

Supplementary Materials

## Ionothermal Synthesis of Triclinic SAPO-34 Zeolites

Li Han <sup>1,2,\*</sup>, Xinxin Yan <sup>2</sup>, Lulu Guo <sup>2</sup>, Yanan Duan <sup>2</sup>, Zheng Wang <sup>3</sup>, Tianliang Lu <sup>2</sup>, Jun Xu <sup>2</sup>, Yuzhong Zhan <sup>2</sup> and Jianfeng Wang <sup>1,\*</sup>

<sup>1</sup> School of Ecology and Environment, Zhengzhou University, Zhengzhou 450001, China

<sup>2</sup> School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China;  
xinxinyan0131@163.com (X.Y.); gllzzu@163.com (L.G.); DuanYN\_ZZU@163.com (Y.D.);  
lutianliang@zzu.edu.cn (T.L.); jxuzzu@sohu.com (J.X.); zhanyz@zzu.edu.cn (Y.Z.);

<sup>3</sup> State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Institute of  
Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China; wzheng@nxu.edu.cn

\* Correspondence: lihan@zzu.edu.cn (L.H.); wangjf@zzu.edu.cn (J.W.)

**Table S1.** XRD date of different samples.

AlPO <sub>4</sub> -34		S-Si-0.1		S-Si-0.3		S-Si-0.5	
2θ	d	2θ	d	2θ	d	2θ	d
9.61	9.19	9.82	9.00	9.70	9.11	9.73	9.08
15.77	5.61	15.98	5.54	15.82	5.59	15.86	5.58
25.74	3.46	25.95	3.43	25.87	3.45	25.95	3.43
30.87	2.90	31.05	2.87	31.02	2.87	31.01	2.88

**Table S2.** Structural parameters of SAPO-34 molecular sieves

Sam-ples	Molar composition <sup>a</sup>	S <sup>b</sup> <sub>BET</sub> (m <sup>2</sup> /g)	S <sup>c</sup> <sub>micro</sub> (m <sup>2</sup> /g)	S <sup>c</sup> <sub>ext</sub> (m <sup>2</sup> /g)	V <sup>c</sup> <sub>micro</sub> (cm <sup>3</sup> /g)	V <sup>d</sup> <sub>meso</sub> (cm <sup>3</sup> /g)	D <sup>e</sup> <sub>avg</sub> (nm)
S-Si-0.1	Al <sub>0.476</sub> P <sub>0.518</sub> Si <sub>0.006</sub> O <sub>2</sub>	562.69	532.34	30.35	0.26	0.10	11.50
S-Si-0.3	Al <sub>0.476</sub> P <sub>0.505</sub> Si <sub>0.019</sub> O <sub>2</sub>	526.02	470.74	55.28	0.23	0.17	10.35
S-Si-0.5	Al <sub>0.466</sub> P <sub>0.511</sub> Si <sub>0.023</sub> O <sub>2</sub>	511.89	455.04	56.85	0.22	0.17	8.28

a Measured by energy dispersive spectrometry (EDS).

b S<sub>BET</sub> (total surface area) calculated by applying the BET equation using the linear part (0.05 < P/P<sub>0</sub> < 0.30) of the adsorption isotherm.c S<sub>micro</sub> (micropore area), S<sub>ext</sub> (external surface area) and V<sub>micro</sub> (micropore volume) calculated using the t-plot method.d V<sub>meso</sub> (mesopore volume).e D<sub>avg</sub> (average diameter) calculated using the BJH method (from desorption).**Table S3.** Synthesis conditions in [EMIm]Cl

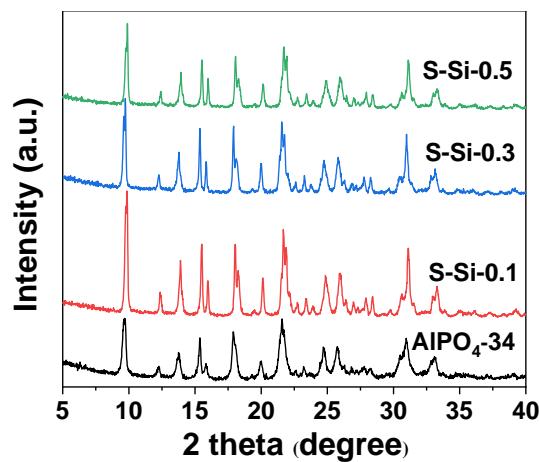
Sample	Raw material molar ratio	Crystallization	Crystallization
		Temperature	Time
S1(150 °C)	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	150 °C	48 h
S1(180 °C)	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S1(200 °C)	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	200 °C	48 h
S1-Si-0.1	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S1-Si-0.3	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.3Si	180 °C	48 h
S1-Si-0.5	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.5Si	180 °C	48 h
S1-F-0	39[EMIm]Cl: 1TEA: 1Al: 3P: 0HF: 0.1Si	180 °C	48 h
S1-F-0.3	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.3HF: 0.1Si	180 °C	48 h
S1-F-0.7	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S1-F-1.0	39[EMIm]Cl: 1TEA: 1Al: 3P: 1.0HF: 0.1Si	180 °C	48 h
S1-3 h	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	3 h
S1-6 h	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	6 h
S1-12 h	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	12 h
S1-24 h	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	24 h
S1-48 h	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h

**Table S4.** Synthesis conditions in different ionic liquids

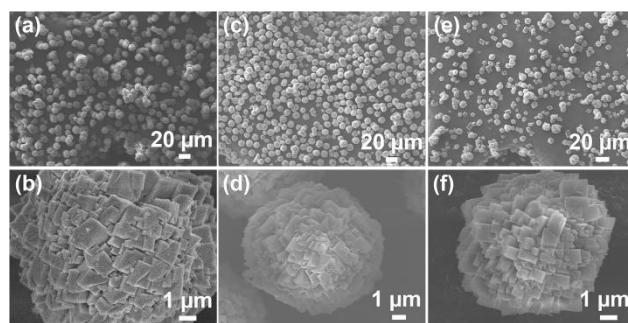
Sample	Raw material molar ratio	Crystallization Temperature	Crystallization Time
S-EM-C	39[EMIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si(op)	180 °C	48 h
S-EM-B	39[EMIm]Br: 1TEA: 1Al: 3P: 0.7HF: 0.1S(op)	180 °C	48 h
S-BM-C	21[BMIIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si(cl)	180 °C	48 h
S-BM-B	21[BMIIm]Br: 1TEA: 1Al: 3P: 0.7HF: 0.1Si(cl)	180 °C	48 h
S-EMM-B	39[EMMIm]Br: 1TEA: 1Al: 3P: 0.7HF: 0.1Si(cl)	180 °C	48 h
S-BMM-B	39[BMMIm]Br: 1TEA: 1Al: 3P: 0.7HF: 0.1Si(cl)	180 °C	48 h

**Table S5.** Synthesis conditions in different templates

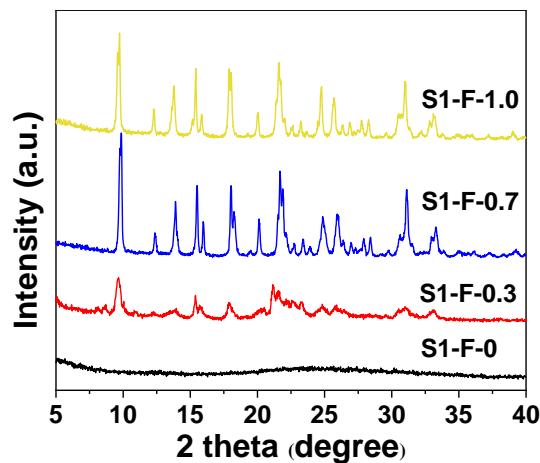
Sample	Raw material molar ratio	Crystallization Temperature	Crystallization Time
S1-T-0	39[EMIm]Cl: 0TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S1-T-0.5	39[EMIm]Cl: 0.5TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S1-T-1.0	39[EMIm]Cl: 1.0TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S1-T-1.5	39[EMIm]Cl: 1.5TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-T-0	21[BMIIm]Cl: 0TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-T-0.5	21[BMIIm]Cl: 0.5TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-T-1.0	21[BMIIm]Cl: 1.0TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-T-1.5	21[BMIIm]Cl: 1.5TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-TME	21[BMIIm]Cl: 1TEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-DEA	21[BMIIm]Cl: 1DEA: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-MOR	21[BMIIm]Cl: 1MOR: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-N-MIM	21[BMIIm]Cl: 1N-MIM: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h
S2-TEAOH	21[BMIIm]Cl: 1TEAOH: 1Al: 3P: 0.7HF: 0.1Si	180 °C	48 h



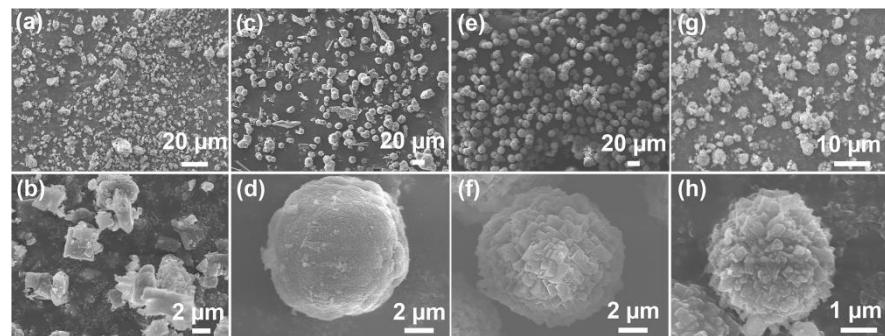
**Figure S1.** XRD patterns of samples under different molar amounts of Si.



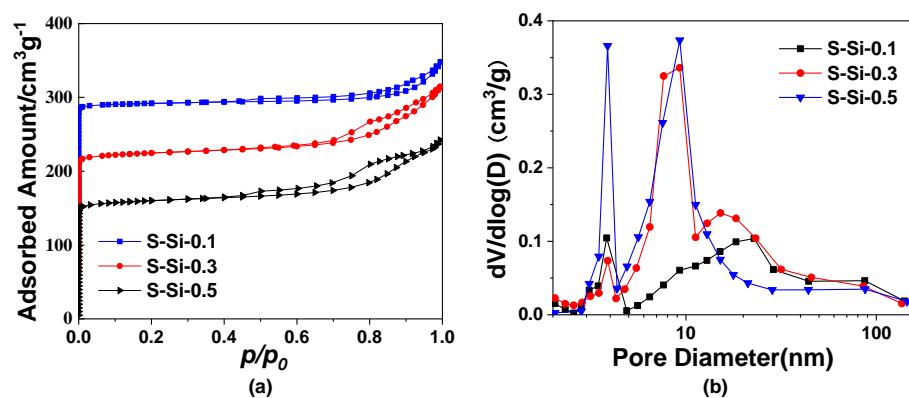
**Figure S2.** SEM images of samples under different molar amounts of Si (**a, b** for S-Si-0.1, **c, d** for S-Si-0.3, and **e, f** for S-Si-0.5).



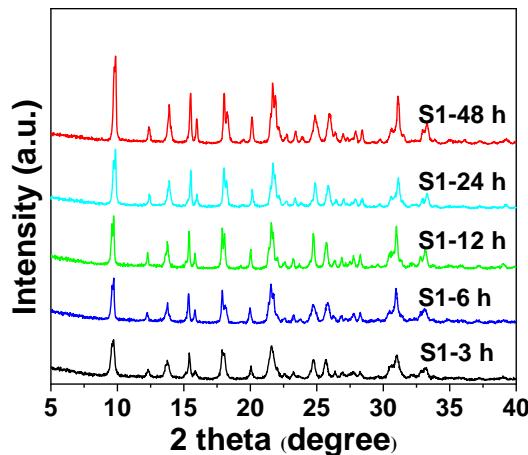
**Figure S3.** XRD patterns of samples under different molar amounts of HF.



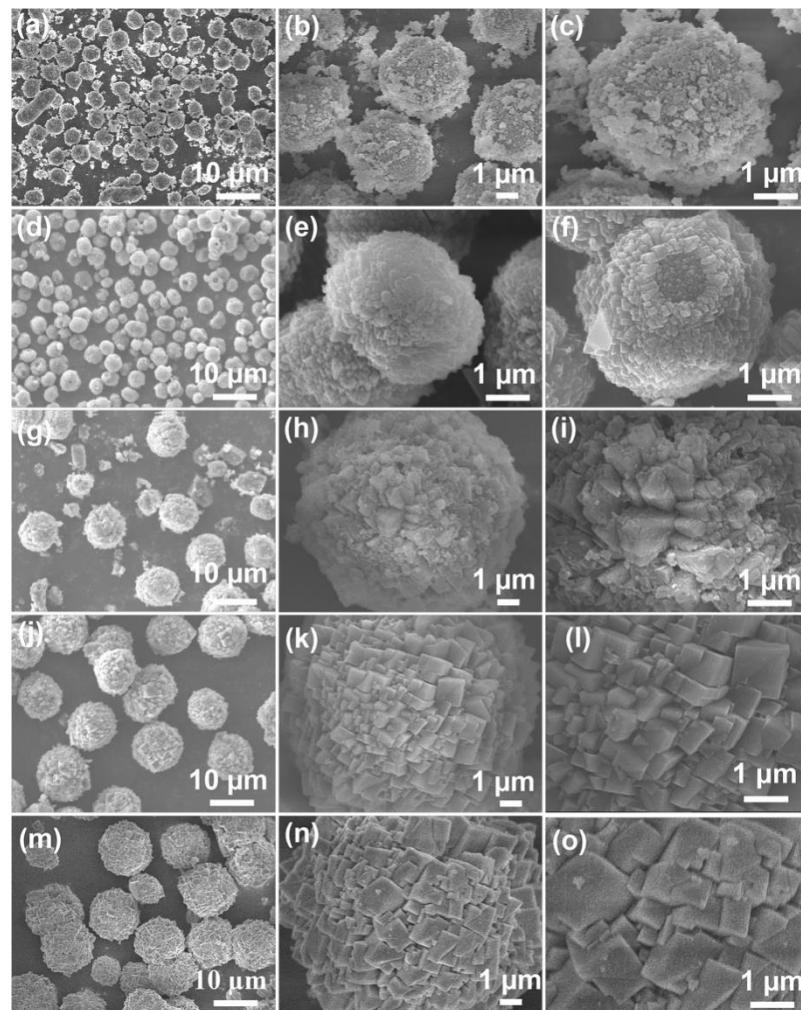
**Figure S4.** SEM images of samples under different molar amounts of HF (**a, b** for S1-F-0, **c, d** for S1-F-0.3, **e, f** for S1-F-0.7, and **g, h** for S1-F-1.0).



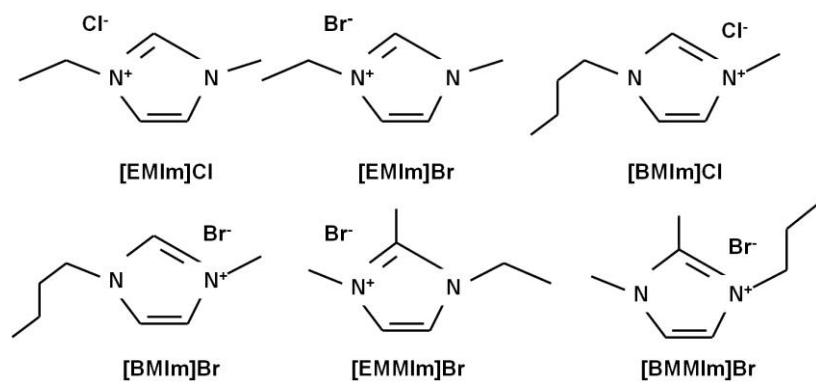
**Figure S5.** (a)  $\text{N}_2$  adsorption-desorption isotherms and (b) BJH pore size distributions of triclinic SAPO-34 molecular sieves.



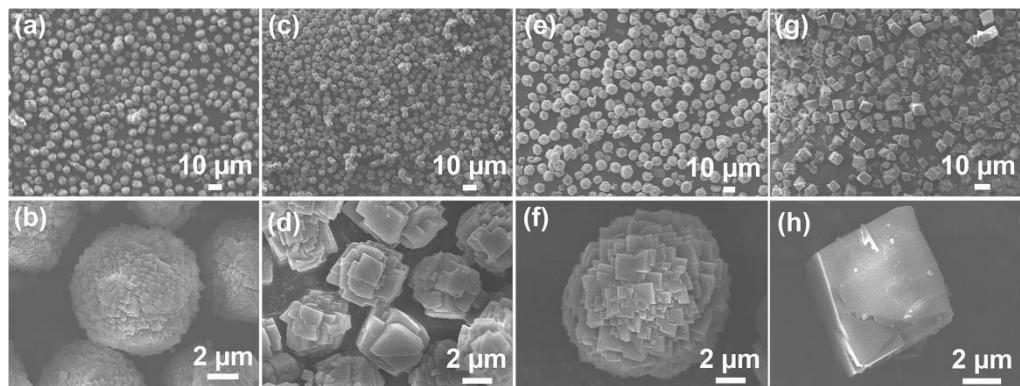
**Figure S6.** XRD patterns of samples at different crystallization times.



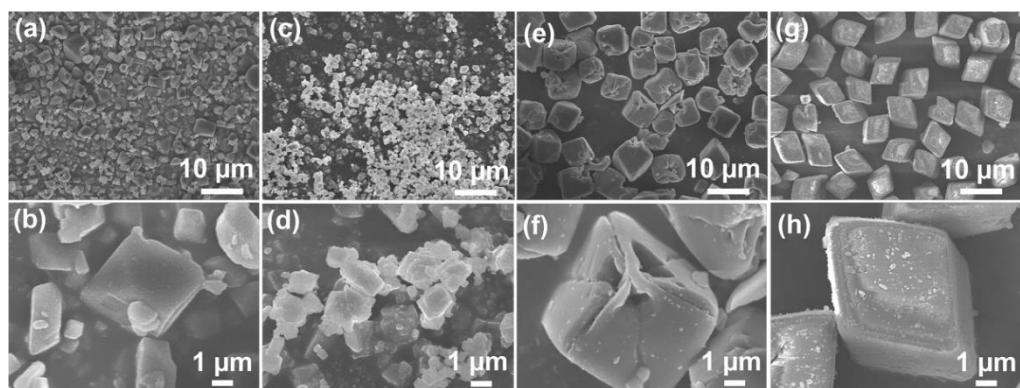
**Figure S7.** SEM images of samples at different crystallization times (**a~c** for S1-3 h, **d~f** for S1-6 h, **g~i** for S1-12 h, **j~l** for S1-24 h, and **m~o** for S1-48 h).



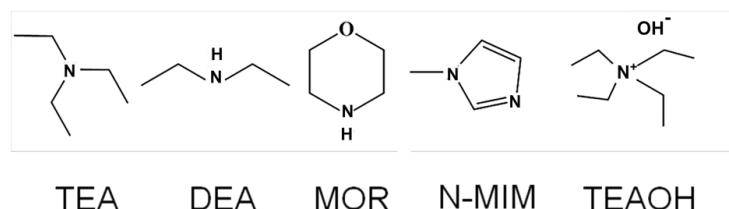
**Figure S8.** Structure of ionic liquids.



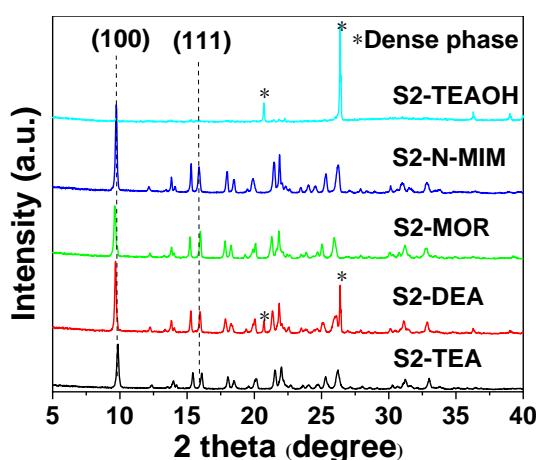
**Figure S9.** SEM images of samples under different molar amounts of TEA (**a, b** for S1-T-0, **c, d** for S1-T-0.5, **e, f** for S1-T-1.0, and **g, h** for S1-T-1.5).



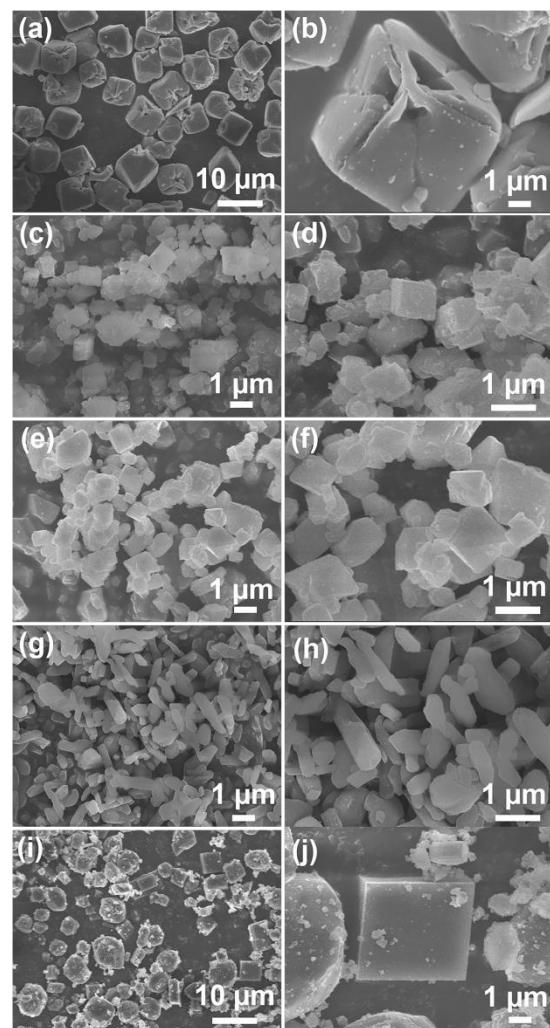
**Figure S10.** SEM images of samples at different molar amounts of TEA (**a, b** for S2-T-0, **c, d** for S2-T-0.5, **e, f** for S2-T-1.0, and **g, h** for S2-T-1.5).



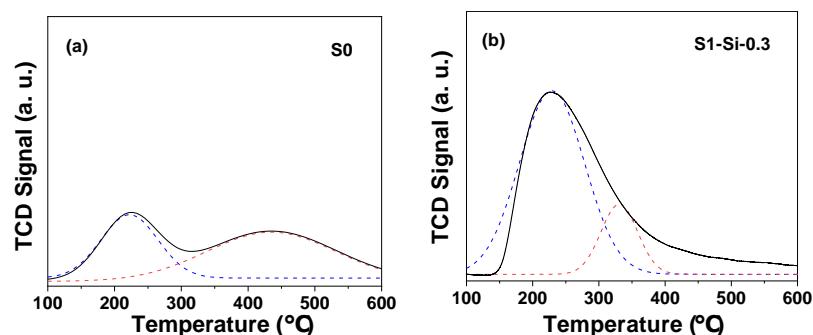
**Figure S11.** Structure of different templating agents.



**Figure S12.** XRD patterns of samples under different types of template.



**Figure S13.** SEM images of samples under different types of template (**a, b** for S2-TEA, **c, d** for S2-DME, **e, f** for S2-MOR, **g, h** for S2-N-MIM, and **i, j** for S2-TEAOH).



**Figure S14.** NH<sub>3</sub>-TPD patterns of SAPO-34 molecular sieves.