Supporting Information

Synthesis of TS-1 zeolites from a polymer containing titanium and silicon

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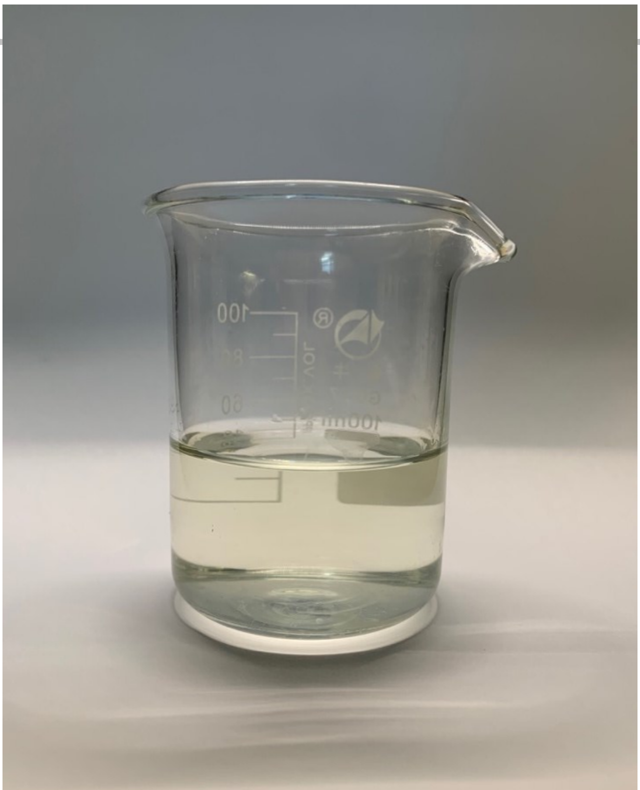


Figure S1. Ti-PEG-Si polymer was dissolved in water at room temperature.

For example, tetraethyl titanate (TEOT), a quite easily hydrolyzed ester, was used as a raw material to synthesize the Ti-PEG-Si polymer with PEG as diol reactant. The obtained polymer was stably present and dissolved in water and did not hydrolyze after more than 12 months at room temperature.

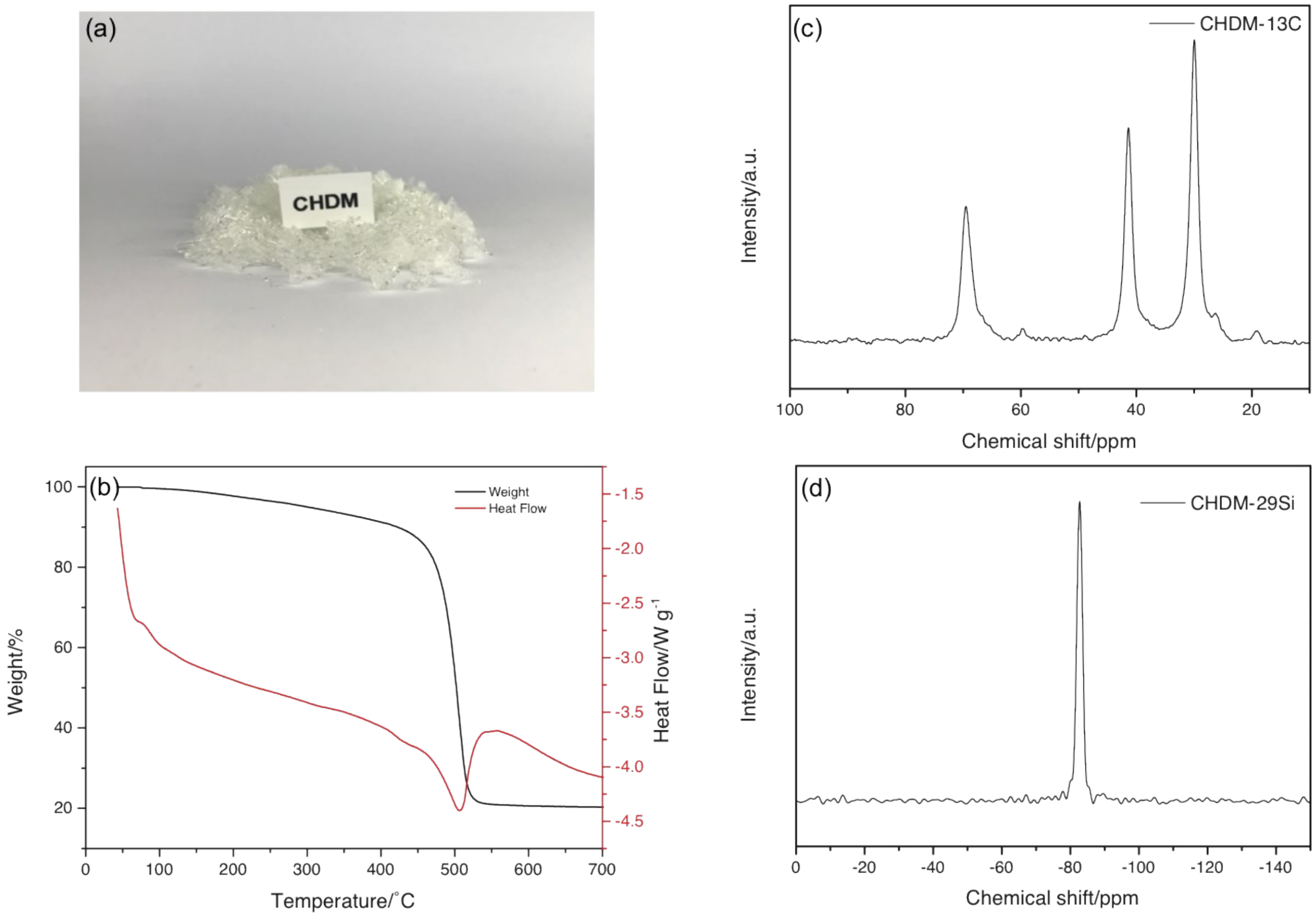


Figure S2. photo of Ti-CHDM-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-CHDM-Si polymer.

In Fig S2a, it is a photograph of the Ti-CHDM-Si polymer, and the Ti-CHDM-Si polymer is a transparent solid with certain toughness. Fig S2b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 500 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions. The main peaks on ^{13}C MAS NMR appeared at 69.2, 41.5 and 30.2 ppm are the peaks of carbon atoms on CHDM.

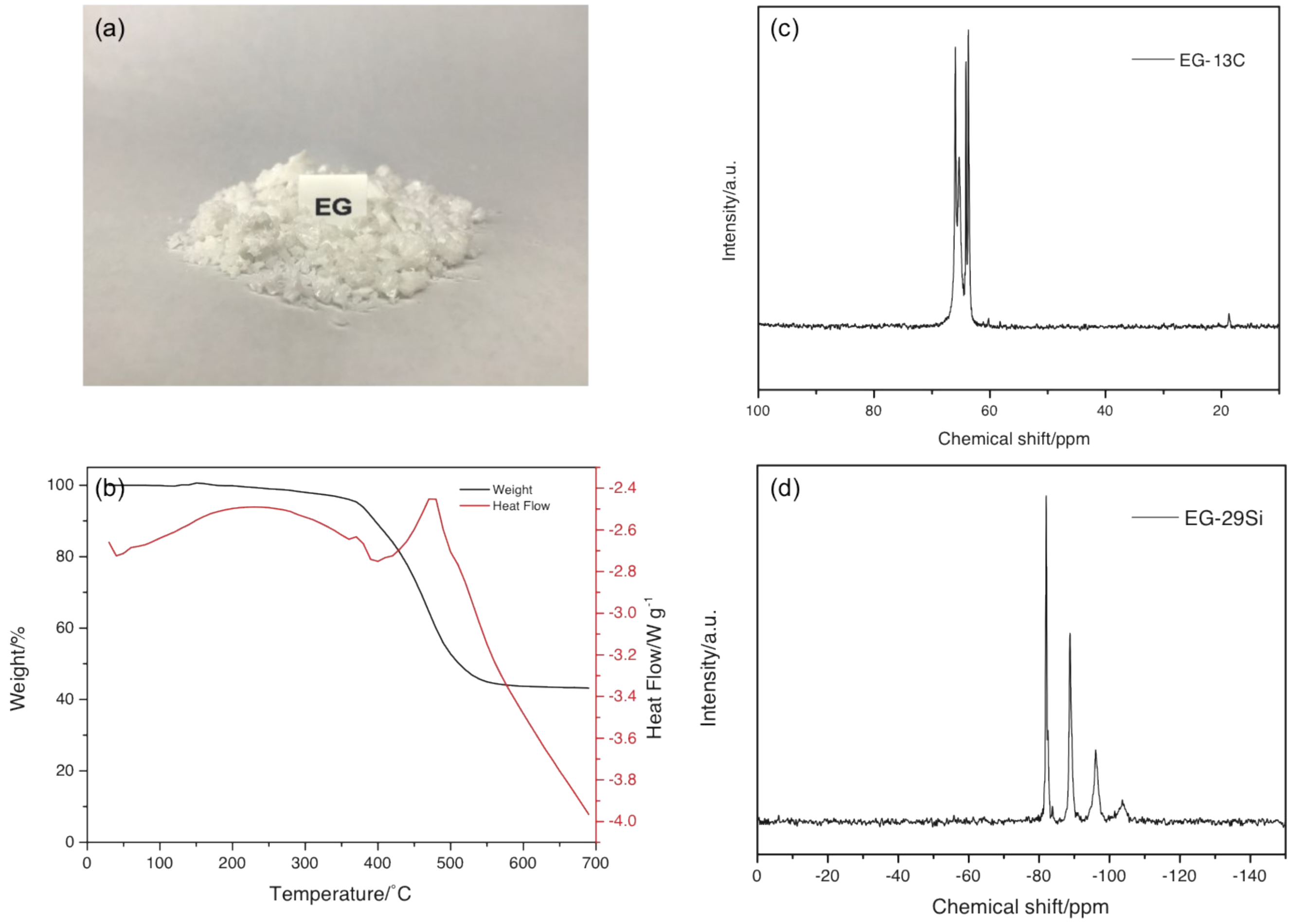


Figure S3. photo of Ti-EG-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-EG-Si polymer**.**

In Fig S3a, it is a photograph of the Ti-EG-Si polymer, and the Ti-EG-Si polymer is a transparent solid with certain toughness. Fig S3b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 430 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions.

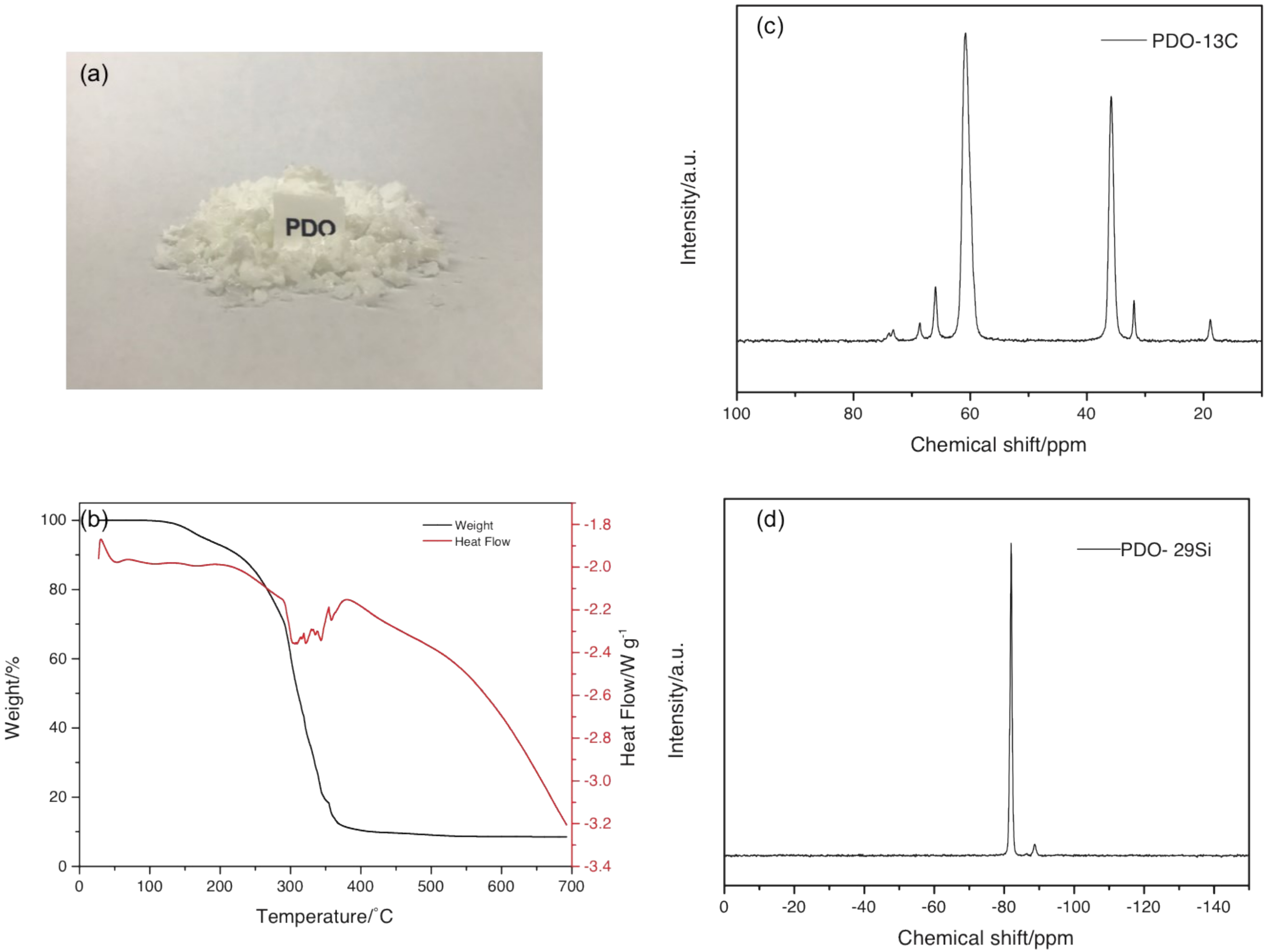


Figure S4. photo of Ti-PDO-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-PDO-Si polymer**.**

In Fig S4a, it is a photograph of the Ti-PDO-Si polymer, and the Ti-PDO-Si polymer is a transparent solid with certain toughness. Fig S4b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 330 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions. The main peaks on ^{13}C MAS NMR appeared at 60.1 and 35.0 ppm are the peaks of carbon atoms on PDO.

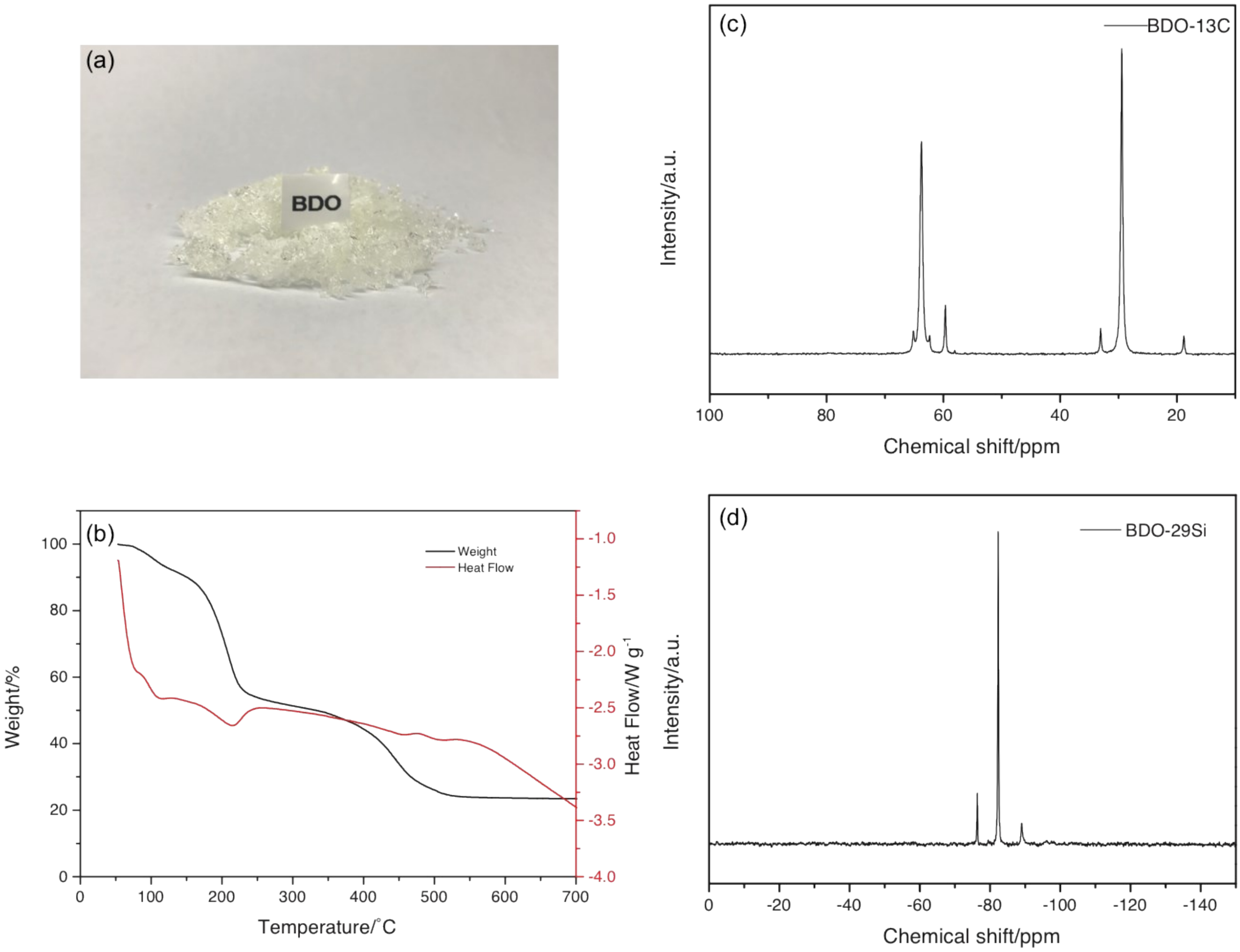


Figure S5. photo of Ti-BDO-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-BDO-Si polymer**.**

In Fig S5a, it is a photograph of the Ti-BDO-Si polymer, and the Ti-BDO-Si polymer is a transparent solid with certain toughness. Fig S5b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 430 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions. The main peaks on ^{13}C MAS NMR appeared at 63 and 29.5 ppm are the peaks of carbon atoms on BDO.

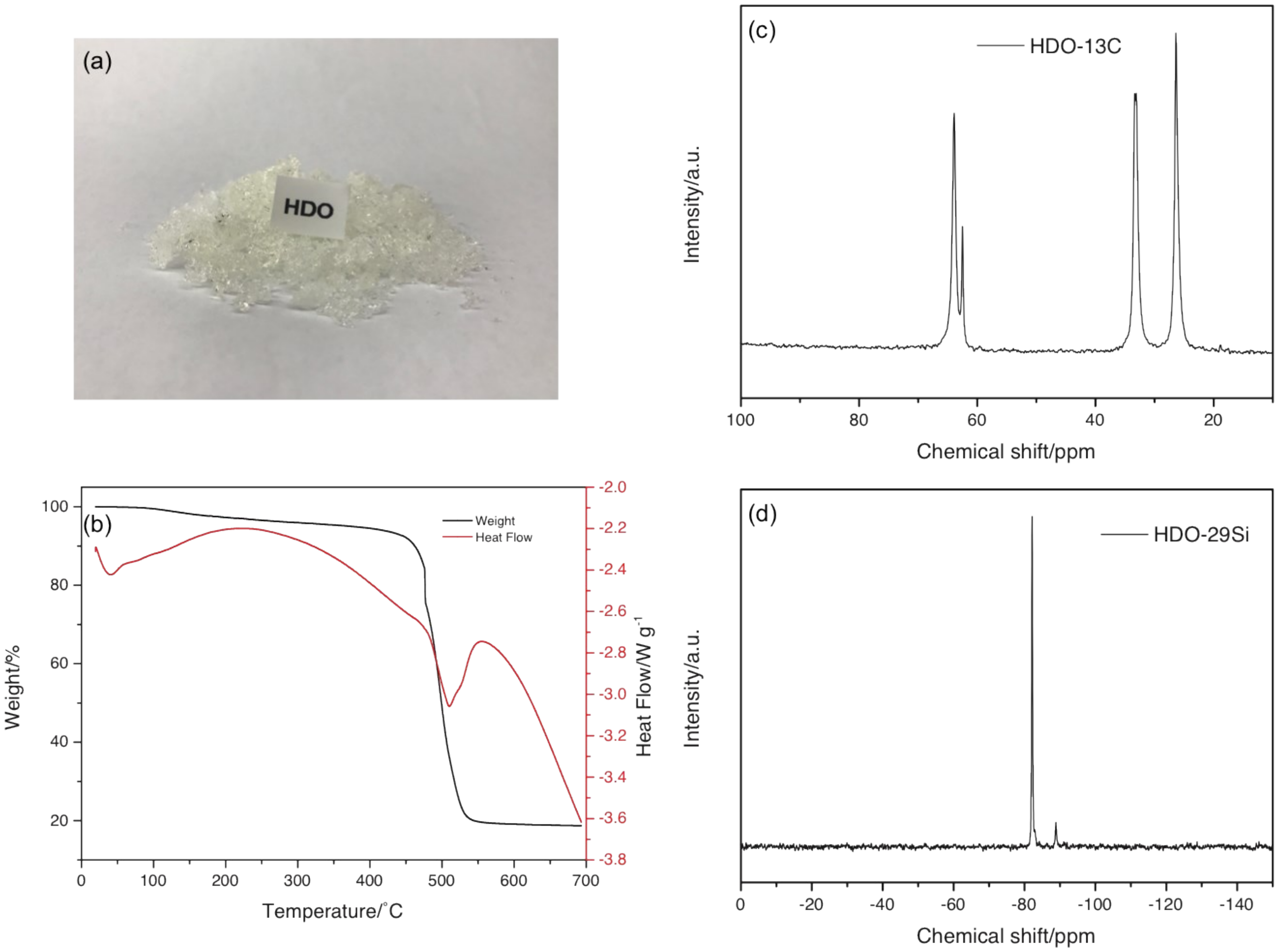


Figure S6. photo of Ti-HDO-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-HDO-Si polymer**.**

In Fig S6a, it is a photograph of the Ti-HDO-Si polymer, and the Ti-HDO-Si polymer is a transparent solid with certain toughness. Fig S6b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 500 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions. The main peaks on ^{13}C MAS NMR appeared at 62, 33.2 and 26.1 ppm are the peaks of carbon atoms on HDO.

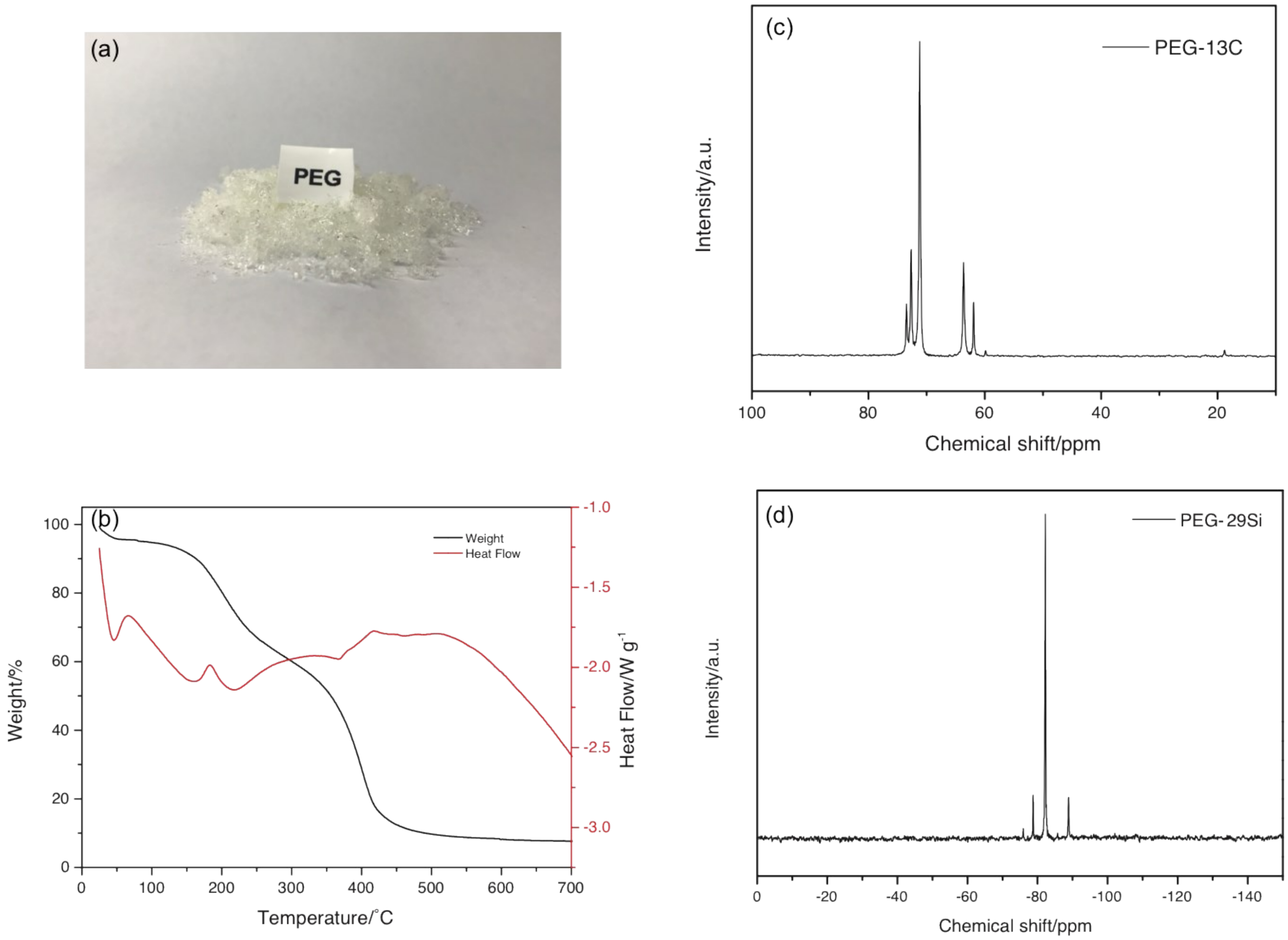


Figure S7. photo of Ti-PEG-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-PEG-Si polymer**.**

In Fig S7a, it is a photograph of the Ti-PEG-Si polymer, and the Ti-PEG-Si polymer is a transparent solid with certain toughness. Fig S7b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 400 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions.

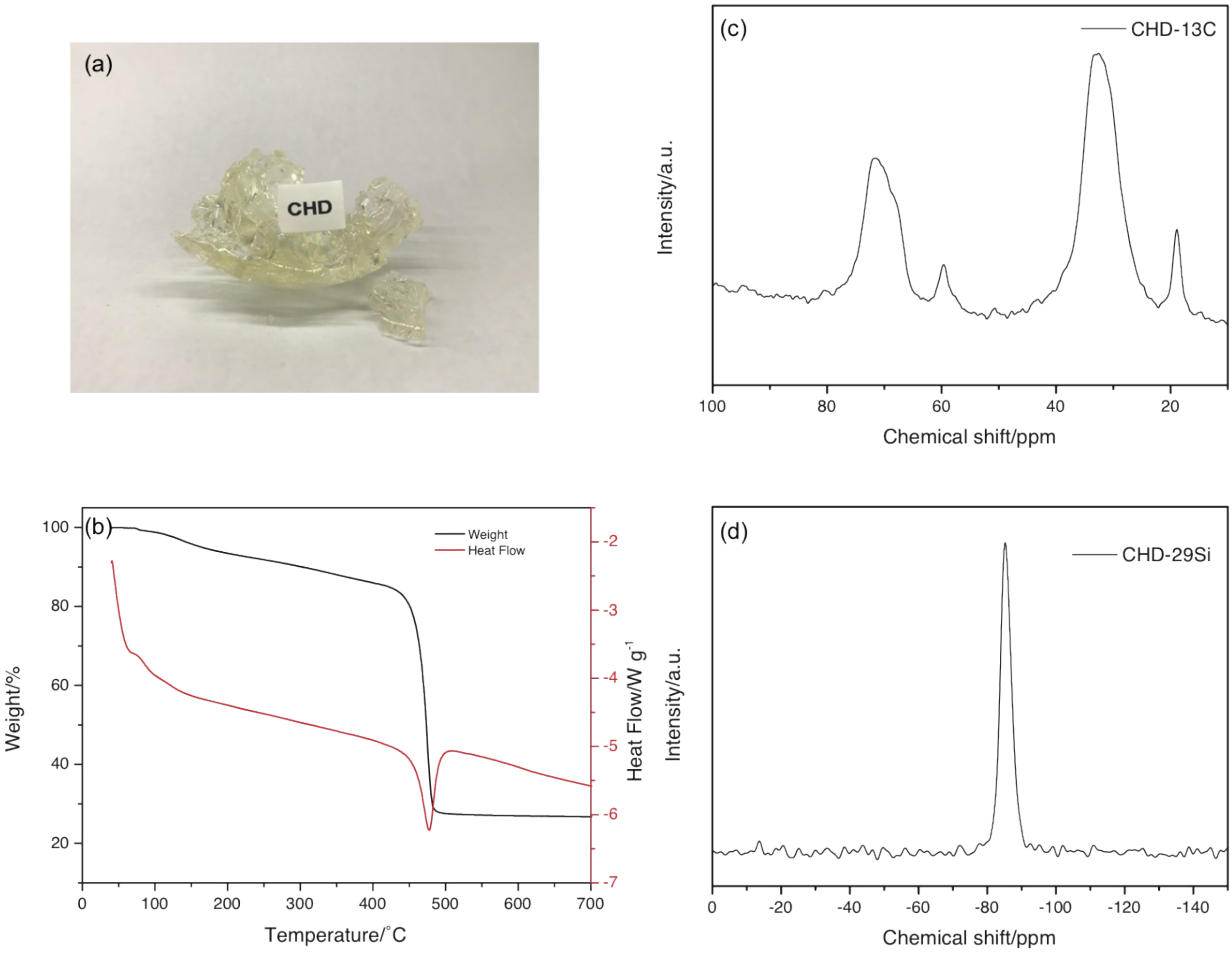


Figure S8. photo of Ti-CHD-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-CHD-Si polymer**.**

In Fig S8a, it is a photograph of the Ti-CHD-Si polymer, and the Ti-CHD-Si polymer is a transparent solid with certain toughness. Fig S8b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 470 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions. The main peaks on ^{13}C MAS NMR appeared at 70 and 35.8 ppm are the peaks of carbon atoms on CHD.

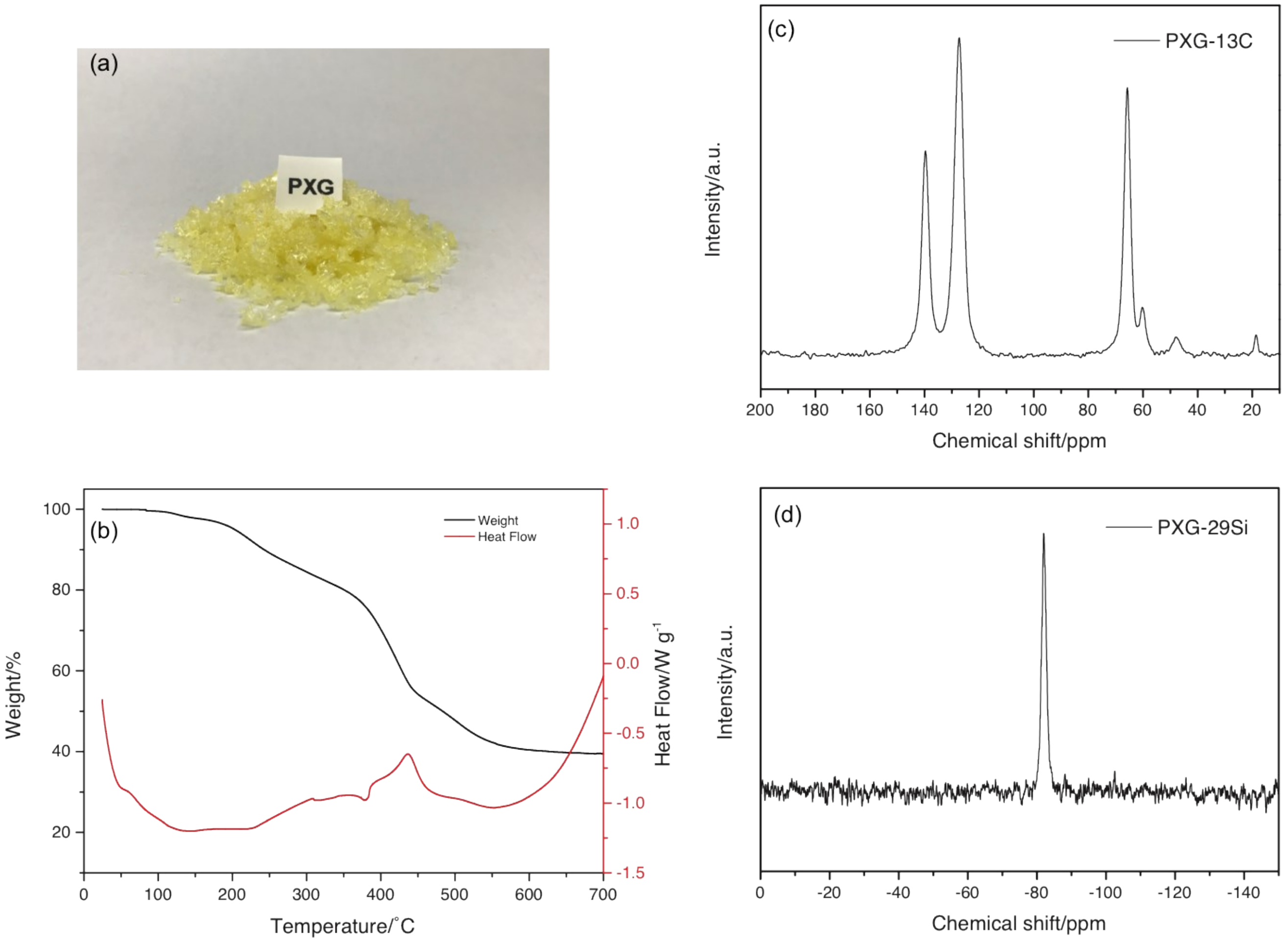


Figure S9. photo of Ti-PXG-Si polymer (a) TGA analysis (b) ^{13}C MAS NMR (c) ^{29}Si MAS NMR (d) of Ti-PXG-Si polymer**.**

In Fig S9a, it is a photograph of the Ti-PXG-Si polymer, and the Ti-PXG-Si polymer is a transparent solid with certain toughness. Fig S9b is the thermogravimetric analysis of the polymer. It can be seen that the sample decomposes significantly at around 430 °C, which means that the polymer has quite high thermal stability, and it is also an obvious evidence of successful polymerization of titanium and silicon esters with diol species. The ^{13}C MAS NMR analysis shows that the peaks of methylene and methyl groups on the silicon ester and the titanium ester are significantly weakened and lowered at 58.2 and 18.2 ppm, respectively, which proves that the ethyl groups of the original tetraethyl orthosilicate and tetraethyl titanate are removed in the transesterification reactions. The main peaks on ^{13}C MAS NMR appeared at 139.9, 125.5 and 65 ppm are the peaks of carbon atoms on PXG.

Table S1. Decomposition temperature and degree of polymerization of the polymers.

Polymer	EG	PDO	BDO	HDO	PEG	CHD	CHDM	PXG
Decomposition temperature/°C[a]	430	330	430	500	400	470	500	430
degree of polymerization[b]	15	10	10	13	15	11	12	12

[a] Decomposition temperature, judged by thermogravimetric weight loss. [b] Degree of polymerization is based on the quality of the distilled ethanol.

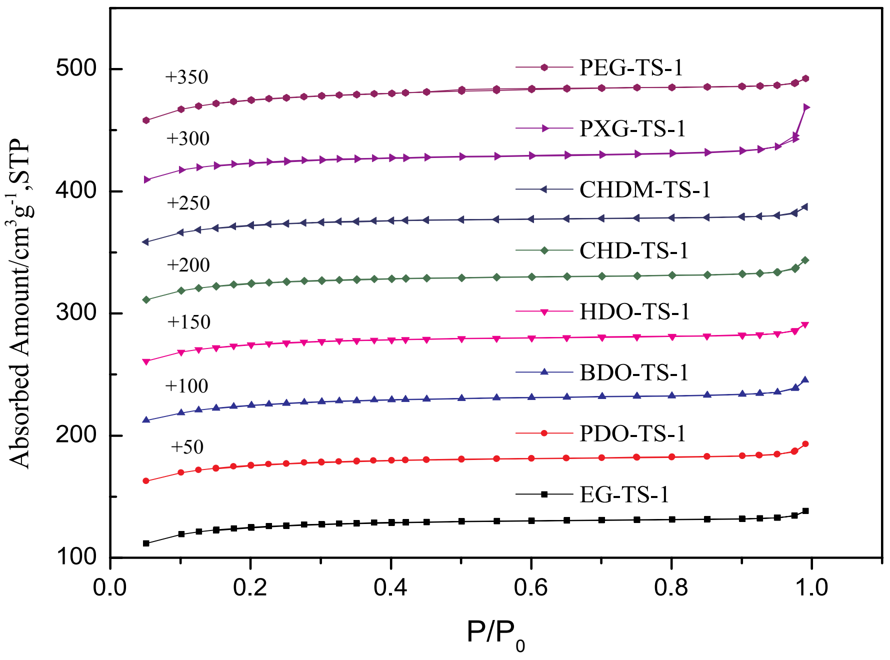


Figure S10. The N_2 adsorption-desorption isotherms of the TS-1 zeolites synthesized by different polymers.

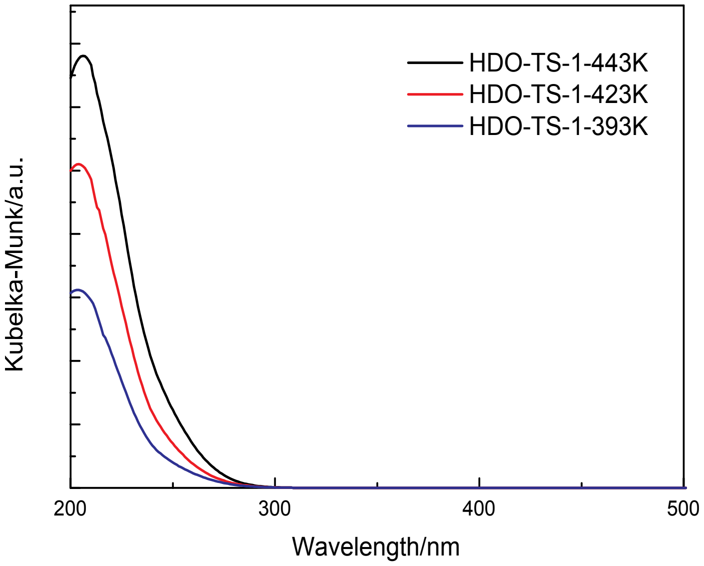


Figure S11. UV-Vis spectra of TS-1 synthesized by HDO polymers under different crystallization temperatures.

From the UV-Vis spectroscopy, there were no significant absorption bands between 240 and 330 nm in TS-1 samples which synthesized under different crystallization temperatures, 120 ° C, 150 ° C and 170 ° C. It is proved that most of the titanium ions in TS-1 exist in a tetracoordinate form and was absorbed at a wavelength of 210 nm.

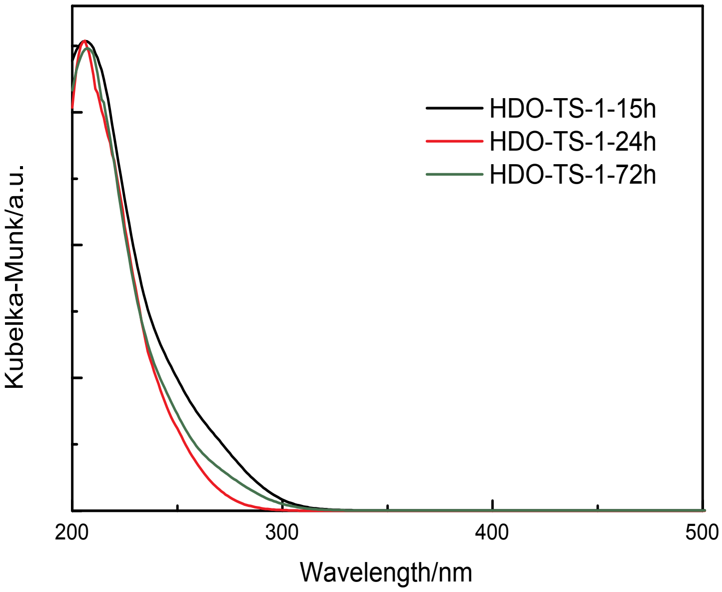


Figure S12. UV-Vis spectra of TS-1 synthesized by HDO polymers under different crystallization times.

The crystallization time was 15h, 24h and 72h, respectively, it can be seen that all the TS-1 zeolites have a strong absorption band at a wavelength of 210 nm. The absorption peak here represents the tetrahedrally coordinated titanium in the framework. At the wide band between 240 and 280 nm as well as 330 nm, it is generally considered to be the extraframework titanium species. All the TS-1 samples have no absorption band here, which proves that the extraframework titanium species in TS-1 is not significantly formed during crystallization.

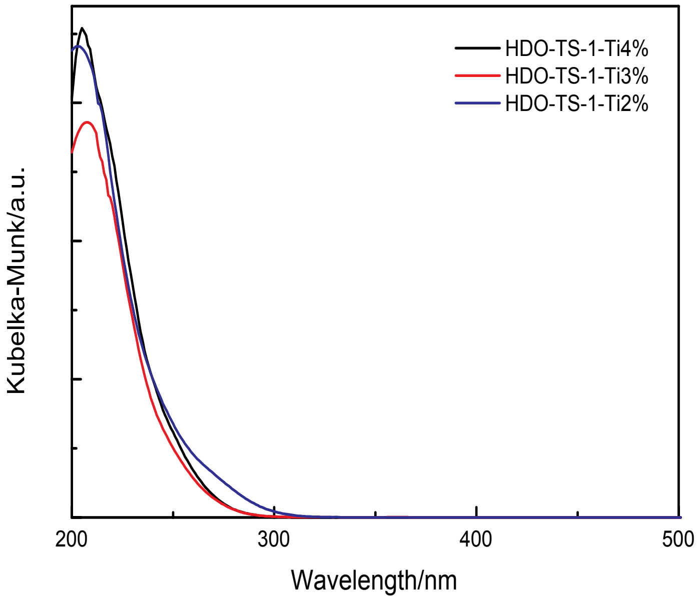


Figure S13. UV-Vis spectra of TS-1 synthesized by HDO polymers with different titanium contents.

Ti-HDO-Si polymers with titanium content of 2% and 3% were also used as raw materials for synthesizing TS-1 zeolites. The UV-Vis spectroscopy did not show absorption bands between 240 and 330 nm, which proved that the extraframework titanium species in TS-1 is not significantly formed during crystallization.

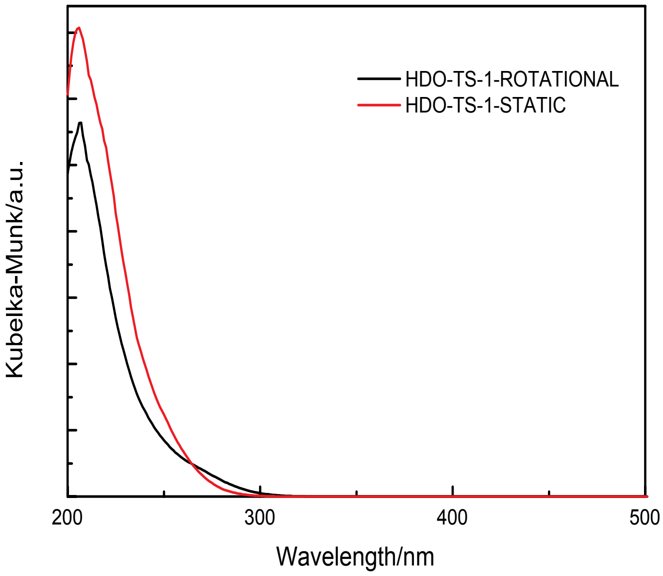


Figure S14. UV-Vis spectra of TS-1 synthesized by HDO polymers under static and rotational crystallization condition.

Rotational crystallization was more advantageous than static crystallization in controlling particle sizes. Rotational crystallization used the same crystallization temperature and crystallization time, crystallizing at 170 ° C for 1 d with a rotation rate of 35 rpm. The Si/Ti molar ratio of the rotationally crystallized TS-1 by ICP was 53.3 slightly higher than that of the statically crystallized samples with 48.8. The UV-Vis spectroscopy did not show absorption bands between 240 and 330 nm, which proved that the extraframework titanium species in TS-1 is not significantly formed during crystallization.

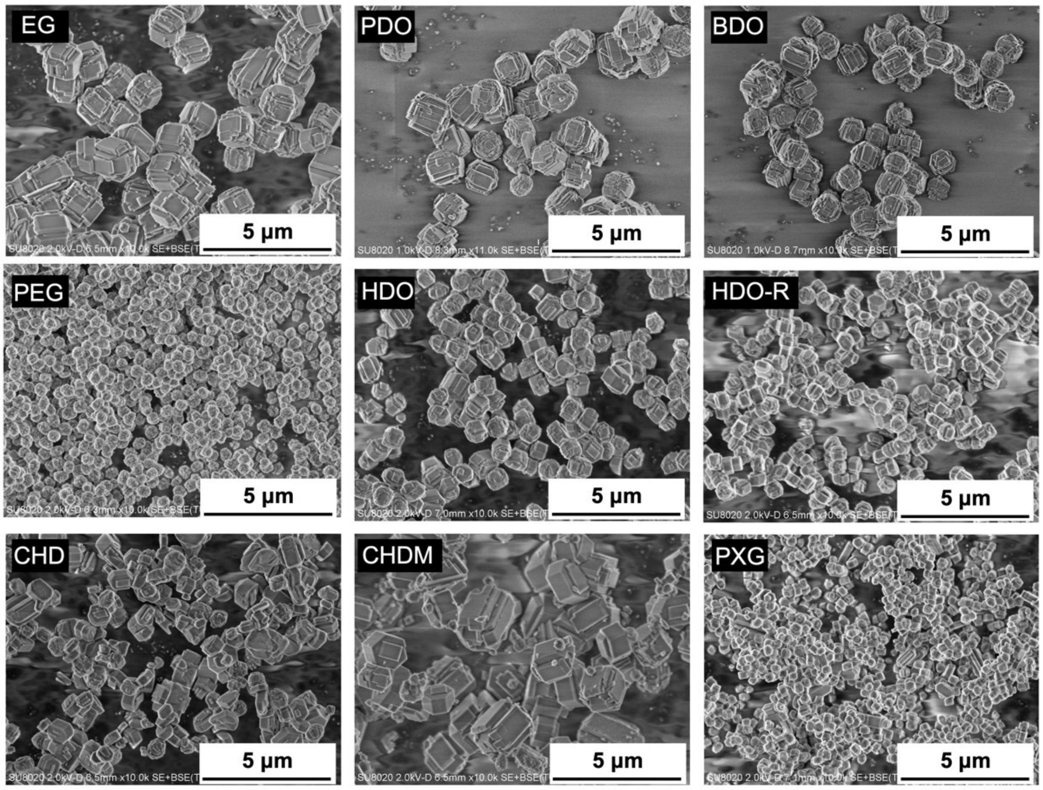


Figure S15. SEM images of TS-1 synthesized from different Ti-diol-Si polymers.

Table S2. Catalytic Results of Prepared TS-1 for the Oxidation of 1-Hexene. [a]

sample	Si/Ti ratio[b] in catalyst	Conv. [%] based on 1-hexene	Sel. [%]		H_2O_2	
			epoxide	others	Conv. [%]	Sel. [%]
EG-TS-1	48.6	40.3	95.8	4.2	45.5	85.5
PDO-TS-1	52.8	41.2	96.4	3.6	43.6.	88.5
BDO-TS-1	55.0	38.5	96.1	3.9	44.7	87.6
HDO-TS-1	48.8	44.7	97.3	2.7	48.4	89.7
CHD-TS-1	52.1	34.7	95.7	4.3	40.7	80.1
CHDM-TS-1	55.0	32.3	95.2	4.8	38.2	78.0
PXG-TS-1	52.0	31.6	94.3	5.7	36.4	67.5
PEG-TS-1	35.8	43.2	97.1	2.9	47.2	84.9
HDO-TS-1-R	53.3	45.6	97.7	2.3	45.9	94.5
TS-1-C[c]	43.3	21.3	96.3	3.7	35.7	77.1

[a] Reaction conditions: 0.05 g of catalyst, 60 °C, 2 hrs., 10 mL of CH_3OH as solvent, 10 mmol of 1-hexene, 10 mmol of H_2O_2 (30% in aqueous solution). [b] The elemental compositions in TS-1 are determined by ICP. [c] TS-1 synthesized by conventional processes.

Table S3 Yields of the TS-1 zeolites synthesized from polymers.

Samples	EG	PDO	BDO	HDO	CHD	CHDM	PXG	PEG	Con[b]
Yields[a] [wt. %]	94	92	92	94	92	92	93	95	89

[a] Calculated based on initially added amounts of SiO_2 and TiO_2. [b] TS-1 zeolites synthesized from conventional methods.

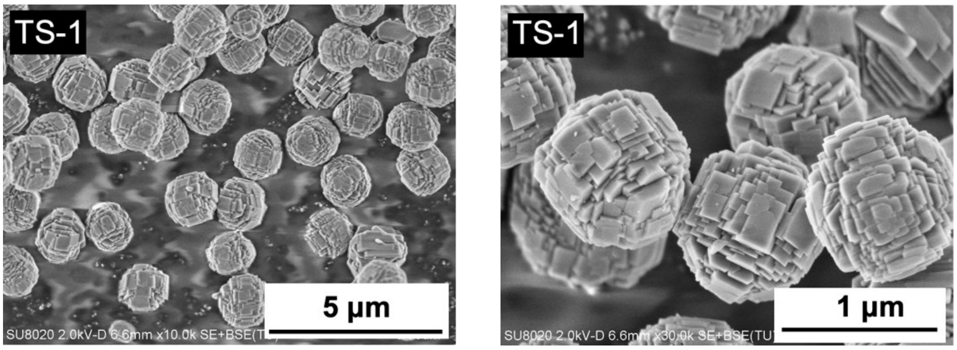


Figure S16. SEM images of TS-1 synthesized from Ti-PEG-Si polymers under low concentration of TPAOH.

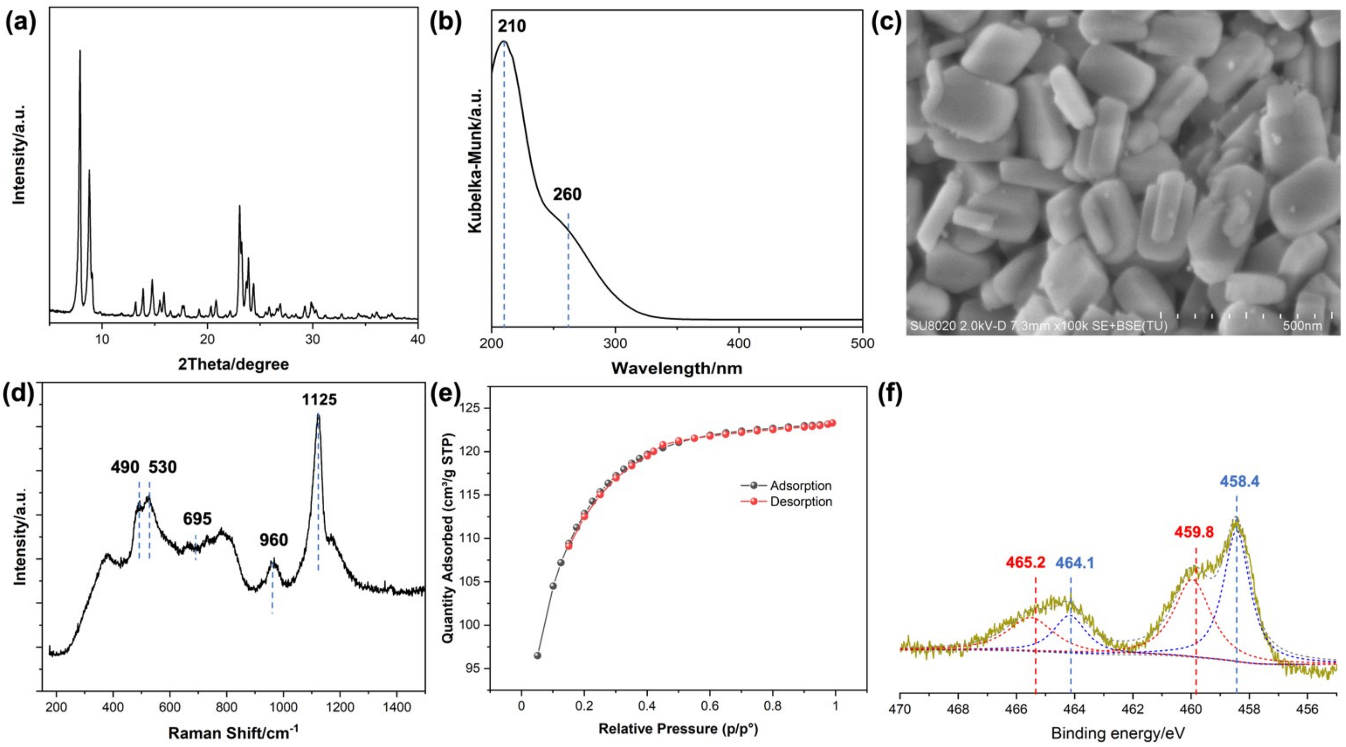


Fig. S17. (a) XRD patterns; (b) UV-Vis spectra; (c) SEM image; (d) UV Raman spectra excited at 244 nm; (e) N_2 adsorption-desorption isotherms and (f) Ti 2p XPS of conventional TS-1 samples.

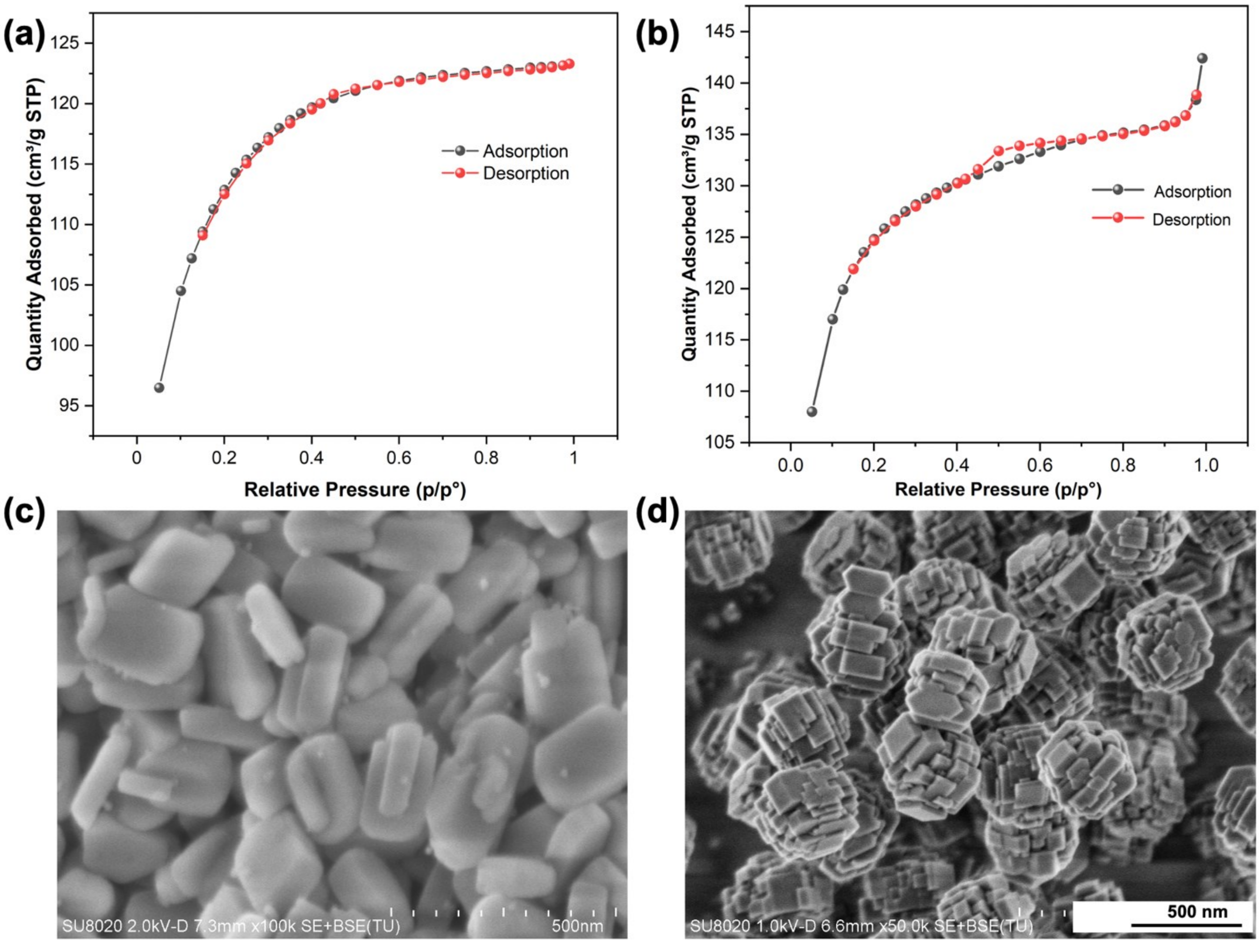


Fig. S18. (a) N_2 adsorption-desorption isotherms and (c) SEM image of the conventional TS-1 samples. (b) N_2 adsorption-desorption isotherms and (d) SEM image of the TS-1 samples synthesized from Ti-PEG-Si polymers.

Table S4. Catalytic Results of Prepared TS-1 zeolites for the Oxidation of Cyclohexene. [a]

Sample	Si/Ti ratio[b] in catalyst	Conv. [%] based on cyclohexene	Sel. [%]		H_2O_2	
			Epox	Other	Conv. [%]	Sel. [%]
TS-1-P[c]	35.8	26.3	69.8	30.2	25.7	87.7
TS-1-C[d]	43.3	3.1	71.3	28.7	9.6	41.2

[a] Reaction conditions: 0.1 g of catalyst, 60°C, 4 h, 5 mL of acetonitrile as the solvent, 4.5 mmol of cyclohexene, 4.5 mmol of H_2O_2 (30% in aqueous solution). [b] The elemental compositions in TS-1 are determined by ICP. [c] TS-1 synthesized from Ti-PEG-Si polymers. [d] TS-1 synthesized by conventional processes.

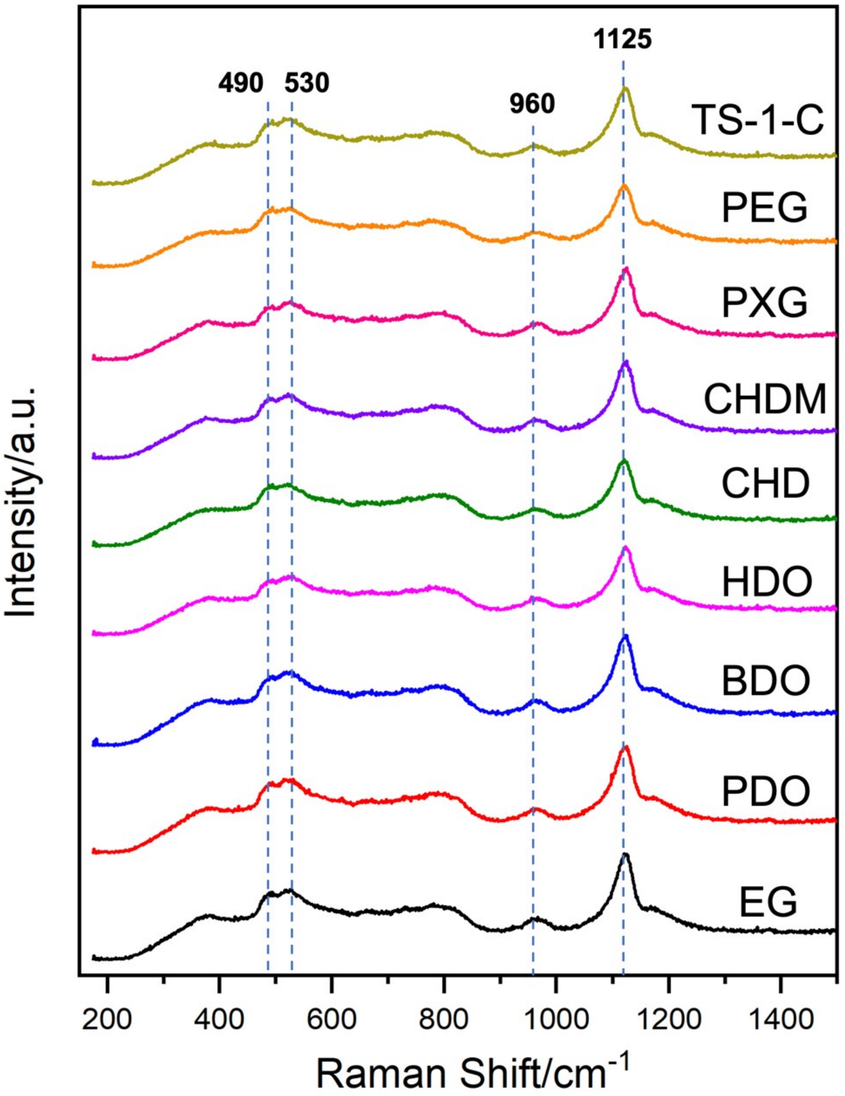


Fig. S19. UV Raman spectra excited at 244 nm of the conventional TS-1 samples (TS-1-C) and the TS-1 samples synthesized from different polymers.

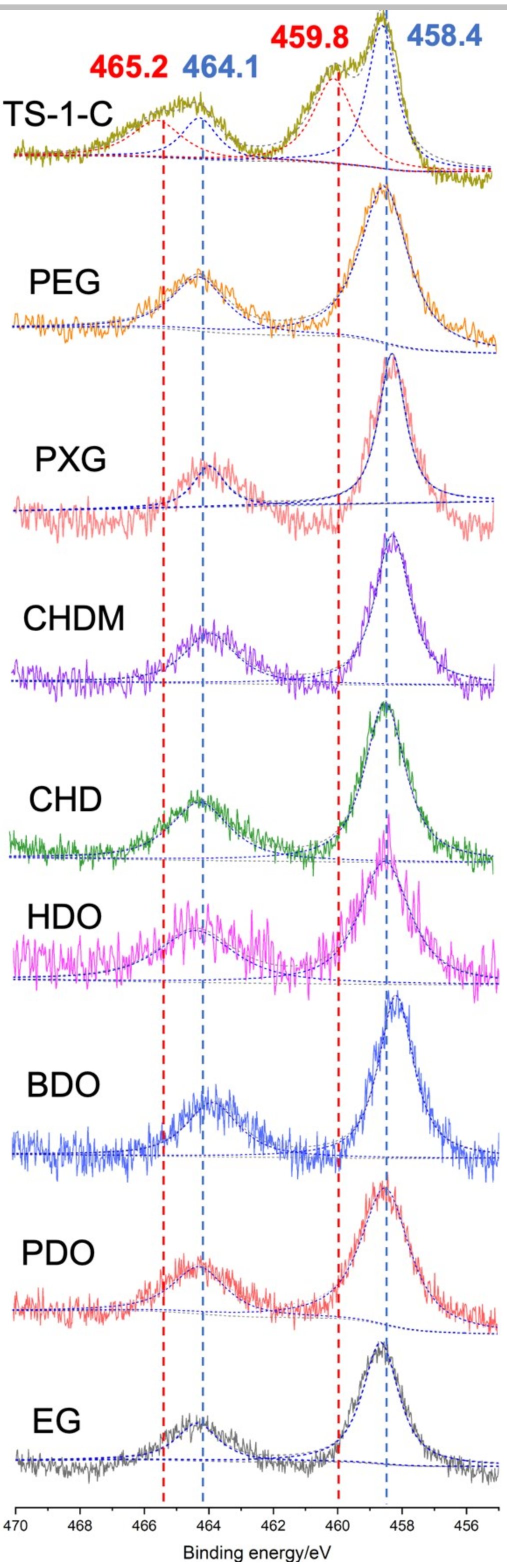


Fig. S20. Ti 2p XPS of the conventional TS-1 samples (TS-1-C) and the TS-1 samples synthesized from different polymers.

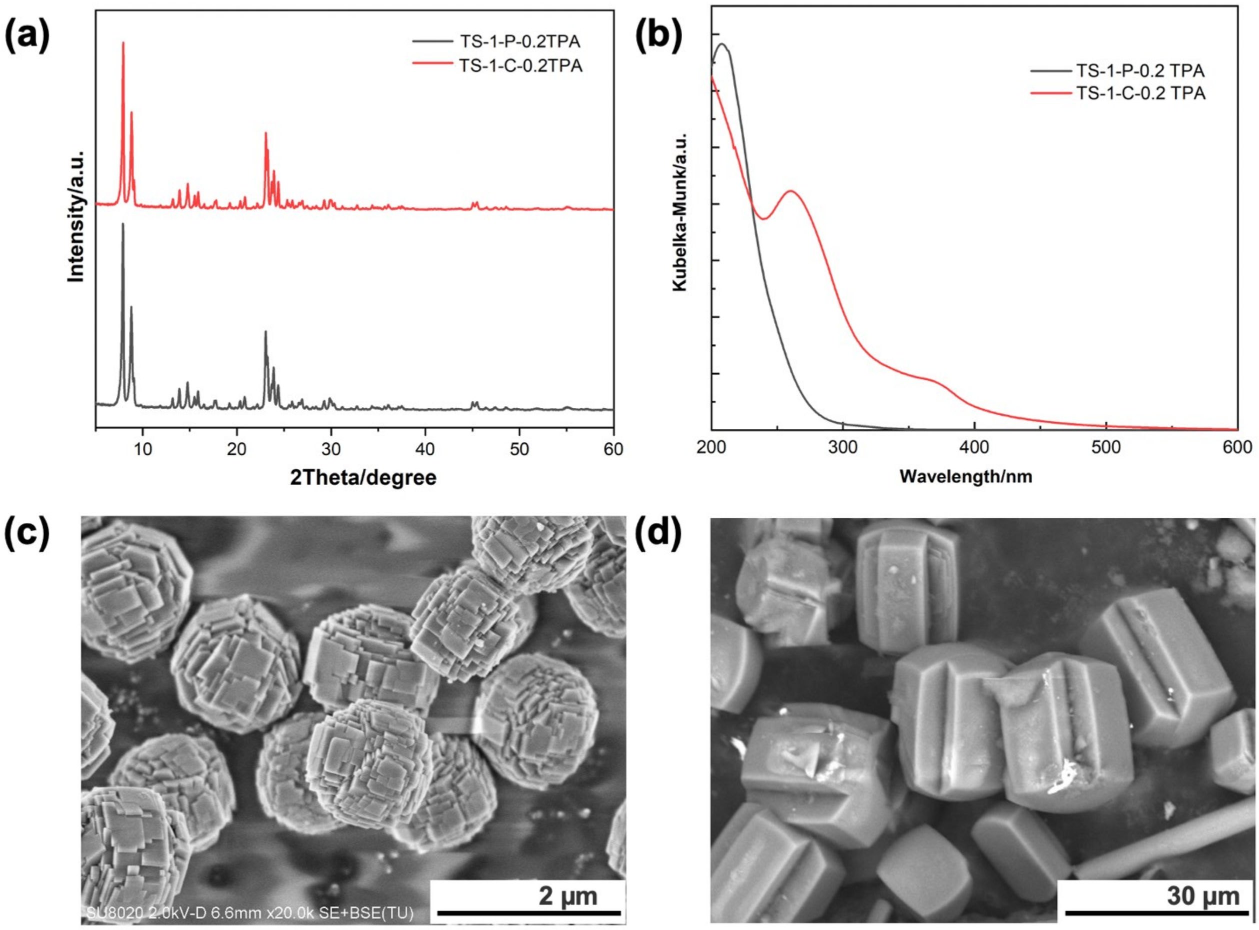


Fig. S21. (a) XRD patterns and (b) UV-Vis spectra of TS-1 synthesized under lower usage of TPAOH. Black: TS-1 zeolites synthesized from polymers (TS-1-P). Red: TS-1 zeolites synthesized from conventional methods (TS-1-C). (c) SEM image of the TS-1 zeolites synthesized from polymers. (d) SEM image of the TS-1 zeolites synthesized by conventional methods.

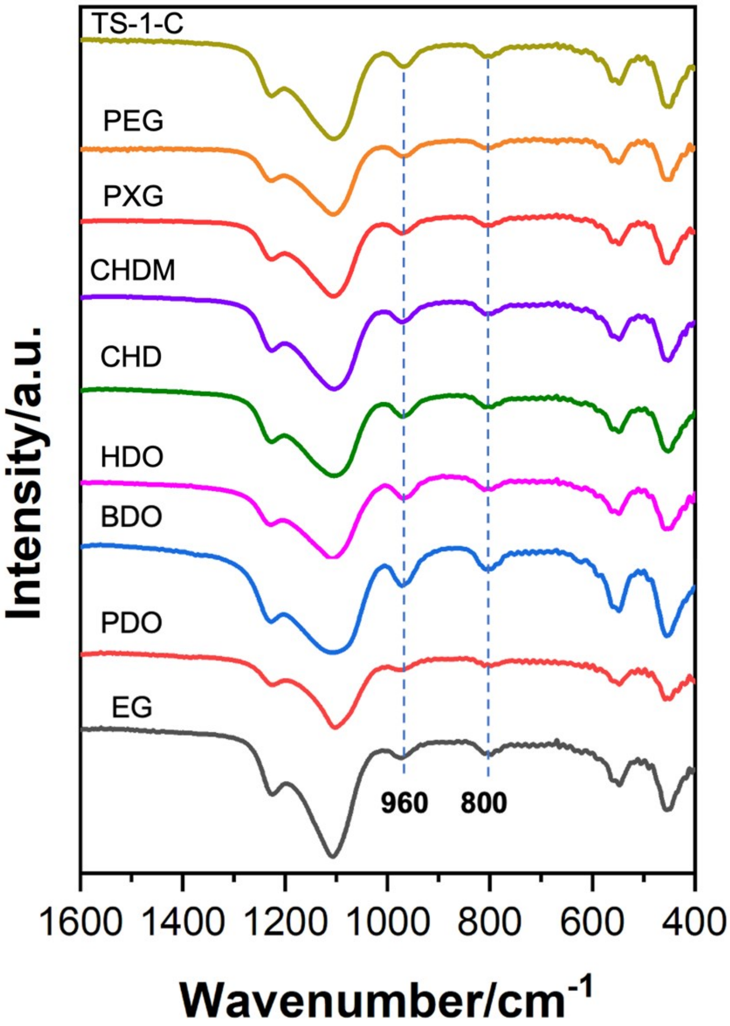


Fig. S22. Fourier Transform infrared spectroscopy (FTIR) of the conventional TS-1 samples (TS-1-C) and the TS-1 samples synthesized from different polymers.

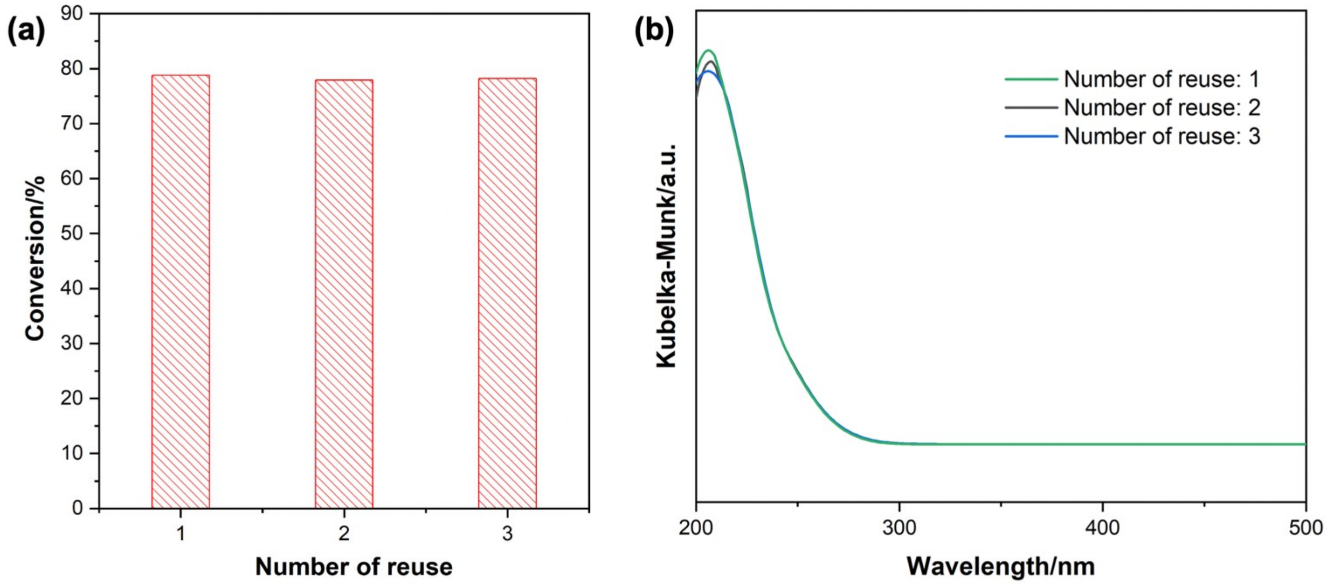


Fig. S23 (a) Changes of n-hexane conversion with the reaction-regeneration cycles on TS-1 zeolites. Reaction conditions for the first run: 0.1 g of catalyst, 60 °C, 4 hrs., 10 mL of CH_3OH as solvent, 10 mmol of n-hexane, 20 mmol of H_2O_2 (30% in aqueous solution). All the catalytic runs proceed at a constant ratio of catalyst-oxidant-solvent. (b) UV-Vis spectra of the TS-1 zeolites carried with different reaction-regeneration cycles

Table S5. Changes of n-hexane conversion with the reaction-regeneration cycles on TS-1 zeolites. [a]

Number of reuse	Si/Ti ratio[b] in catalyst	Conv. [%] based on n-hexene
1	53.3	78.5
2	53.2	77.9
3	53.2	78.2

[a] Reaction conditions for the first run: 0.1 g of catalyst, 60 °C, 4 hrs., 10 mL of CH_3OH as solvent, 10 mmol of n-hexane, 20 mmol of H_2O_2 (30% in aqueous solution). All the catalytic runs proceed at a constant ratio of catalyst-oxidant-solvent. [b] The elemental compositions in TS-1 are determined by ICP.

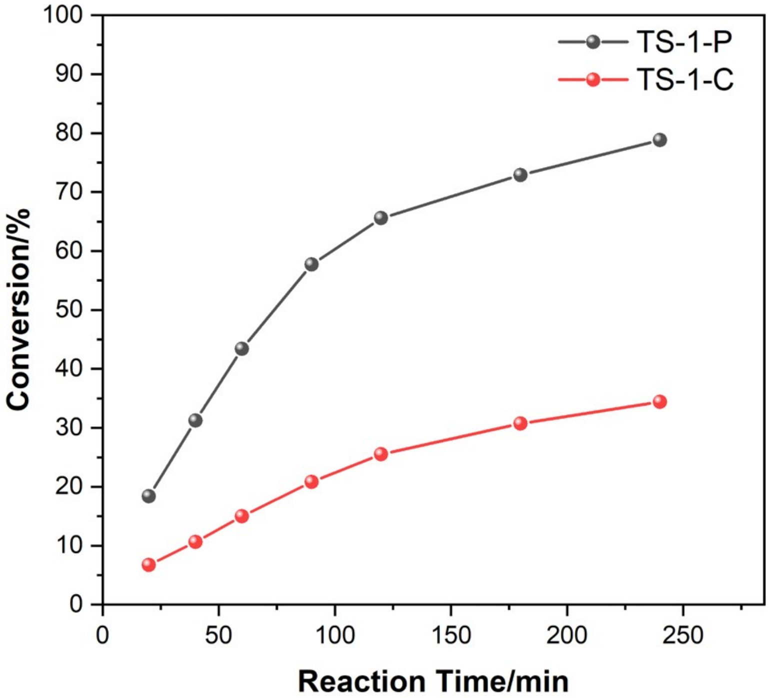
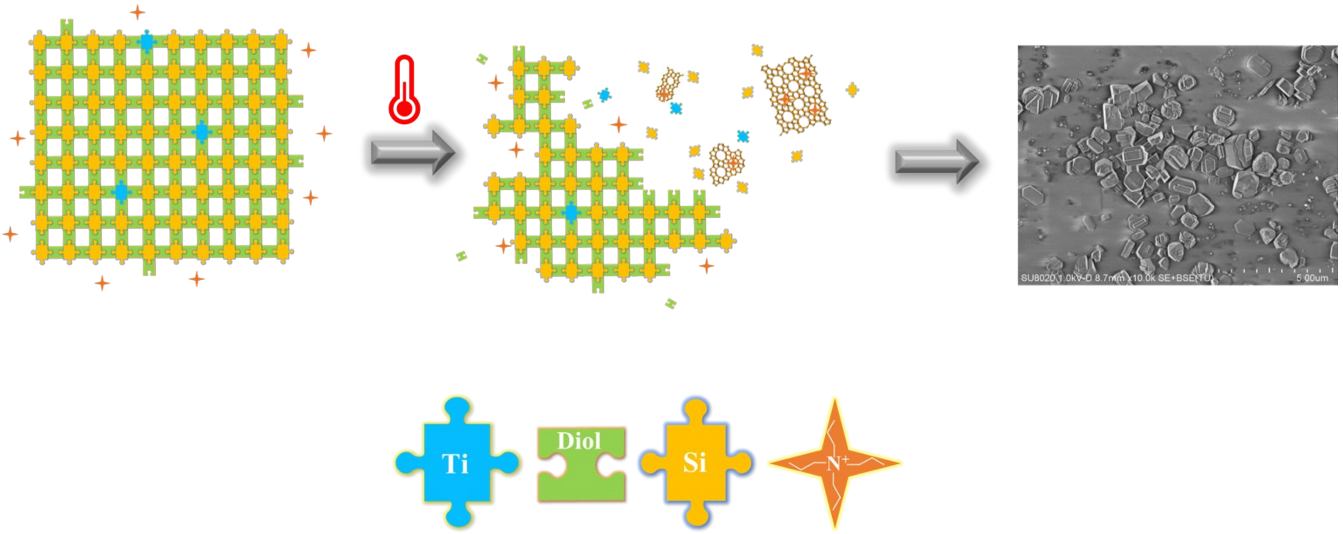
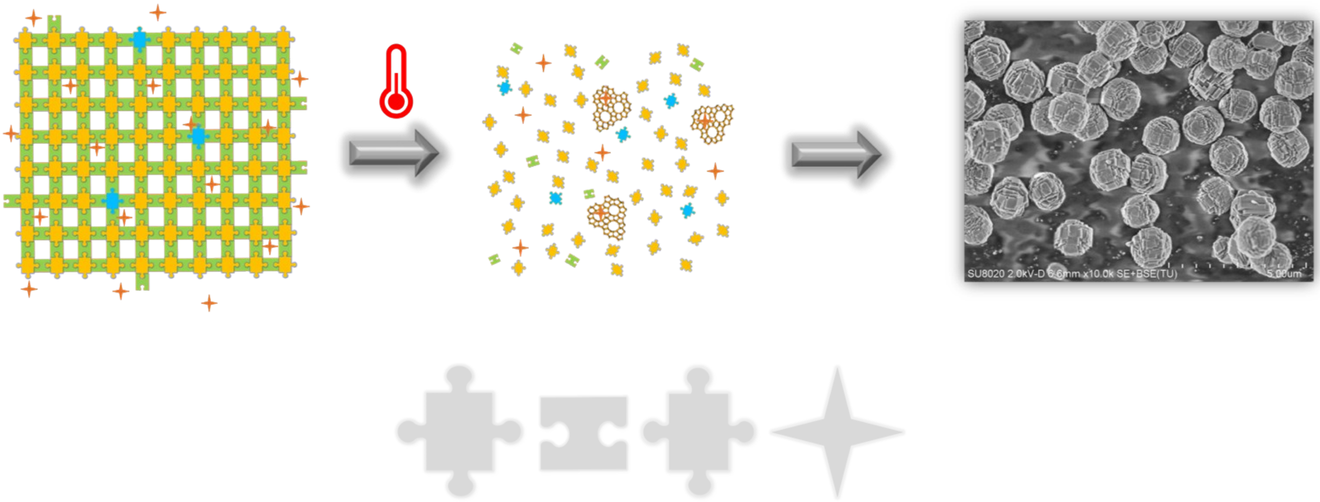


Fig. S24 n-hexane conversion as a function of reaction time during the oxidation of n-hexane using TS-1 zeolites synthesized from Ti-HDO-Si polymers (TS-1-P) and conventional methods (TS-1-C) (Reaction conditions: 0.1 g of catalyst, 60 °C, 10 mL of CH_3OH as solvent, 10 mmol of n-hexane, 20 mmol of H_2O_2 (30% in aqueous solution)).



TS-1 synthesized from Ti-CHD-Si, Ti-CHDM-Si, Ti-PXG-Si polymers had a large particle size and their surfaces were smooth and flat, while the size of zeolite crystal distributed widely. This was mainly because these polymers cannot dissolve in the synthesis solution at room temperature. Then during the crystallization, the outer layers of the solid polymer were gradually decomposed in the autoclave. The polymers provided the titanium and silicon sources layer by layer and from outside to inside. Under the action of the templating agent, the crystals were gradually grown while the unsolved polymers released new sources of titanium and silicon. In this case, a different nucleation time resulted in the size of the particle distributed widely.



For water soluble polymers such as Ti-EG-Si, Ti-HDO-Si, Ti-PEG-Si polymers, etc. The polymers were fully dissolved in the synthesis solution and not hydrolyzed under room temperature. After that, the polymers were uniformly decomposed in the aqueous solution of TPAOH in autoclave, and at the same time, silicon sources and titanium sources were provided, and the crystal grew under the action of the templating agent. Therefore, compared with TS-1 directly synthesized from non-soluble polymers, the particle sizes of TS-1 synthesized by using the soluble polymer were uniform and small