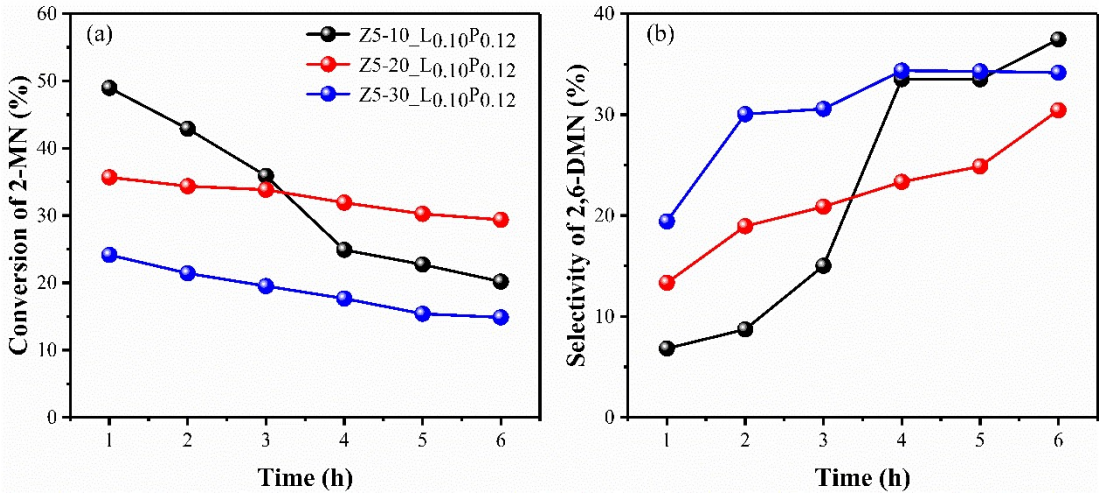

Fig. S17 The catalytic conversion (a) and selectivity (b) of ZSM-5 zeolites with different SiO_2/Al_2O_3 in the alkylation of 2-MN with methanol. Reaction conditions: n(2-MN): n(CH_3OH): n(1,3,5-TMB) = 1:4:4, T = 400 °C, $WHSV_{2\text{-}MN}$ = 1.0 h^{-1}, catalysts weight = 0.5g, time-on-stream = 6 h.

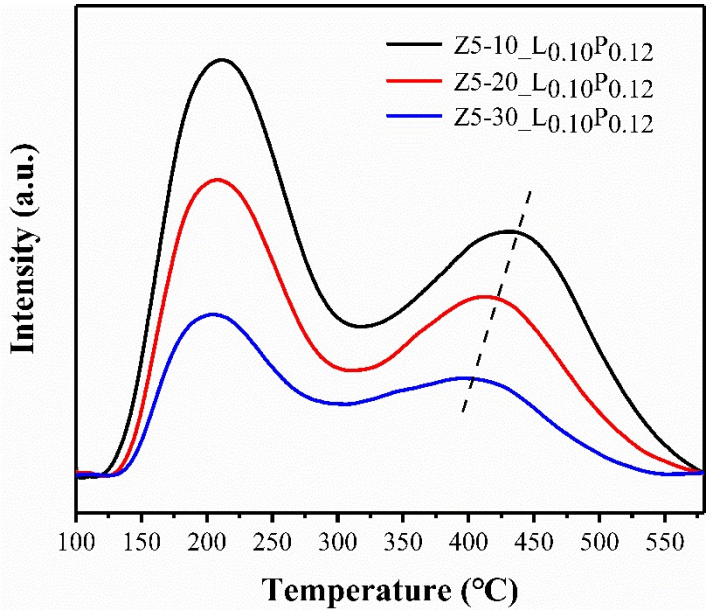

Fig. S18 The NH_3-TPD profiles of the HZSM-5 zeolites with different SiO_2/Al_2O_3.

References

1. L. Jin, T. Xie, S. Liu, Y. Li and H. Hu, *Catal. Commun.*, 2016, **75**, 32-36.
2. L. Jin, X. Zhou, H. Hu and B. Ma, *Catal. Commun.*, 2008, **10**, 336-340.
3. L. Jin, S. Liu, T. Xie, Y. Wang, X. Guo and H. Hu, *React. Kinet., Mech. Catal.*, 2014, **113**, 575-584.
4. L. Jin, H. Hu, X. Wang and C. Liu, *Ind. Eng. Chem. Res.*, 2006, **45**, 3531-3536.
5. L. Jin, Y. Fang and H. Hu, *Catal. Commun.*, 2006, **7**, 255-259.
6. C. Zhang, X. W. Guo, Y. N. Wang, X. S. Wang and C. S. Song, *Chin. Chem. Lett.*, 2007, **18**, 1281-1284.
7. J. Li, Q. Gong, H. Lian, Z. Hu and Z. Zhu, *Ind. Eng. Chem. Res.*, 2019, **58**, 12593-12601.
8. L. Zhao, H. Wang, M. Liu, X. Guo, X. Wang, C. Song and H. Liu, *Chem. Eng. Sci.*, 2008, **63**, 5298-5303.
9. C. Zhang, X. Guo, C. Song, S. Zhao and X. Wang, *Catal. Today*, 2010, **149**, 196-201.
10. F. Güleç, F. Sher and A. Karaduman, *Petr. Sci.*, 2018, **16**, 161-172.