Supplementary Information

A Significant Enhancement of Catalytic Activities in Oxidations with H_2O_2 over TS-1 Zeolite by Adjusting the Catalyst Wettability

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Experiment section

Materials. All reagents were used without purification. Tetra-*n*-butyl titanate (TBOT), tetraethyl orthosilicate (TEOS), $NaAlO_2$, and isopropyl alcohol (IPA) were obtained from Shanghai Chemical Reagent Company. Tetrapropylammonium hydroxide (TPAOH, *ca.* 12.6 %), and dimethyl dimethoxy silicane (DDS) were supplied by Changling Catalyst Company. 1-hexene, benzyl alcohol, benzaldehyde, 1,2-epoxypropane, 1,2-propanediol, hexane, 2-hexanol, 2-hexanone, MeOH, EtOH, 3-hexanone, and phenol were obtained from the Aladdin Chemical Reagent Company. 3-hexanol and 1,2-epoxyhexene was obtained from Sigma-Aldrich Company.

Synthesis of C-TS-1 sample. The various TS-1 catalysts were hydrothermally synthesized from starting titanosilicate gels with molar ratios of $SiO_2/0.02TBOT/0.3TPAOH/40H_2O/0.33IPA$. As a typical run for the synthesis of C-TS-1, (1) 0.154 g of TBOT was dissolved in 0.448 g of IPA, followed by the addition of 6.65 mL of TPAOH (19.42 *wt*%) and 3.61 mL of water; (2) After stirring at room temperature for 1.5 h, 6 mL of water was added and stirred for another 15 min; (3) After adding 5 mL of TEOS into the gel and stirring for overnight, the gel was transferred into an autoclave to crystallize at 180 °C for 3 days; (4) After filtrating, drying, and calcining at 550 °C for 4 h, the C-TS-1 sample was obtained.

Synthesis of H-TS-1-x samples. The H-TS-1-*x* samples were synthesized from similar method to C-TS-1 except for using DDS and TEOS as a silica source where *x%* stands for molar ratio of DDS to total silica source. For example, in the synthesis of H-TS-1-7.5, 4.63 mL of TEOS and 0.24 mL of DDS were used as a silica source in the starting gel.

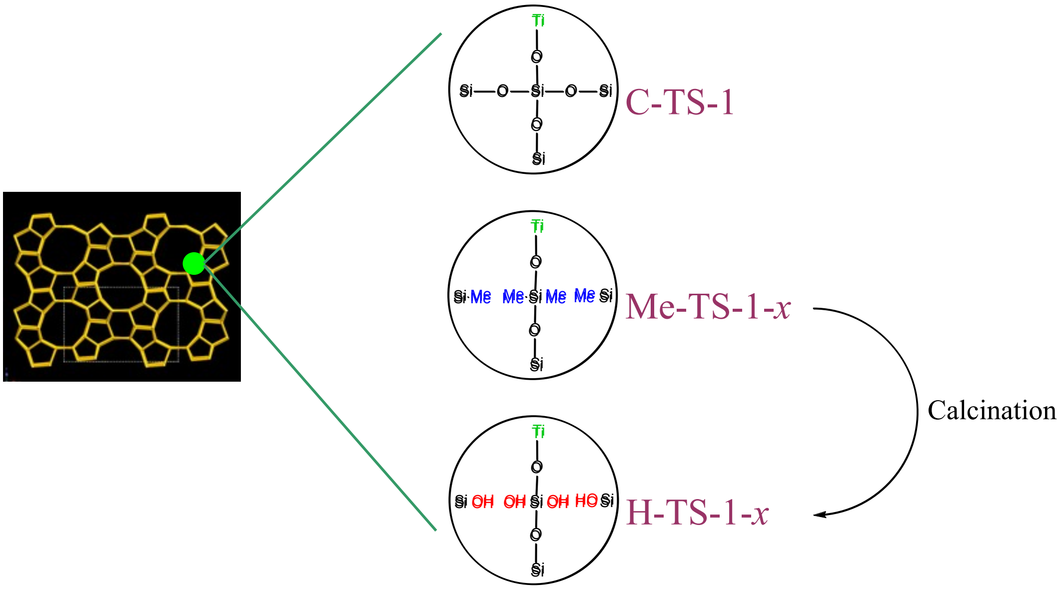
Synthesis of ZSM-5 sample. In a typical run for the synthesis of C-ZSM-5 zeolite, (1) 8 mL of TAPOH (19.42 *wt*%) and 0.08 g of $NaAlO_2$ were added into 20 mL of water; (2) After stirring at room temperature for 2 h, 7 mL of TEOS was added; (3) After stirring for overnight, the gel was transferred into an autoclave to crystallize at 180 °C for 3 days; (4) After filtrating, drying, and calcining at 550 °C for 4 h, the C-ZSM-5 sample was obtained.

Synthesis of H-ZSM-5-7.5 sample. In a typical run for the synthesis of H-ZSM-5-7.5 zeolite, (1) 8 mL of TAPOH (19.42 *wt*%) was added in to 10 mL of water, followed by addition of 6.475 mL of TEOS and 0.336 mL of DDS; (2) After stirring for overnight, 0.08 g of $NaAlO_2$ and 10 mL of water were introduced to the gel; (3) After stirring for 6 h, the gel was transferred into an autoclave to crystallize at 180 °C for 10 days; (5) After filtrating, drying, and calcining at 550 °C for 4 h, the H-ZSM-5-7.5 sample was obtained. The H-form C-ZSM-5 and H-ZSM-5-7.5 zeolites were used for the characterization and catalysis.

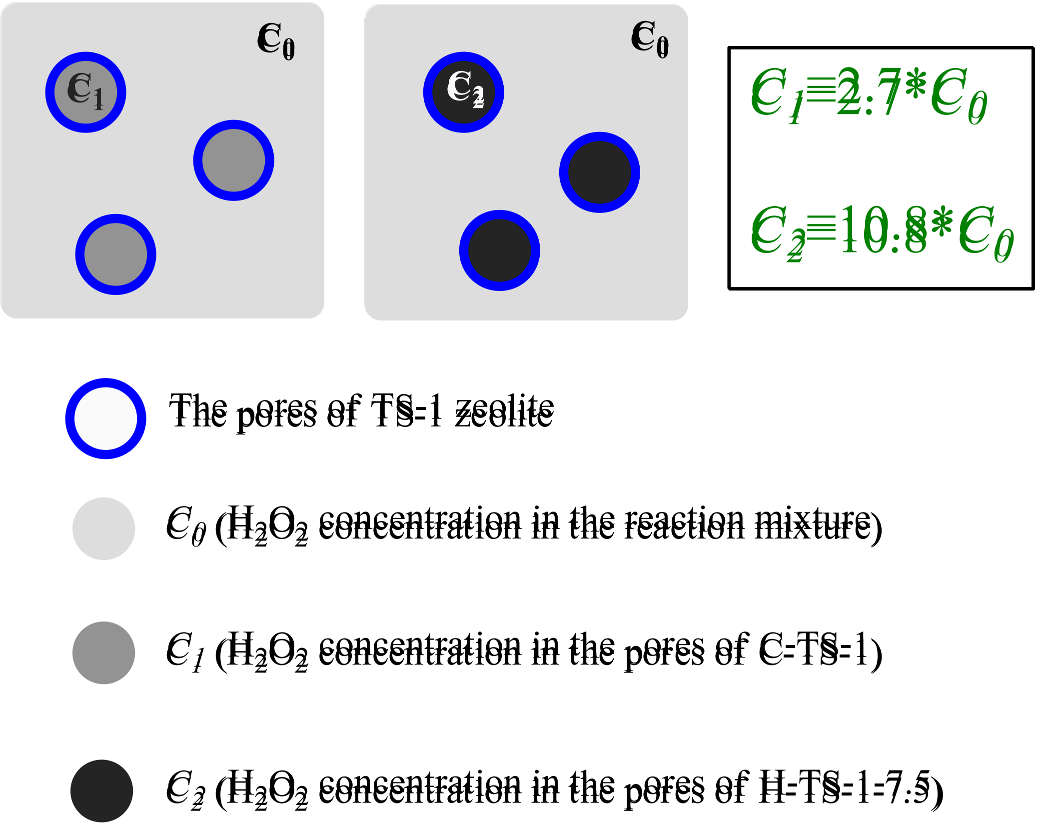
Characterizations. X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu KR radiation (λ=1.5418 Å). Si/Ti and Si/Al ratios were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020 system. ^{29}Si MAS NMR spectra were recorded on Bruker Avance III-600 spectrometer at 119.2 MHz with a spinning rate of 6 kHz, 500 scans, and a recycle delay of 4 s. ^{1}H MAS NMR spectra were collected on the same instrument at 600.1 MHz with a spinning rate of 12 kHz, 32 scans, and a recycle delay of 5 s. ^{29}Si and ^{1}H NMR Chemical shifts were referenced to tetramethylsilane (TMS). UV-Vis spectra were measured on a PERKIN ELMER Lambda 20 spectrophotometer. FT-IR spectra were recorded with a Bruker 66V FTIR spectrometer. The contact angles of water and 1-hexene droplets on the solid surface were measured on an Optical Contact Angle Meter (SL200KB). The enrichment of H_2O_2 on C-TS-1 and H-TS-1-7.5 were calculated by the pore volume of TS-1 samples and the change of H_2O_2 concentration in the mixture before and after adding the samples. As a typical run, 0.1 g of dried TS-1 catalyst, 5 mmol of H_2O_2 were added into MeOH solvent (total volume at 3 mL). After stirring at 0 °C in dark for 40 min, the change of the H_2O_2 concentration in liquor was measured by $KMnO_4$ titration method. The water or 1-hexene adsorption capacities were tested at room temperature for 24 h, the solid samples were outgassed at 100 °C under vacuume for 8 h before the test.

Catalytic tests. The oxidations of 1-hexene, hexane, and phenyl alcohol were performed in a 40-mL glass reactor with a magnetic stirrer (900 rpm). Typically, organic substrate, solvent, and catalyst were mixed in the reactor, After increasing the temperature (the temperature was measured with a thermometer in an oil bath), H_2O_2 solution (35 *wt*%) was introduced. After reaction, the products were analyzed by gas chromatography (GC-14C, Shimadzu, FID) with a flexible quartz capillary column (FFAP and OV-17).

Schemes and tables



Scheme S1. Scheme of various TS-1 samples. After calcination of Me-TS-1-*x* at 550 °C, the organic template was removed, and the methyl groups were transformed into hydroxyl groups, forming H-TS-1-*x*.



Scheme S2. Enrichment of H_2O_2 concentration in C-TS-1 and H-TS-1-7.5 catalysts. The H_2O_2 concentration in the reaction mixture (C_0) was measured to be 1.61 mol L^{-1} by the $KMnO_4$ titration method. The H_2O_2 concentrations in C-TS-1 ($C_1 \approx 4.35$ mol L^{-1}) and H-TS-1-7.5 ($C_2 \approx 17.4$ mol L^{-1}) were calculated by the pore volume of TS-1 catalysts and the change of H_2O_2 concentration in the mixture before and after adding the solid samples.

Table S1. Textural parameters of various TS-1 samples.

Samples	DDS loading[a]	Si/Ti[b]	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
C-TS-1	1.0	52	435	0.54	0.13
H-TS-1-5	5.0	55	422	0.53	0.14
H-TS-1-7.5	7.5	58	403	0.54	0.13
H-TS-1-10	10.0	60	414	0.54	0.15
H-TS-1-20	20.0	57	434	0.53	0.15

[a] Molar ratio of DDS to total silica in the starting gel; [b] By ICP.

Table S2. Textural parameters and catalytic data in hydration of 1,2-epoxypropane by water to 1,2-propanediol over various ZSM-5 samples.

Samples	Si/Al[a]	S_{BET} (m^2/g)[b]	Pore size (nm)	Pore volume (cm^3/g)	Conv. (%)[c]	Sel. (%)[d]
C-ZSM-5	42	345 (54)	0.54	0.15	14.5	>99.0
H-ZSM-5-7.5	46	412 (46)	0.54	0.17	25.9	>99.0
C-ZSM-5-Poisoned[e]					13.9	94.9
H-ZSM-5-7.5-Poisoned[e]					22.0	96.5

[a] By ICP; [b] Total BET surface area (external surface area); [c] Conversion of 1,2-epoxypropane. Reaction conditions: 0.1 g of catalyst, 2.9 g of 1,2-epoxypropane, 9 g of water, 40 ºC, 6 h; [d] the selectivity to 1,2-propanediol, and the by-products are $C_{>3}$ species; [e] 1 mmol of 2,6-di-tert-butylpyridine into the reaction mixture.

Figure Captions

Figure S1. Experimental points correlating the concentration of H_2O_2 with the initial reaction rates over C-TS-1 catalyst.

Figure S2. XRD patterns of various TS-1 samples.

Figure S3. SEM images of various samples.

Figure S4. N_2 sorption isotherms of various TS-1 samples.

Figure S5. UV-visible spectra of various TS-1 samples.

Figure S6. Contact angles of water and 1--hexene droplets on the surface of various TS-1 samples.

Figure S7. (A) FT-IR spectra of various TS-1 samples exposed in wet air; (B) Water adsorption capacities over various TS-1 samples.

Figure S8. Experimental points correlating the concentration of H_2O_2 with the initial reaction rates over H-TS-1-7.5 catalyst.

Figure S9. The 1-hexene adsorption capacities over various TS-1 samples.

Figure S10. (A) The turnover numbers and (B) H_2O_2 efficiency over various catalysts.

Figure S11. Catalytic oxidation of 1-hexene in a fixed-bed reactor.

Figure S12. Recyclable test of H-TS-1-7.5 catalyst in the oxidation of 1-hexene.

Figure S13. XRD patterns of C-ZSM-5 and H-ZSM-5-7.5.

Figure S14. SEM images of a) C-ZSM-5 and b) H-ZSM-5-7.5.

Figure S15. N_2 sorption isotherms of C-ZSM-5 and H-ZSM-5-7.5 samples.

Figure S16. Contact angles of water droplets on the surface of C-ZSM-5 and H-ZSM-5-7.5 samples.

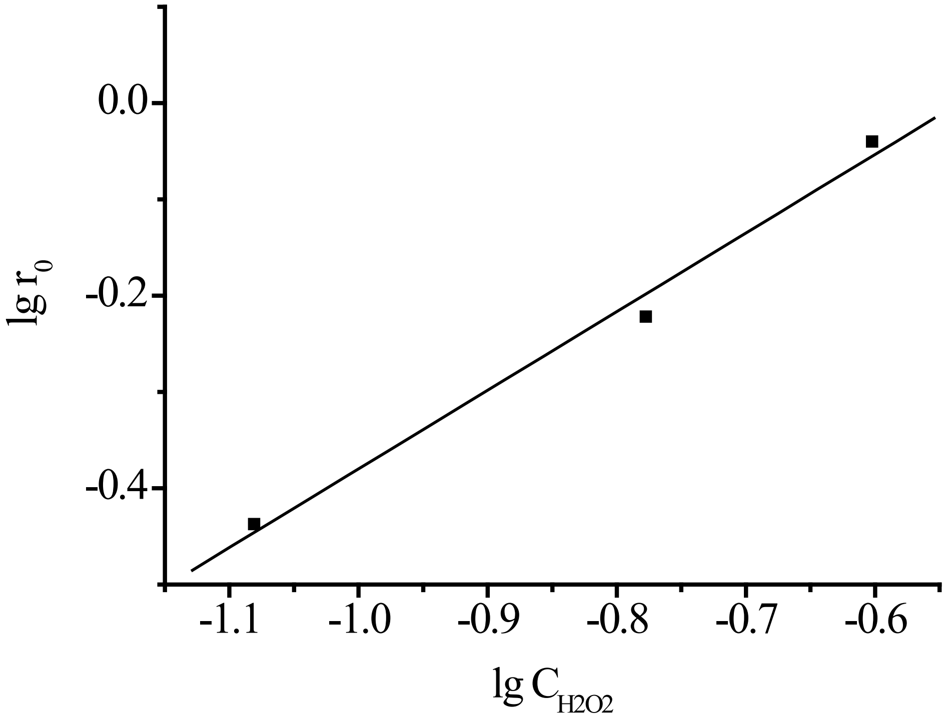


Figure S1. Experimental points correlating the concentration of H_2O_2 (lg C_{H2O2}) with the initial reaction rates (lg r_0) over C-TS-1 catalyst. The straight line was made with the best fitting of the experimental points. Reaction conditions: 10 mmol of 1-hexene, 10 mL of methanol, 50 mg of catalyst, 60 ºC, reaction time at 5 min. According to the chemical reaction rate equation, the reaction order is calculated to be 0.71 for the concentration of H_2O_2.

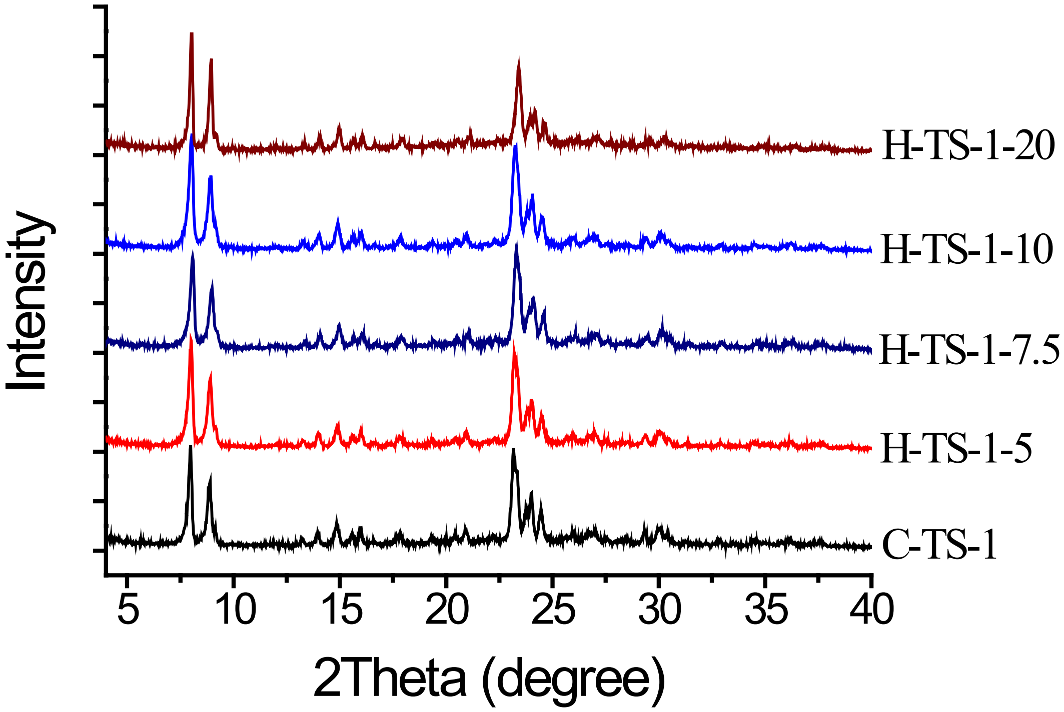


Figure S2. XRD patterns of various TS-1 samples.

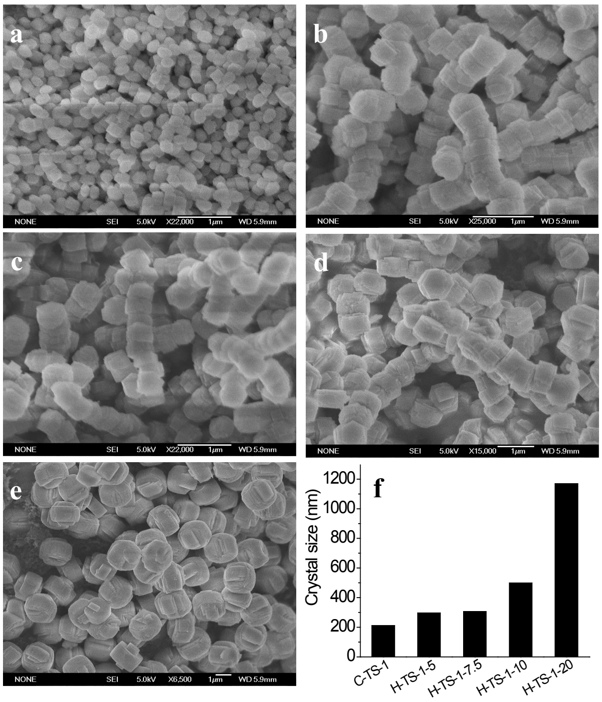


Figure S3. SEM images of (a) C-TS-1, (b) H-TS-1-5, (c) H-TS-1-7.5, (d) H-TS-1-10, and (e) H-TS-1-20; (f) Average crystal sizes of various samples. The scale bars in all images are 1μm. The H-TS-1-5, H-TS-1-7.5, and H-TS-1-10 samples exhibited chain-like morphology, which is quite different from the crystal morphology of TS-1 zeolite. This result might be related to the use of DDS in the synthesis.

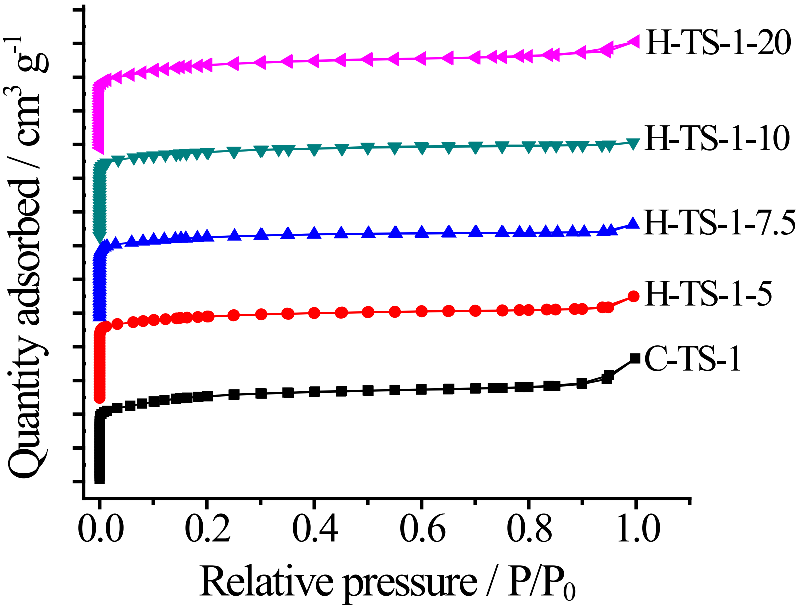


Figure S4. N_2 sorption isotherms of various TS-1 samples.

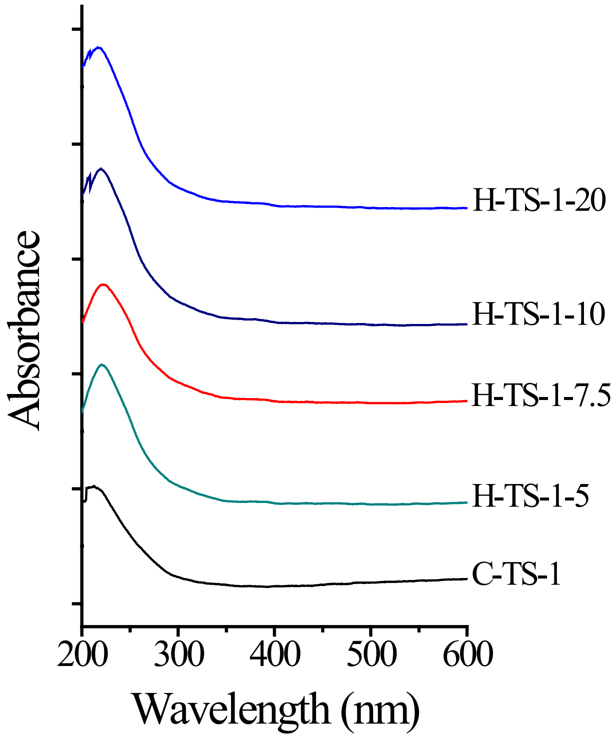


Figure S5. UV-visible spectra of various TS-1 samples.

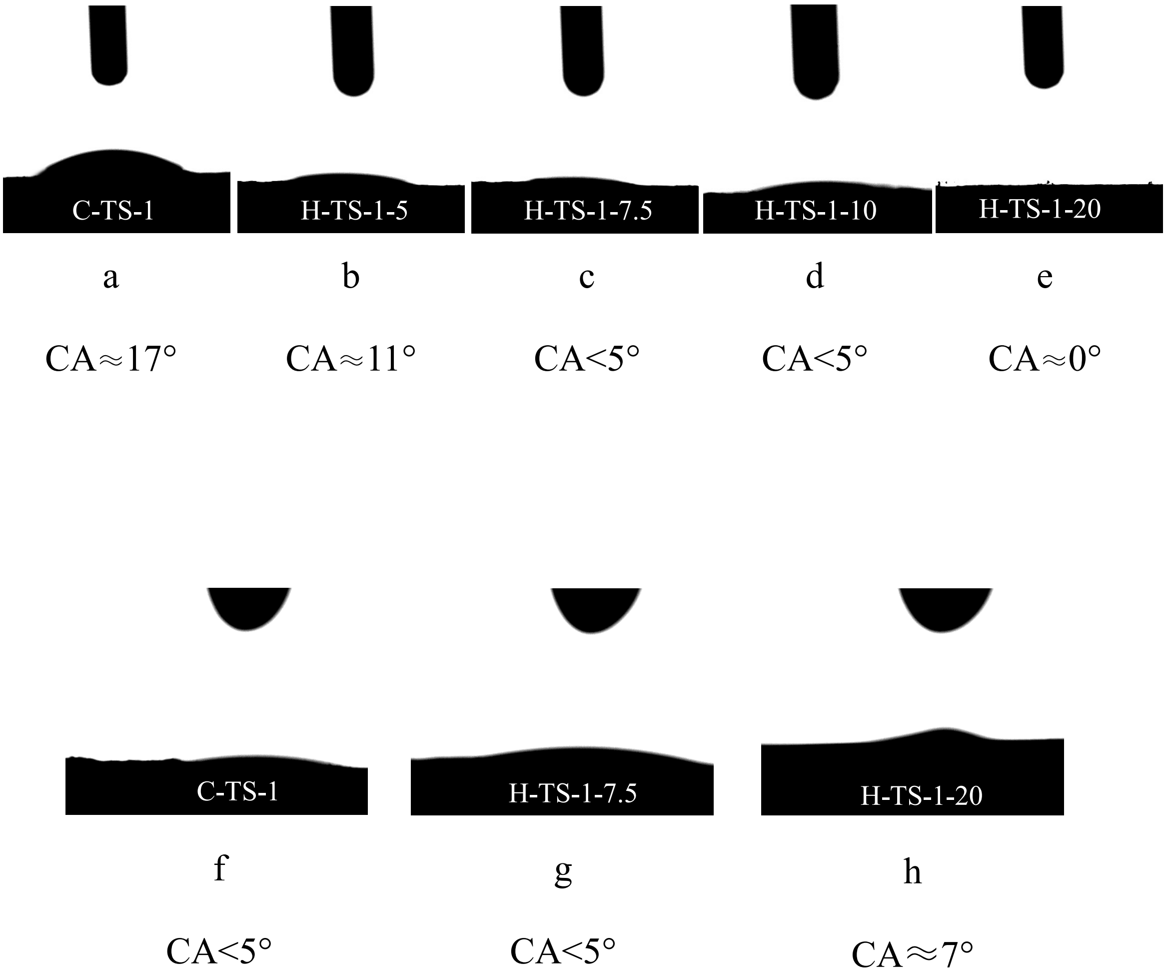


Figure S6. Contact angles of (a-e) water and (f-h) 1-hexene droplets on the surface of various TS-1 samples. The photos were collected at about 0.2 and 0.5s after the droplet touching the solid surface for water and 1-hexene, respectively.

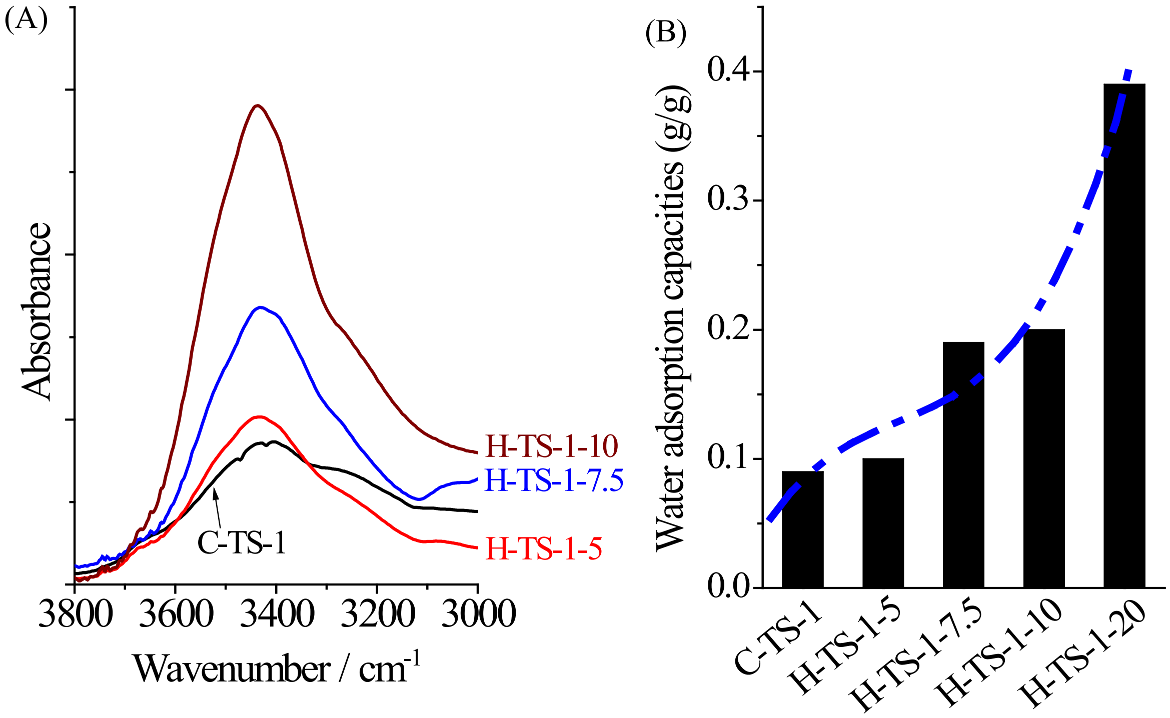


Figure S7. (A) FT-IR spectra of various TS-1 samples exposed in wet air. The intensity order of the peaks associated with adsorbed water species is in the following: *H-TS-1-10 > H-TS-1-7.5 > H-TS-1-5 > C-TS-1*, which is in good agreement with the order of hydroxyl content in the various TS-1 samples. (B) Water adsorption capacities over various TS-1 samples. The water adsorption capacities increased with the order of hydroxyl content in the various TS-1 samples, in good agreement with the phenomenon over the IR spectra. These results indicate that the TS-1 zeolite with more hydroxyl groups could adsorb and enrich more water species.

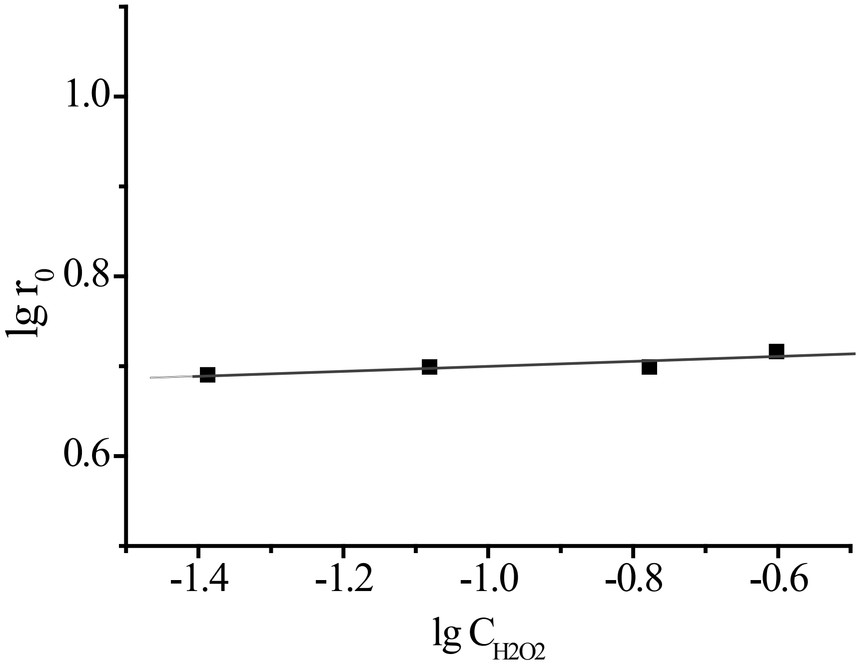


Figure S8. Experimental points correlating the concentration of H_2O_2 (lg C_{H2O2}) with the initial reaction rates (lg r_0) over H-TS-1-7.5 catalyst. The straight line was made with the best fitting of the experimental points. Reaction conditions: 10 mmol of 1-hexene, 10 mL of methanol, 50 mg of catalyst, 60 ºC, reaction time at 5 min. According to the chemical reaction rate equation, the reaction order is calculated to be 0.11 for the concentration of H_2O_2.

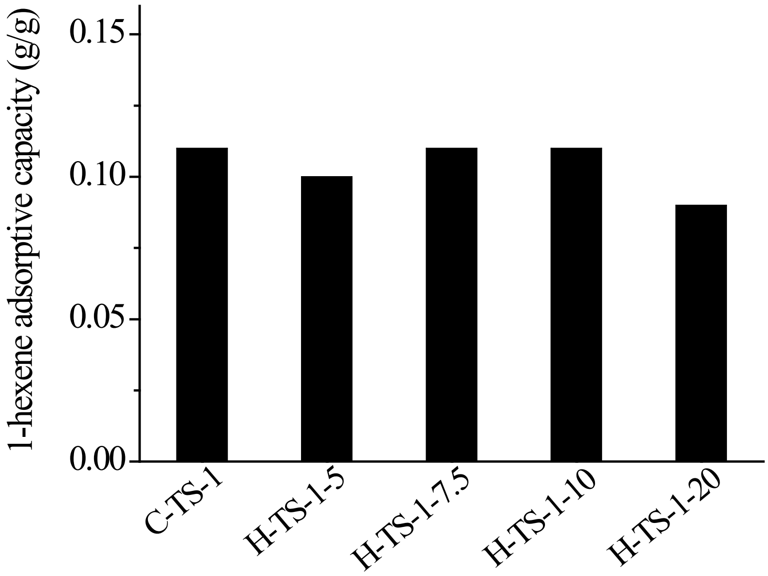


Figure S9. The 1-hexene adsorption capacities over various TS-1 samples.

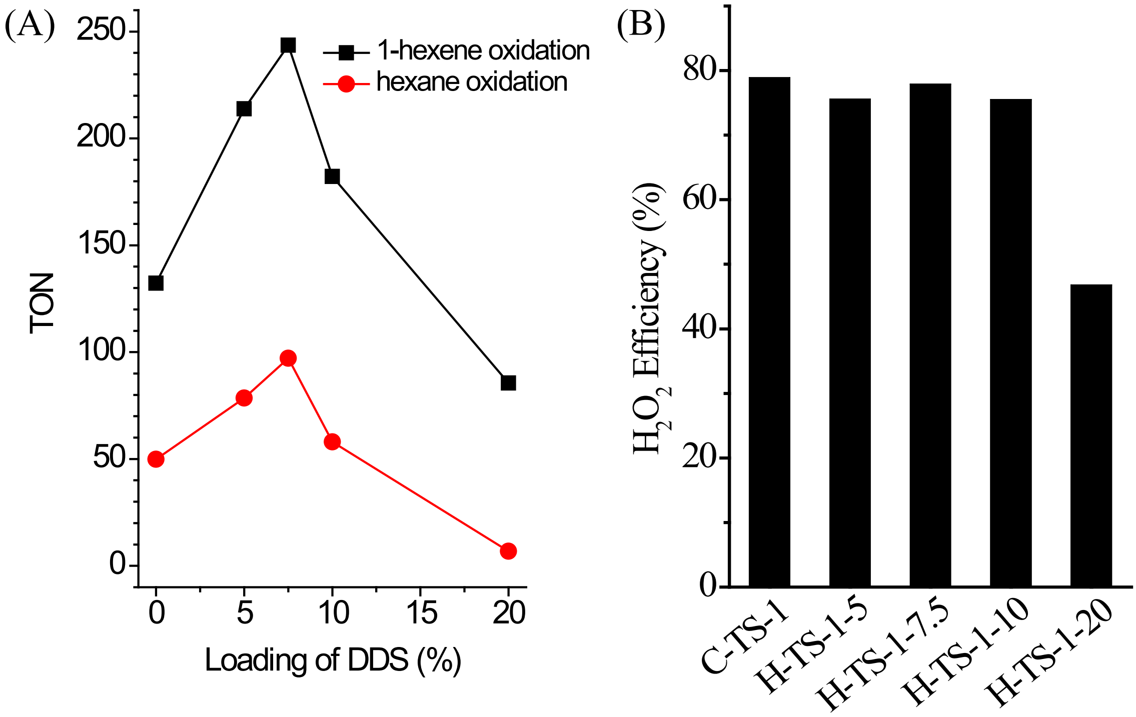


Figure S10. (A) The turnover numbers (TON = moles of converted substrate / moles of Ti species) of the catalysts with different DDS loading (molar ratios of DDS / total silica in the starting gel); (B) H_2O_2 efficiency over various catalysts in the oxidation of 1-hexene. The reaction conditions are the same as that in Table 1. C-TS-1. H-TS-1-5, H-TS-1-7.5, and H-TS-1-10 gave similar H_2O_2 efficiencies at 72.5-78.9%, much higher than that (46.8%) over H-TS-1-20.

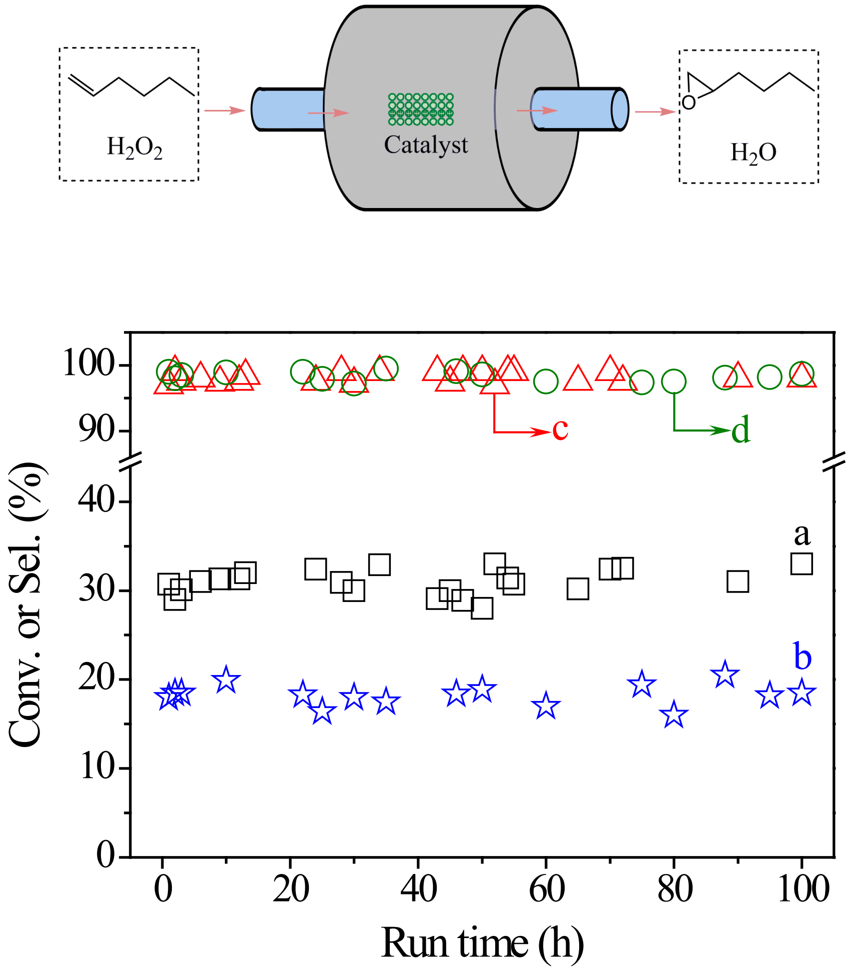


Figure S11. Catalytic oxidation of 1-hexene in a fixed-bed reactor. Conversion of 1-hexene over (a) H-TS-1-7.5 and (b) C-TS-1 catalysts, and selectivity of 1,2-epoxyhexene over (c) H-TS-1-7.5 and (d) C-TS-1 catalysts. Reaction conditions: 0.15 g of C-TS-1 or H-TS-1-7.5 catalyst, 1-hexene and H_2O_2 in MeOH solution (8.54 wt% of 1-hexene, molar ratio of 1-hexene and H_2O_2 at 1:1), 60 °C, 0.2 mL min-1. The solution was placed in an ice bath before pumping into the reactor.

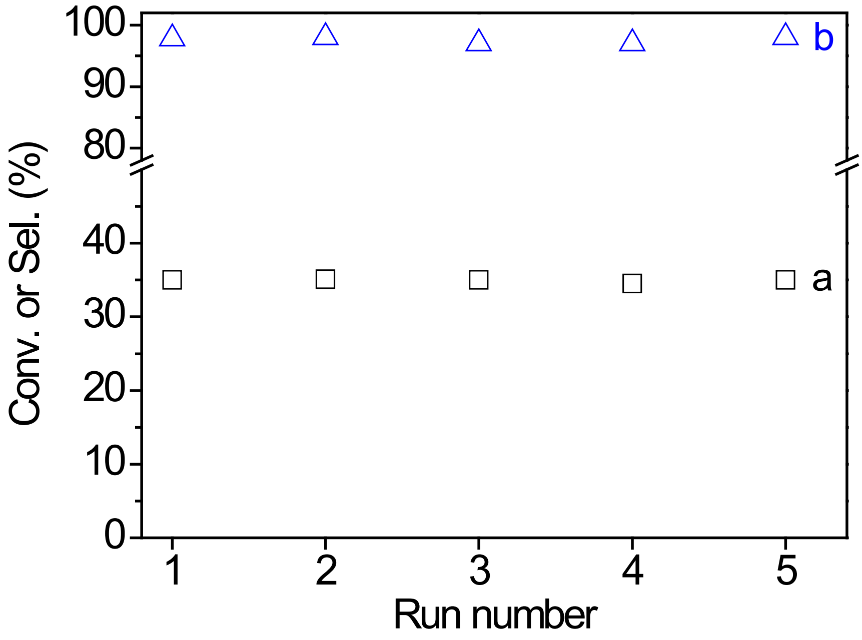


Figure S12. Recyclable test of H-TS-1-7.5 catalyst in the oxidation of 1-hexene. (a) Conversion of 1-hexene and (b) selectivity of 1,2-epoxyhexene. Ever after four recycles, we cannot observe obvious loss for 1-hexene conversion and 1,2-epoxyhexene selectivity, indicating that the H-TS-1-7.5 catalyst has a good recyclability.

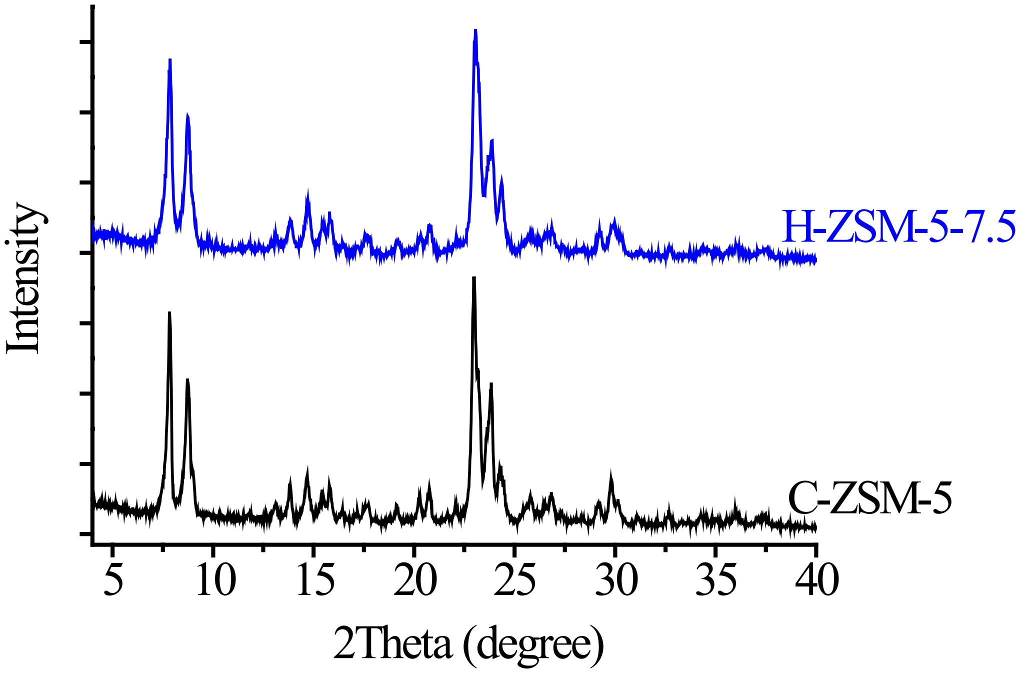


Figure S13. XRD patterns of C-ZSM-5 and H-ZSM-5-7.5. Both samples exhibited good crystalline associated with typical MFI structure.

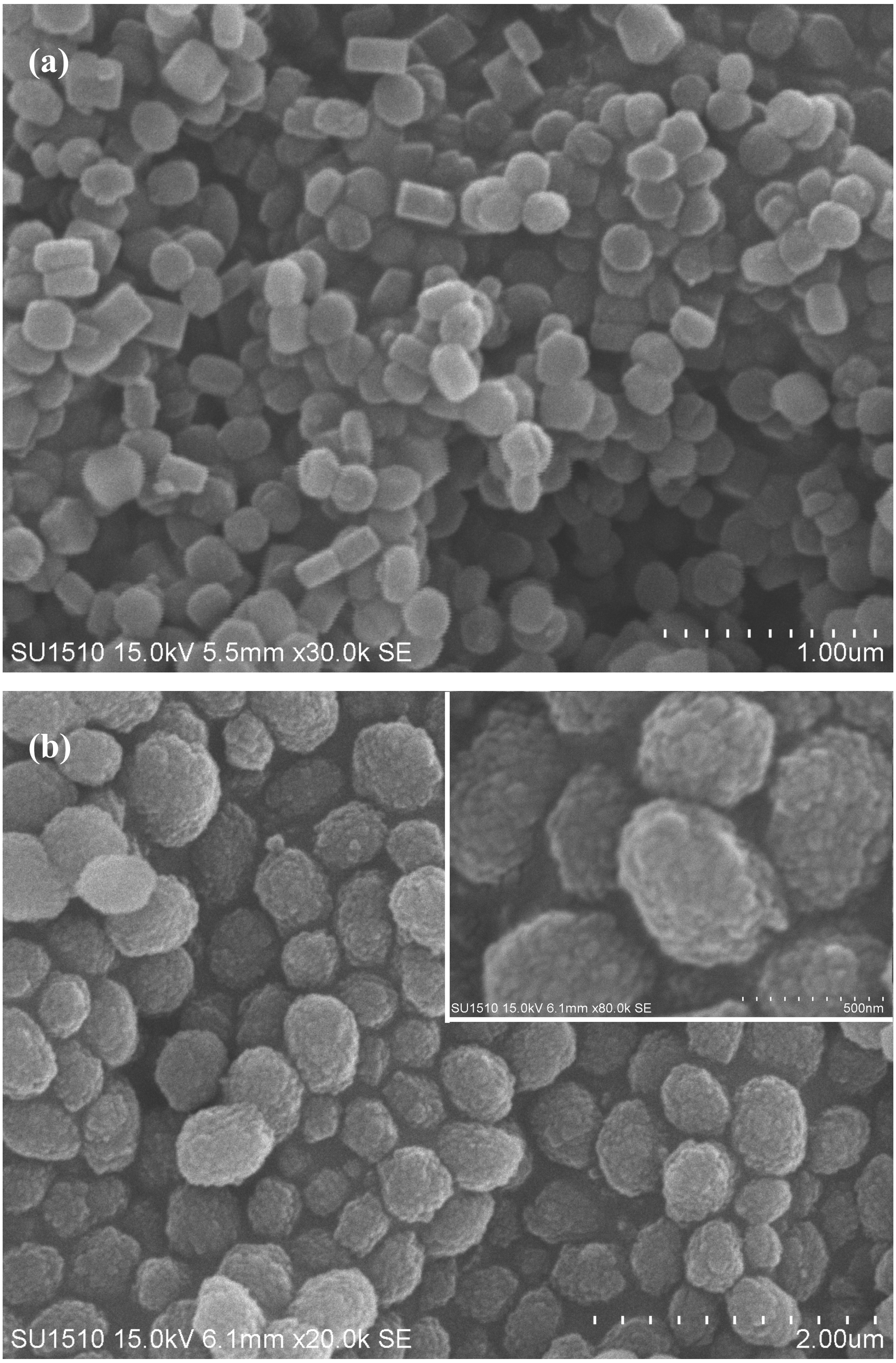


Figure S14. SEM images of a) C-ZSM-5 and b) H-ZSM-5-7.5. The C-ZSM-5 and H-ZSM-5-7.5 samples give average crystal sizes at 185 and 494 nm, respectively. Notably, the H-ZSM-5-7.5 crystals exhibit rough surface, which is due to the presence of DDS in the starting gel for synthesizing H-ZSM-5-7.5.

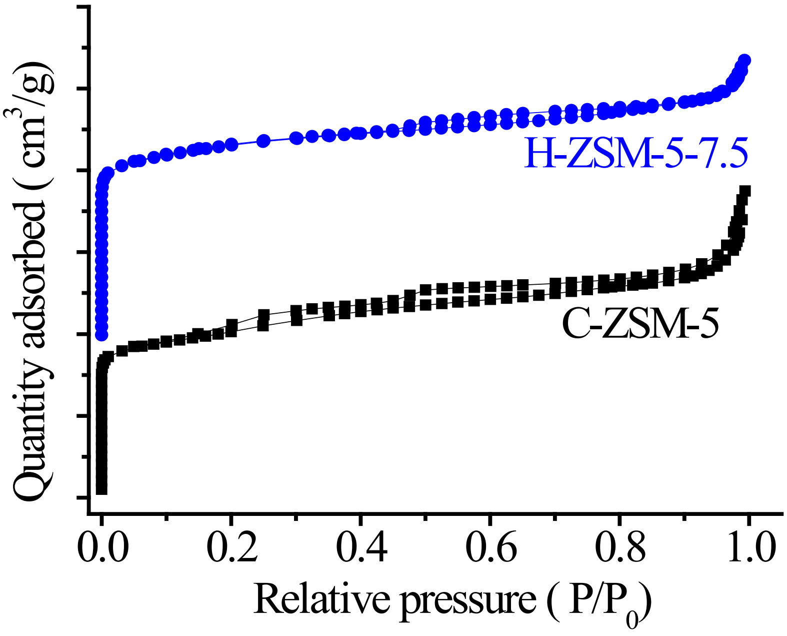


Figure S15. N_2 sorption isotherms of C-ZSM-5 and H-ZSM-5-7.5 samples. Both samples exhibit very similar sorption curves, thus giving similar surface area, pore size distribution, and pore volume (Table S2).

a

b

CA≈15°

CA<5°

Figure S16. Contact angles of water droplets on the surface of C-ZSM-5 and H-ZSM-5-7.5 samples. The photos were collected at about 0.2s after the water droplet touching the solid surface. The H-ZSM-5-7.5 gives smaller contact angle than C-ZSM-5, indicating that H-ZSM-5-7.5 has better water wettability than C-ZSM-5.

As shown in Figure 1B-a, the ^{1}H NMR spectrum of H-TS-1-7.5 gives a weak signal at 0.9 ppm, which is associated with the presence of small amount of methyl groups. Further calcination at higher temperature for a long time (8 h at 600°C) could completely eliminate these methyl groups, but the higher temperature calcination also partially removes the hydroxyl groups in the catalyst. Therefore, calcination at 550 °C for 4 h in oxygen was chosen as a suitable condition to remove the organic template and methyl groups, minimizing the loss of hydroxyl groups in the catalysts.

It is worth noting that the concept on synthesis of zeolites with rich hydroxyl groups is not only limited to the titanosilicate TS-1, but also extended to various frameworks of zeolites. For example, we can use this route to synthesize aluminosilicate ZSM-5 with rich hydroxyl groups from a mixture of TEOS and DDS, forming relatively hydrophilic H-ZSM-5-7.5. Interestingly, the hydrophilic H-ZSM-5-7.5 exhibited much higher activity in hydration of 1,2-epoxypropane than the conventional ZSM-5 (C-ZSM-5) under the same reaction conditions (Figs. S13-S16, Table S2). The synthesis of hydrophilic zeolites would open a new door for developing alternative active catalyst in the future.

In the hydration of 1,2-epoxypropane by water to 1,2-propanediol, H-ZSM-5-7.5 gives higher 1,2-epoxypropane conversion at 25.9% than that of C-ZSM-5 (14.5%). Additionally, when the external surface areas of the catalysts are poisoned by 2,6-di-tert-butylpyridine (a bulky molecule can only poison the external acid site of the catalyst crystals),[1] the H-ZSM-5-7.5 still shows much higher 1,2-epoxypropane conversion (22.0%) than C-ZSM-5 catalyst (13.9%). This result indicates that the higher activity of H-ZSM-5-7.5 than C-ZSM-5 should origin from the internal active sites in the micropores, which is owing to the excellent wettability of H-ZSM-5-7.5 to water (Fig. S16).

Supporting reference

1. X. Zhang, D. Liu, D. Xu, S. Asahina, K. A. Cychosz, K. V. Agrawal, Y. Al Wahedi, A. Bhan, S. Al Hashimi, O. Terasaki, M. Thommes, M. Tsapatsis, *Science,* 2012, **336***,* 1684