Supplementary Information for

Boosting the growth kinetics of extra-large pore zeolite ZEO-1

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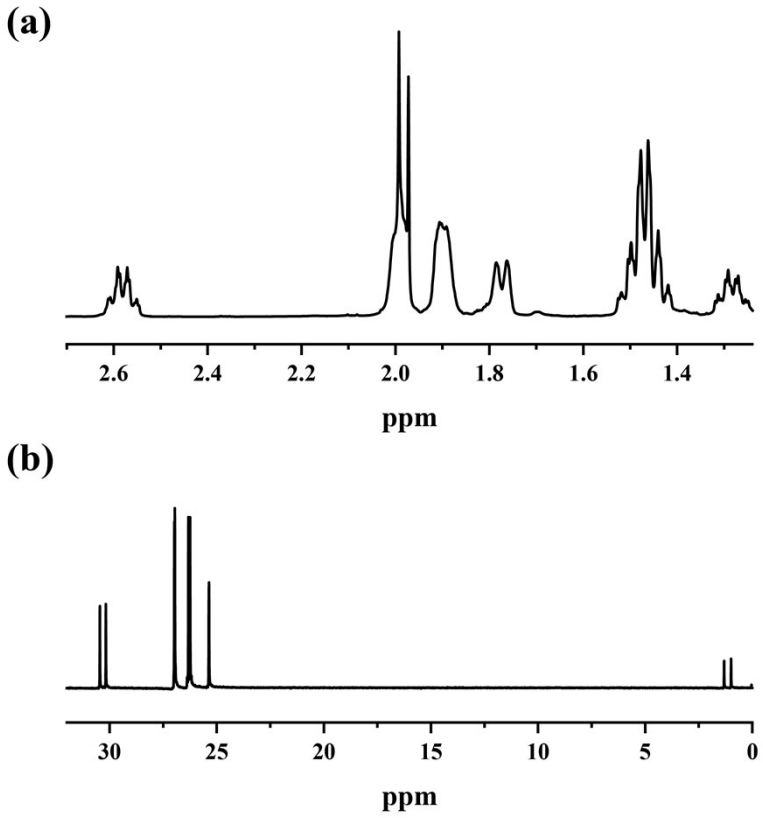

Fig. S1. Liquid phase ^{1}H NMR (a) and ^{13}C NMR (b) spectra of $TCyMP^{+}$ in $CDCl_3$.

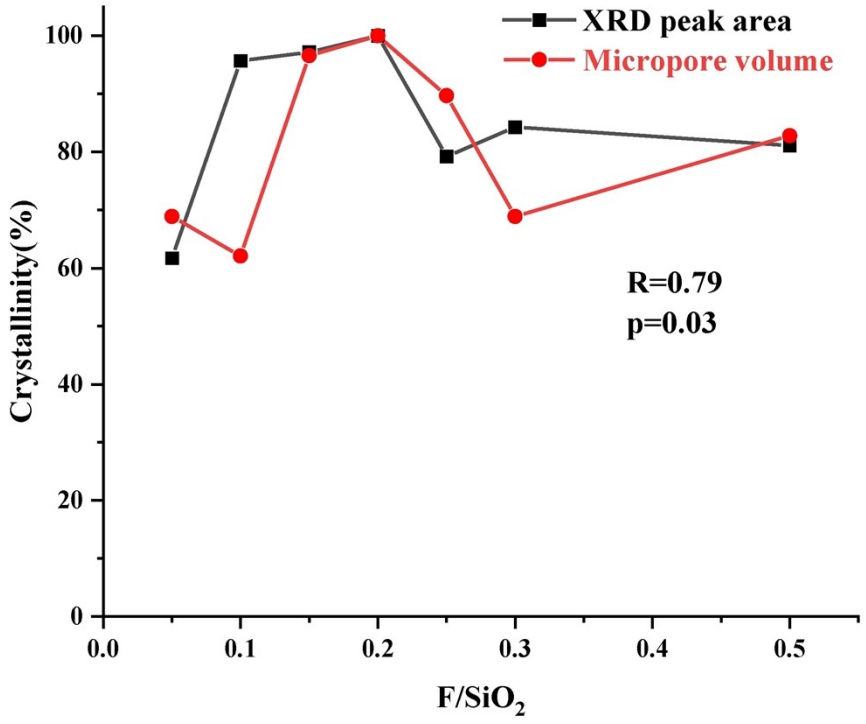

Fig. S2. The variation of crystallinity (%) with the F/SiO_2 ratio calculated by XRD peak area method (black square) and micropore volume method (red dot).

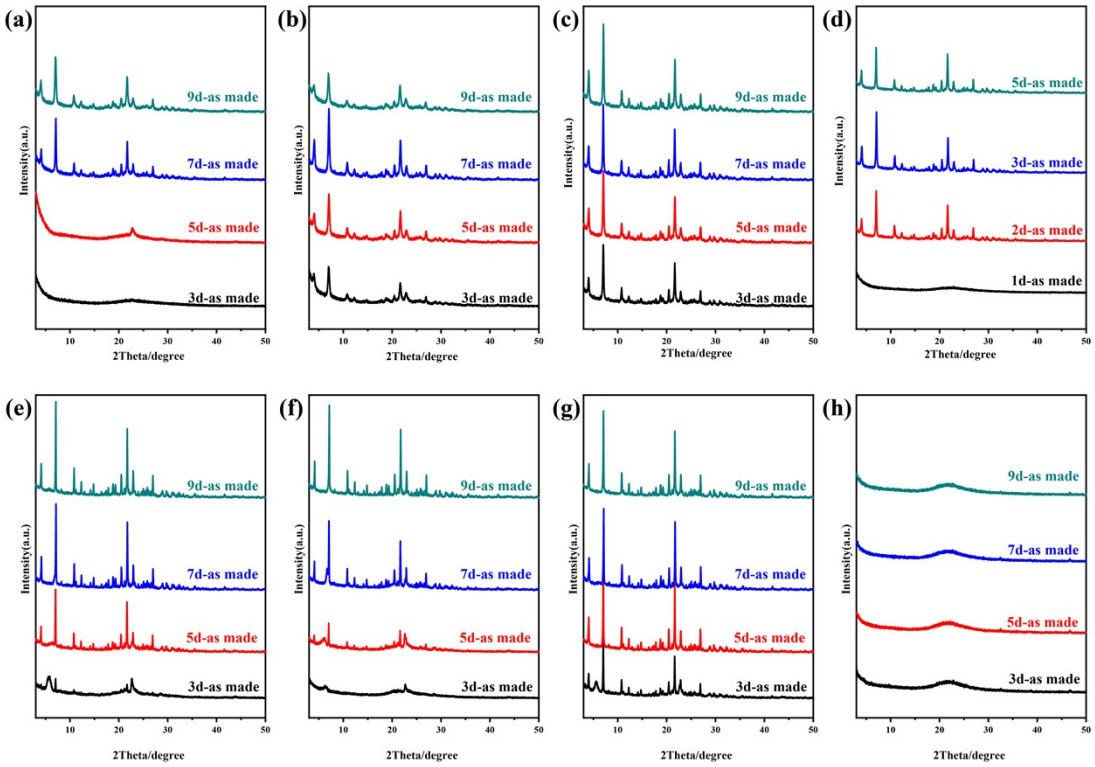

Fig. S3. PXRD patterns of products obtained with a gel F/SiO_2 ratio of 0.05 (a), 0.10 (b), 0.15 (c), 0.20 (d), 0.25 (e), 0.30 (f), 0.50 (g) and 0.70 (h) using HF as fluoride source.

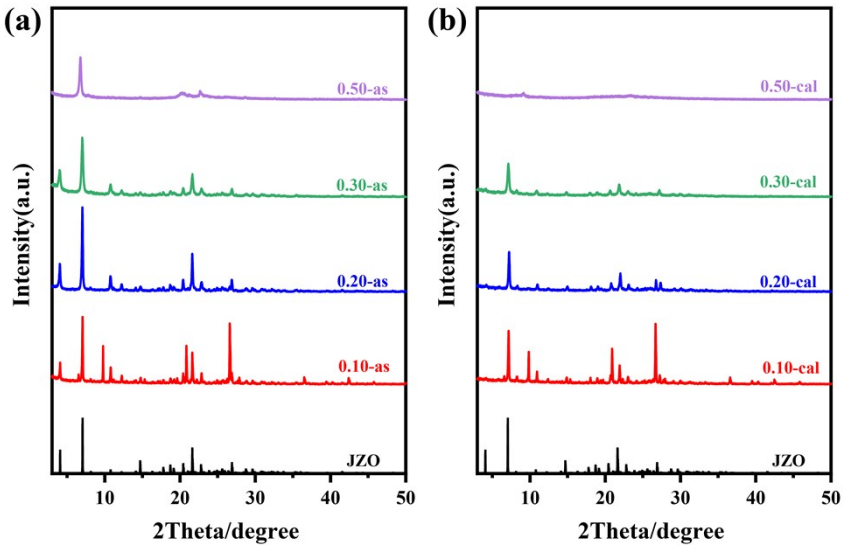

Fig. S4. PXRD patterns of as-made (a) and calcined (b) ZEO-1 zeolites obtained with different F/SiO_2 ratios using NH_4F as the fluoride source. The gel molar composition is 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* NH_4F:10 H_2O, *x* = 0.1-0.5.

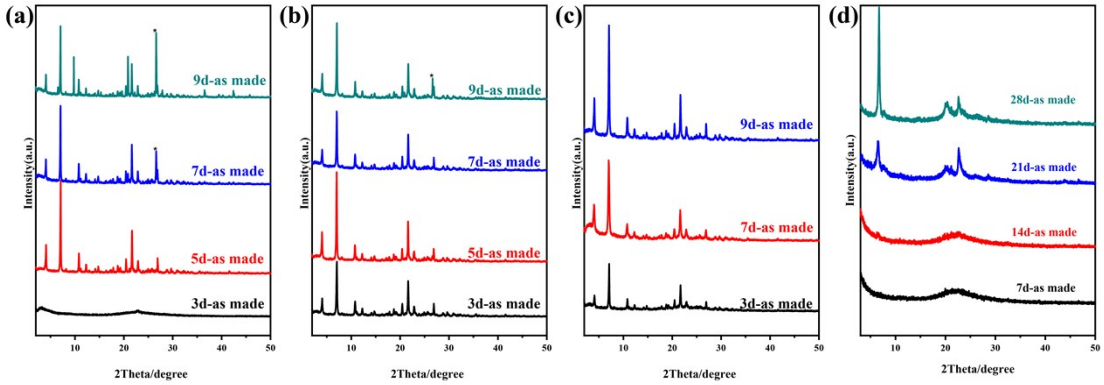

Fig. S5. PXRD patterns of products obtained with a gel F/SiO_2 ratio of 0.10 (a), 0.20 (b), 0.30 (c) and 0.50 (d) using NH_4F as fluoride source. The asterisk symbols (*) indicate quartz phase.

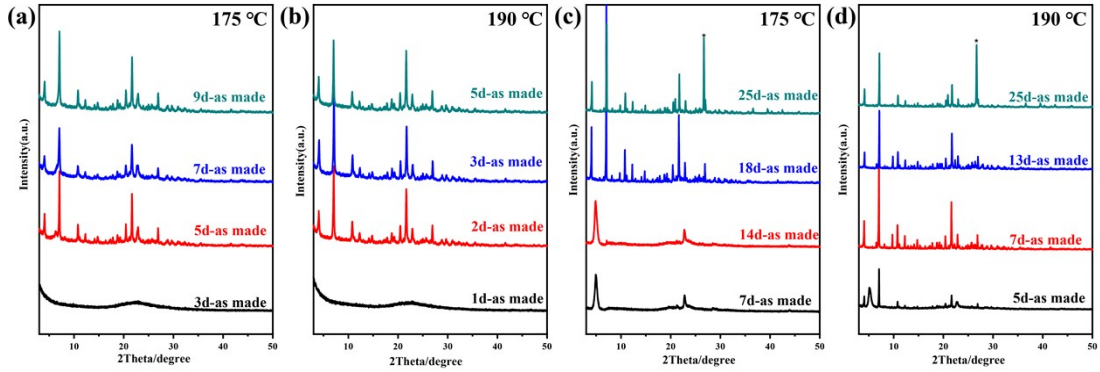

Fig. S6. PXRD patterns of ZEO-1 zeolites obtained using HF (a, c) and in OH^- medium (b, d). The gel molar composition is 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* HF:10 H_2O, *x* = 0 or 0.2. The asterisk symbols (*) indicate quartz phase.

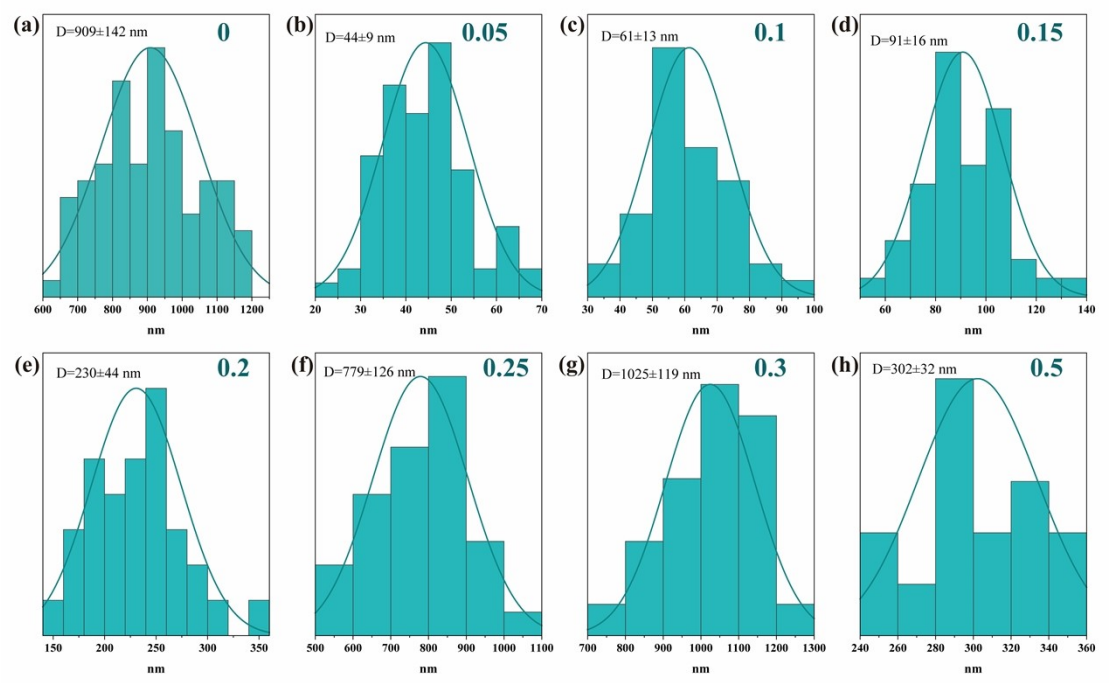

Fig. S7. Particle size distribution of ZEO-1 zeolites obtained with F/SiO_2 ratios of 0 (a), 0.05 (b), 0.10 (c), 0.15 (d), 0.20 (e), 0.25 (f), 0.30 (g) and 0.50 (h) using HF as fluoride source. The gel molar composition is 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* HF:10 H_2O, *x* = 0-0.5.

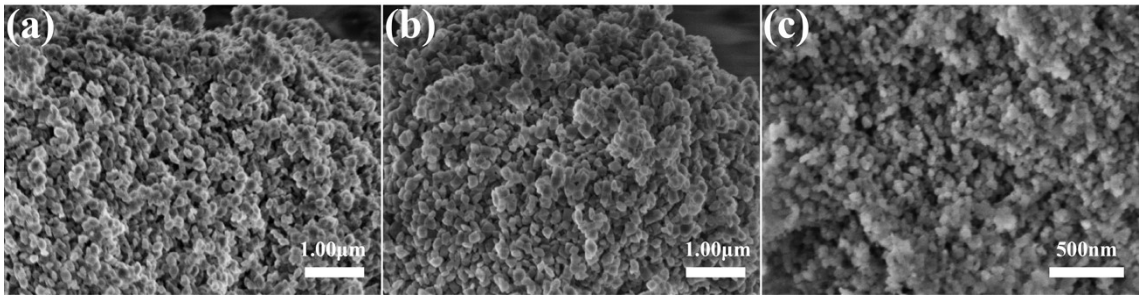

Fig. S8. SEM images of ZEO-1 zeolites obtained with a F/SiO_2 of 0.10 (a), 0.20 (b), and 0.30 (c) using NH_4F as fluoride source. The gel molar composition is 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* NH_4F:10 H_2O, *x* = 0.1-0.3.

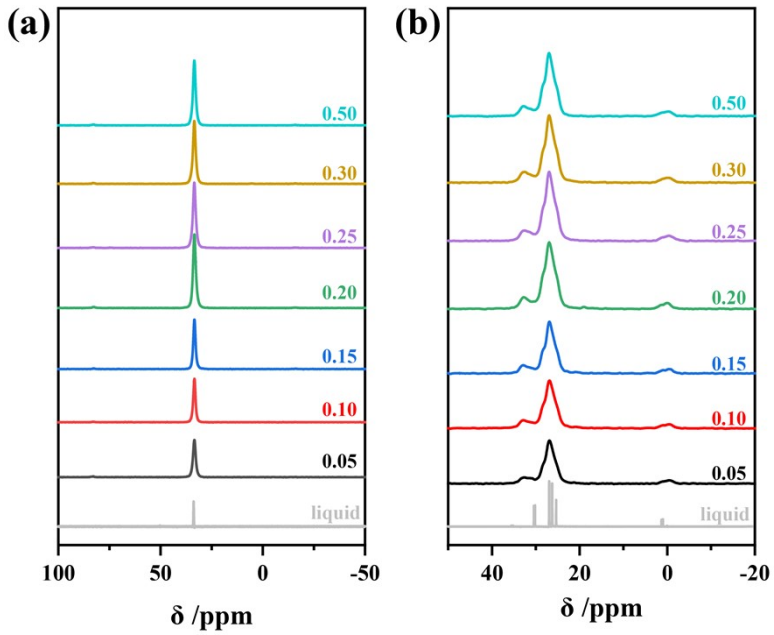

Fig. S9. (a) ^{31}P and (b) ^{13}C MAS solid state nuclear magnetic resonance (NMR) analysis of as-made ZEO-1 zeolite with a gel molar composition of 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* HF:10 H_2O, *x* = 0.05-0.5. The gray lines are the liquid NMR spectra of pristine OSDA.

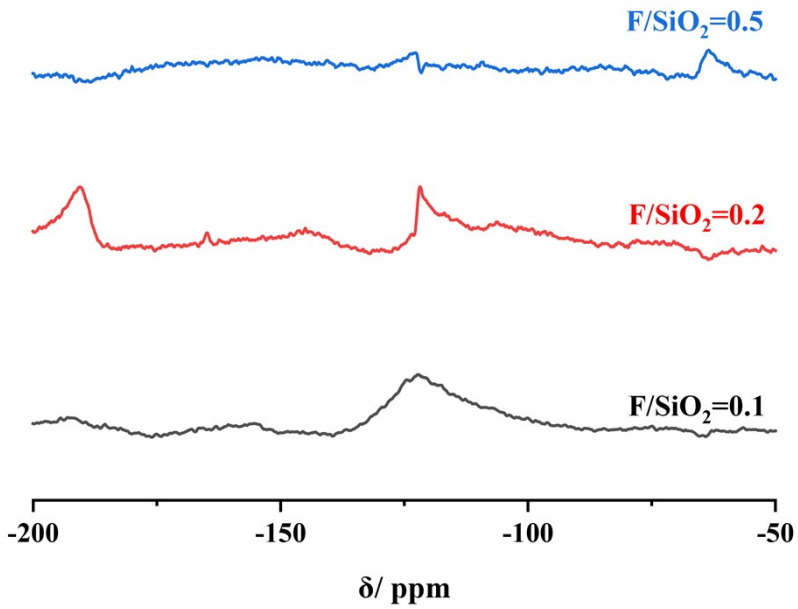

Fig. S10. ^{19}F MAS NMR spectra of as-made ZEO-1 zeolites obtained with a gel molar ratio of 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* HF:10 H_2O, *x* = 0-0.5.

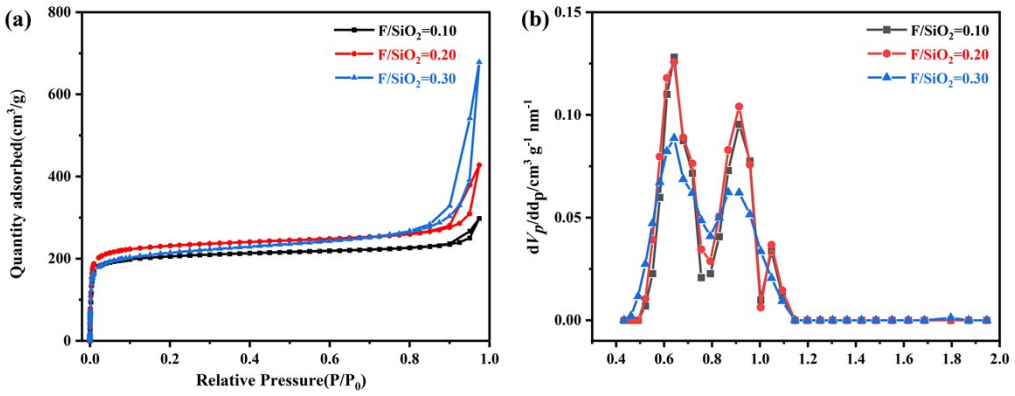

Fig. S11. Ar adsorption-desorption isotherms (a) and corresponding (d) pore size distribution calculated using on NLDFT method of the calcined and NH_4Cl washed ZEO-1 zeolites. The gel molar composition is 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:*x* NH_4F:10 H_2O, *x* =0.10-0.30.

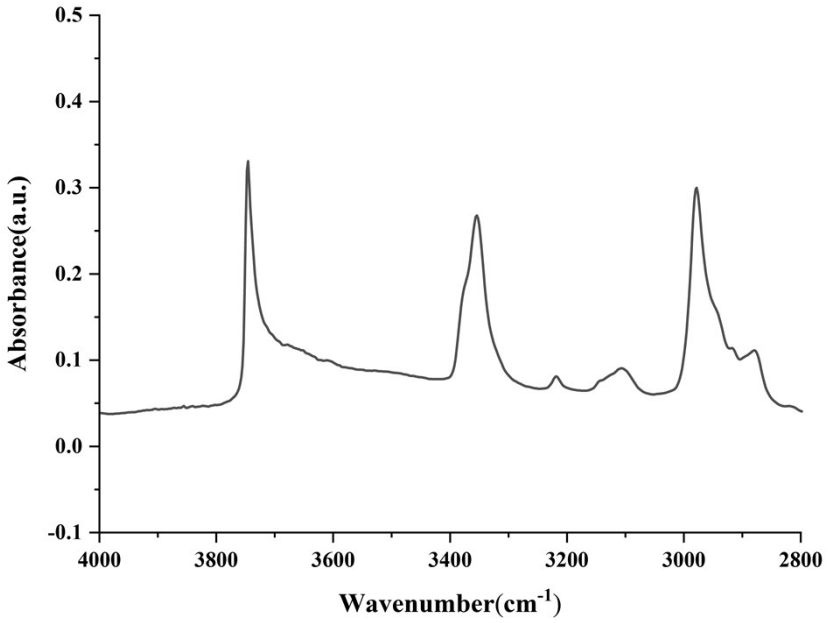

Fig. S12. DTBPy-FTIR spectra of P-free ZEO-1 zeolite with a gel molar ratio of 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:0.2 HF:10 H_2O.

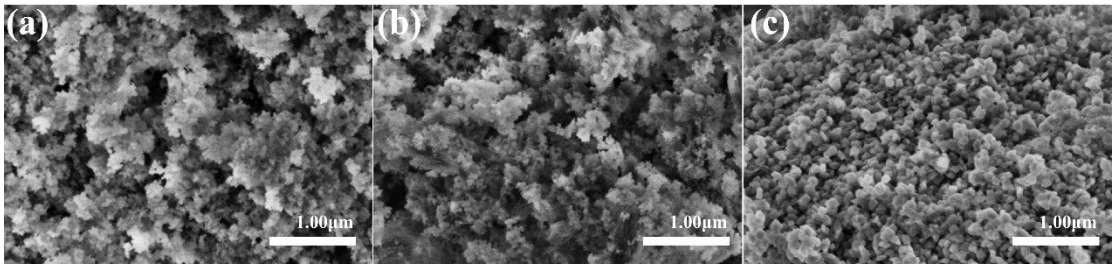

Fig. S13. SEM images of as-made ZEO-1 zeolites obtained with H_2O/SiO_2 of 10 at F/SiO_2 = 0.20 after heating for 36 h (a), 42 h (b), 54 h (c).

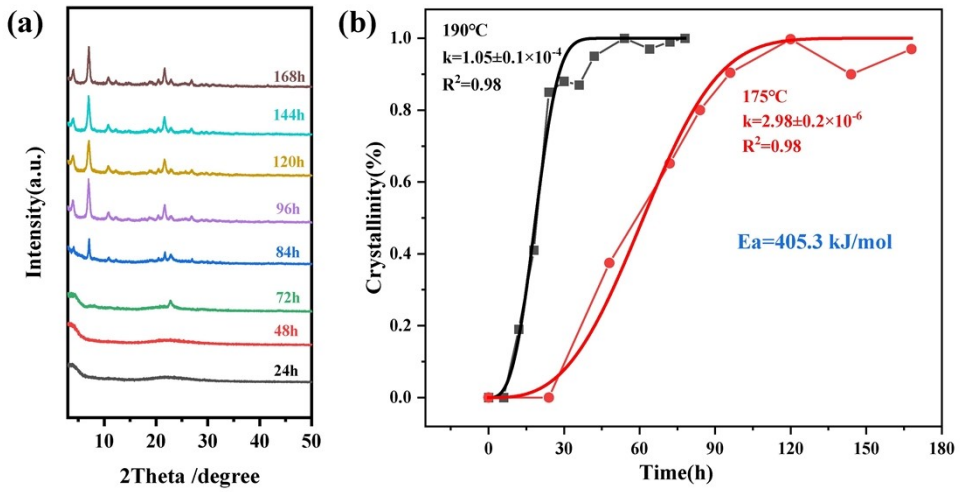

Fig. S14. PXRD patterns of zeolites obtained with a gel molar ratio of 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:0.2 HF:5 H_2O at 175 ℃ (a). Crystallization kinetics curves of ZEO-1 zeolite with different temperature (b).

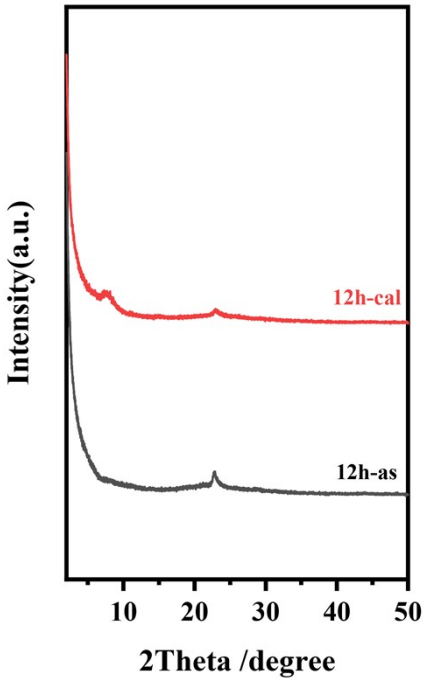

Fig. S15. PXRD patterns of zeolite after calcination obtained with a gel molar ratio of 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:0.2 HF:5 H_2O.

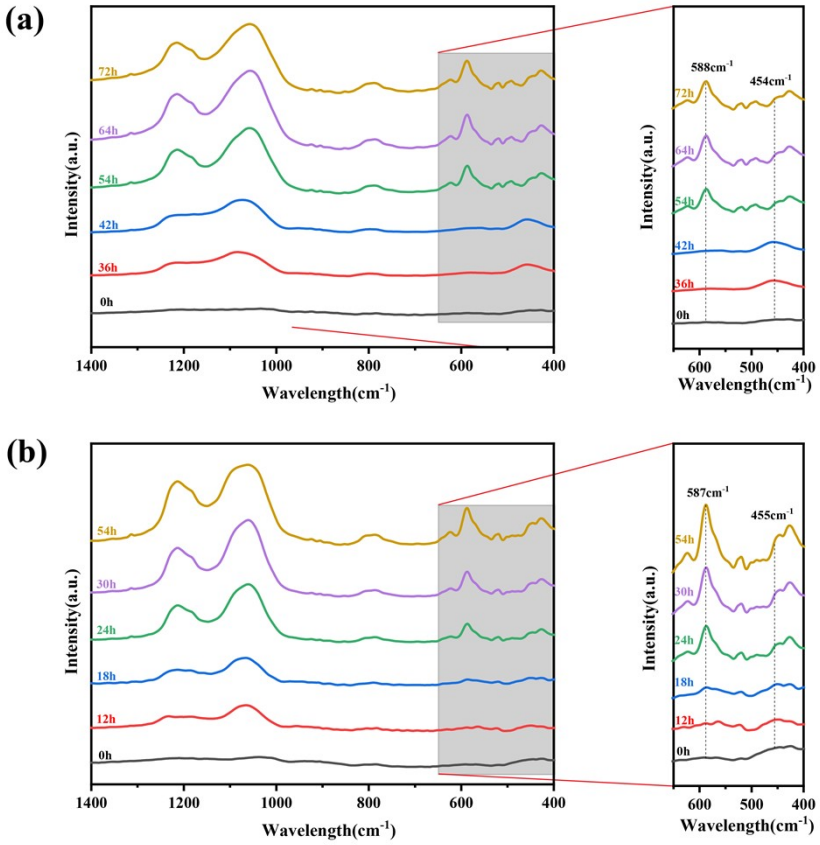

Fig. S16. FTIR spectra (KBr pellets) of as-made products with H_2O/SiO_2 of 5 (a) and 10 (b) at F/SiO_2 of 0.20.

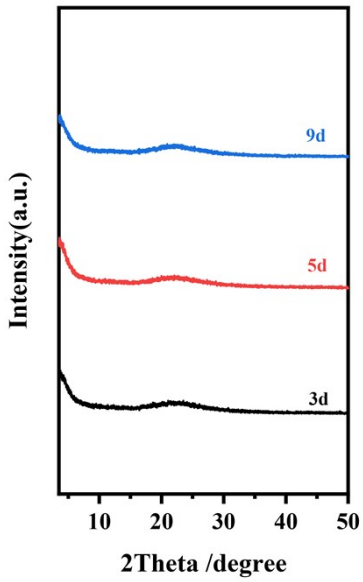

Fig. S17. PXRD patterns of zeolite obtained with a gel molar ratio of 1.0 SiO_2:0.5 SDAOH:0.02 Al_2O_3:0.2 HCl:5 H_2O.

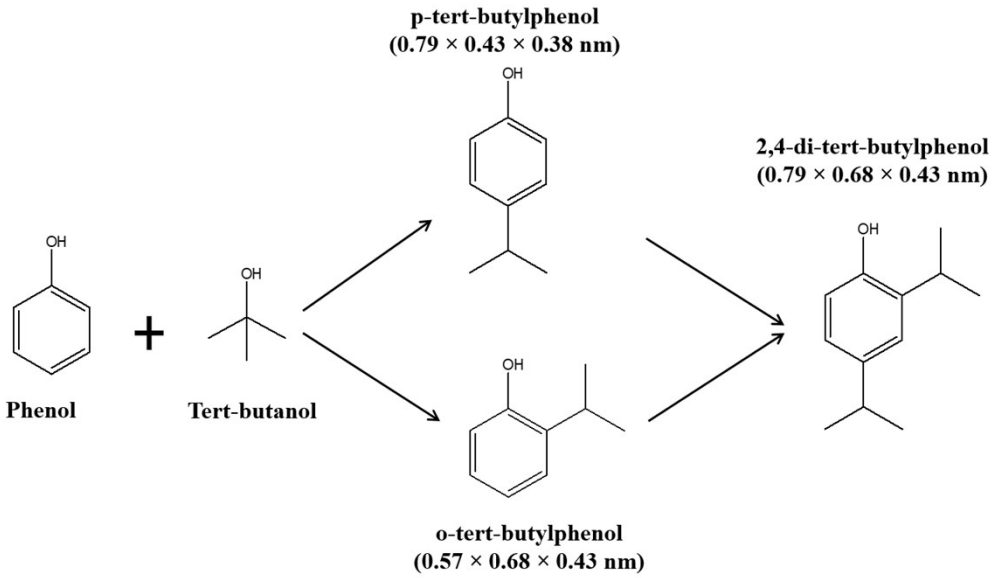

Fig. S18. Schematic representation of reaction mechanism of acid catalysed phenol alkylation by tert-butanol.

Table S1. Textural properties of calcined and NH_4Cl-washed ZEO-1 zeolites.

Sample (F/SiO_2)	S_{BET} (m^2/g)[a]	$V_{micropore}$ ($\pm$SD cm^3/g)[b]
0.15	863.6	0.28±0.007
0.20	847.0	0.29±0.01
0.10[c]	709.1	0.24±0.01
0.20[c]	791.7	0.28±0.005

[a]Apparent surface area calculated using the Roquerol BET criteria. [b]The micropore volume was obtained by Ar@87K adsorption using *t*-plot method. [c]The sample synthesized using NH_4F.

Table S2. Comparison of P content before and after treatment.

Zeolite	P content (%)	
	Untreated	Treated
ZEO-1	2.67 ± 0.06	0.07 ± 0.06

Table S3. Acid sites concentration and strength for P-free ZEO-1 zeolites.

Sample	Peak area			Adsorbed ammonia (μmol/g catalyst)		
	Peak1	Peak2	Peak area ratio	Weak acid	Medium-strong acid	Total mole
F/SiO_2=0.5, H_2O/SiO_2=10	6477	17226	27:73	96.02	255.33	351.35
F/SiO_2=0.2, H_2O/SiO_2=10	4533	15645	22:78	49.51	170.87	220.38
F/SiO_2=0.2, H_2O/SiO_2=5	14602	37702	28:72	151.51	391.20	542.71

Table S4. Selectivity to minor products (wt.%).

Zeolite	**USY**	**Beta**	***ZEO-1$_{LCS}$**	**ZEO-1$_5$**	**ZEO-1$_{10}$**
2,6-DiTBP	0.80	0.00	0.00	0.46	0.45
2,5-DiTBP	0.00	0.00	0.00	0.24	0.24
2,4,6-TriTBP	0.00	0.00	0.00	0.14	0.11

*The sample was synthesized by Laboratoire Catalyse et Spectrochimie.