

Electronic Supplementary Information for

In situ growth-etching synthesis of hierarchical SAPO-34 from recycled mother liquor for ethanol dehydration

Shuhua Liu, Hongxia Zhang, Jianxia Zhang, Zhihao Bian, Fang Wang*, Dezhi Han, Guangjian Wang, Liancheng Bing*

*School of Chemical Engineering, Qingdao University of Science and Technology, Qingdao Shandong 266042, China
E-mail: blc0633@126.com*

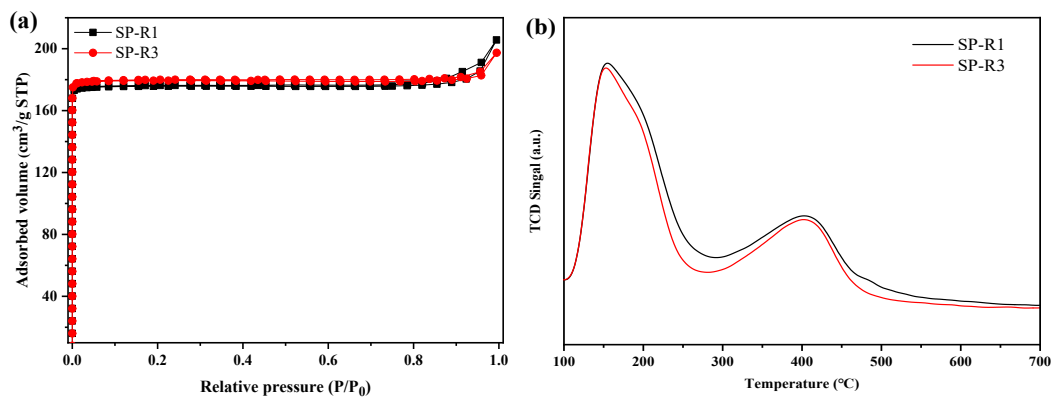


Fig. S1 (a) N₂ adsorption/desorption isotherms (b) NH₃-TPD profiles of SP-R1 and SP-R3.

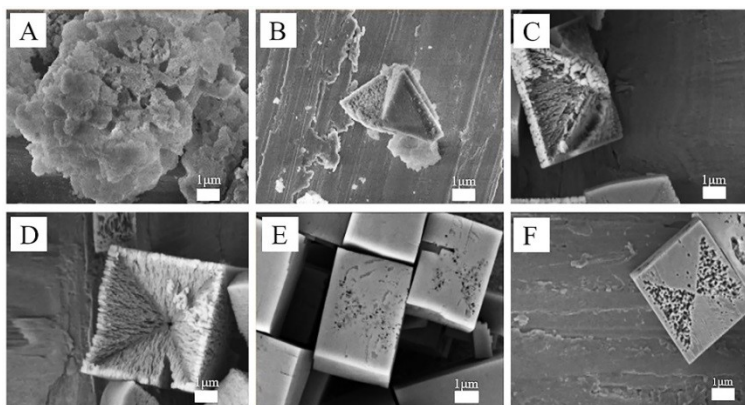


Fig. S2 SEM images of SP-T9 synthesized at (A)1 h, (B) 2 h, (C) 3 h, (D) 6 h, (E) 18 h, and (F) 24 h.

Table S1 Gel composition, pH of synthesis systems and mother liquid composition.

Samples	Gel composition	Mother liquid composition ^[d]	pH
SP-T3	1.00 Al ₂ O ₃ : 1.00 P ₂ O ₅ : 0.20 SiO ₂ : 3.00 TEA: 50 H ₂ O	0.63 Al ₂ O ₃ : 0.55 P ₂ O ₅ : 0.14 SiO ₂ : 2.21 TEA: 35 H ₂ O	7.65
SP-T9	1.00 Al ₂ O ₃ : 1.00 P ₂ O ₅ : 0.20 SiO ₂ : 9.00 TEA: 50 H ₂ O	0.64 Al ₂ O ₃ : 0.57 P ₂ O ₅ : 0.13 SiO ₂ : 8.15 TEA: 36 H ₂ O	9.54
SP-R1	(0.64 ^[a] +0.36 ^[b]) Al ₂ O ₃ : (0.57 ^[a] +0.43 ^[b]) P ₂ O ₅ : (0.13 ^[a] + 0.07 ^[b]) SiO ₂ : 8.15 TEA ^[c] : (36+14) H ₂ O	0.62 Al ₂ O ₃ : 0.56 P ₂ O ₅ : 0.14 SiO ₂ : 7.34 TEA: 34 H ₂ O	8.83
SP-R2	(0.62 ^[a] +0.38 ^[b]) Al ₂ O ₃ : (0.56 ^[a] +0.44 ^[b]) P ₂ O ₅ : (0.14 ^[a] + 0.06 ^[b]) SiO ₂ : 7.44 TEA ^[c] : (34+16) H ₂ O	0.65 Al ₂ O ₃ : 0.54 P ₂ O ₅ : 0.14 SiO ₂ : 6.78 TEA: 36 H ₂ O	8.40
SP-R3	(0.65 ^[a] +0.36 ^[b]) Al ₂ O ₃ : (0.54 ^[a] +0.43 ^[b]) P ₂ O ₅ : (0.14 ^[a] + 0.07 ^[b]) SiO ₂ : 6.82 TEA ^[c] : (36+14) H ₂ O	0.67 Al ₂ O ₃ : 0.60 P ₂ O ₅ : 0.15 SiO ₂ : 6.26 TEA: 37 H ₂ O	8.12

[a] The residual inorganic sources in the mother liquids; [b] Supplemented inorganic sources; [c] The residual amount of TEA in the mother liquids according to TG analysis of the products; [d] Calculated by TG and ICP.

Table S2 Physicochemical properties of SP-R1 and SP-R3.

Samples	Si/Al ^[a]	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{ext} (m ² /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)
SP-R1	Si _{0.07} Al _{0.37} P _{0.57} O ₂	537	532	4	0.270	0.048
SP-R3	Si _{0.06} Al _{0.38} P _{0.58} O ₂	548	545	5	0.276	0.029

[a] Measured by X-ray fluorescence (XRF) spectrometer.

Table S3 Products distribution of ethanol conversion over SP-T3 and SP-T9 catalysts as a function of reaction temperature.

Sample	Temperature (°C)	Product content (%)						
		Ethane	Ethylene	Propane	Propylene	Butene	Butane	Ether
SP-T3	160	3.1	0	58.0	3.8	1.1	0	34.0
	190	4.0	4.5	54.6	5.6	0.9	0	30.4
	220	5.3	17.3	48.7	6.8	2.6	1.2	18.1
	250	2.6	45.1	35.0	3.3	1.8	0.9	11.3
	280	0.9	62.4	26.6	5.3	0.2	0	4.6
	310	1.3	71.0	17.4	5.0	2.6	0.4	2.2
	340	2.2	80.5	12.1	3.4	0.9	0	0.9
	370	0.9	85.3	6.2	2.9	3.7	1.0	0
	400	0.5	88.7	5.5	4.8	0.5	0	0
	SP-T9	160	1.1	6.6	60.2	0	0	0
190		5.7	17.1	43.3	3.2	2.3	1.7	26.7
220		3.7	55.3	18.6	1.7	0.5	0.4	19.8
250		2.2	82.3	6.5	1.6	1.5	0.8	5.1
280		0.3	97.9	0.8	0.1	0	0	0.9
310		0.2	99.3	0.3	0.2	0	0	0
340		0	99.8	0.2	0	0	0	0
370		0	100	0	0	0	0	0
400		0	100	0	0	0	0	0

Table S4 Products distribution of ethanol conversion over SP-R1, R2, and SP-R3 catalysts as a function of reaction temperature.

Sample	Temperature (°C)	Product content (%)						
		Ethane	Ethylene	Propane	Propylene	Butene	Butane	Ether
SP-R1	160	2.9	8.9	52.3	10.8	2	0	23.1
	190	3.6	38.3	34.5	6.3	0	0	17.3
	220	0.5	74.2	16.8	1.8	0.8	0	5.9
	250	1.3	80.3	11.9	3.7	1.2	0.6	1
	280	0.1	98.8	0.8	0.1	0	0	0.2
	310	0	99.9	0.1	0	0	0	0
	340	0.1	98.9	0.7	0.2	0.1	0	0
	370	0.1	98.7	1	0.2	0	0	0
	400	0.1	97.8	1.5	0.2	0.2	0.2	0
SP-R2	160	1.3	2.3	68.5	1.1	0.1	0	26.7
	190	0.8	26.6	46.3	7.7	0	0	18.6
	220	2.2	56.3	22.2	6.2	1.3	0.1	11.7
	250	2.1	74.5	14.2	2.1	0.3	0	6.8
	280	0.7	92.5	3.3	1	0.3	0.1	2.1
	310	0.3	97.8	1.2	0.5	0	0	0.2
	340	0.4	98.7	0.8	0.1	0	0	0
	370	0.1	99	0.5	0.4	0	0	0
	400	0.4	98.4	1.1	0.1	0	0	0
SP-R3	160	3.7	10.6	55.1	2.3	0.2	0	28.1
	190	2.8	15.9	49.3	6.8	2.7	0.4	22.1
	220	3.1	49.3	28.1	3.5	2.1	0.2	13.7
	250	0.6	73.7	12.8	4.9	0.6	0.7	6.7
	280	0.6	87.5	7.6	1.9	0.2	0	2.2
	310	0	92.1	4.7	1.6	0.1	0	1.5
	340	0.2	95.1	4.1	0.3	0	0	0.3
	370	0.1	95.1	4.1	0.7	0	0	0
	400	1.5	95.1	2.5	0.4	0.3	0.2	0