

Synthesis of Hierarchical ZSM-5 Zeolite Using CTAB Interacting with Carboxyl-ended Organosilane as Mesotemplate

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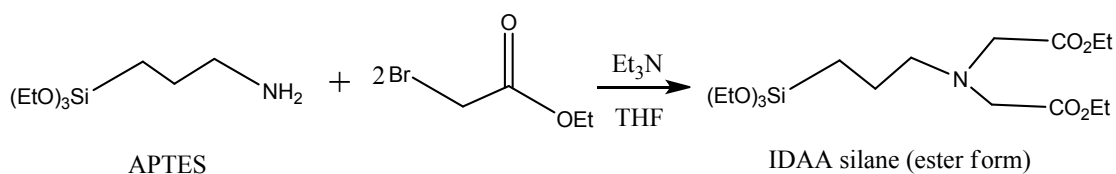
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Supporting information:

Synthesis of IDAA silane (ester form).

Ester form of the iminodiacetic acid (IDAA) terminated organosilane was synthesized by reaction of 3-aminopropyltriethoxysilane (APTES) and ethyl bromoacetate according to the previous literature.¹ The product was identified as IDAA silane (ester form) by ¹H NMR in a CDCl₃ solution with the main peaks of 4.15 (q, 4H, *J* = 7.2 Hz), 3.81 (q, 6H, *J* = 7.2 Hz), 3.55 (s, 4H), 2.71 (pt, 2H, *J* = 7.5 Hz), 1.59 (quintet, 2H, *J* = 8.1 Hz), 1.27 (t, 6H, *J* = 7.2 Hz), 1.22 (t, 9H, *J* = 7.0 Hz), and 0.61 (m, 2H).



Synthesis of ZSM-5 zeolites.

The synthesis of ZSM-5 zeolite samples was adapted from the procedure published elsewhere.² 0.31 g aluminium isopropoxide (AIP; Shanghai Lingfeng Chemical Co., China) was dissolved in 7.42 g tetrapropylammonium hydroxide (TPAOH, 25 wt % aqueous solution; Shanghai Cainorise Chemicals Co., China), followed by the addition of 14.96 g deionized water and 9.50 g Tetraethyl orthosilicate (TEOS, Shanghai Lingfeng Chemical Co., China). After stirring at 30 °C for 5 h, a clear solution with the following molar composition was obtained: AIP: TEOS: TPAOH: H₂O = 1: 30: 6: 750. This solution was precrystallized under reflux with vigorous stirring 90 °C for 24 h. Then 0.90 g IDAA silane (ester form) was added into the clear

solution and further refluxed at 90 °C for 6 h, which is similar to literature.² Thirdly, the above solution was mixed with surfactant solution which contains 0.83 g CTAB in 28.73 g deionized water and kept stirring at 30 °C for 3 h. The final mixture was crystallized in a Teflon-lined stainless steel autoclave at 170 °C for 72 h. The solid products were separated by centrifugation, washed several times, dried overnight at 110 °C and air calcined at 550 °C for 6 h. Hierarchical zeolite was prepared, and the final composition recipe was AIP: TEOS: TPAOH: CTAB: IDAA silane: H₂O = 1: 30: 6: 1.5: 1.5: 1800. The obtained ZSM-5 is denoted as ZSM-5 (NCOO⁻-CTAB), which is short for ZSM-5 (N(CH₂COO⁻)₂-CTAB).

For comparison, we synthesized another two ZSM-5 zeolites, one was added with CTAB without any organosilane, and the other one was added with APTES (5 mol % with respect to the silica content in the gel) instead of IDAA silane (ester form). They are denoted as ZSM-5 (CTAB) and ZSM-5 (NH₂-CTAB), respectively.

Preparation of samples for FT-IR measurement.

The samples for FT-IR measurement were prepared as the following procedures which are schematically shown in Scheme S1:

ZSM-5precursor (NCOO⁻): The precursor solution was obtained after the precrystallization and silanization step. The solid phase was formed by drying the precursor solution under vacuum at 50 °C. So the obtained solid contains the –COO⁻ group both anchored on the zeolite and existing in the solvent.

ZSM-5precursor (NCOOH): The precursor solution was acidified by adding

concentrated hydrochloric acid (HCl) until pH = 1. The solid phase was formed by drying the acidified precursor solution under vacuum at 50 °C. So the obtained solid contains the –COOH group both anchored on the zeolite seeds and existing in the solvent.

ZSM-5seed (NCOOH-CTAB): CTAB was mixed with precursor solution for 3 h after the silanization step, disturbing the colloidal stability of precursor solution. The resultant suspension was acidified by adding concentrated hydrochloric acid (HCl) until pH=1. The zeolite seeds in the acidified suspension were collected by centrifugation, followed by repeated washing with 0.1 mol/L HCl solution to preserve the protonated carboxylic acid group. Then the solid phase was further dried under vacuum at 80 °C. So the obtained solid contains the –COOH group only anchored on the zeolite seeds.

ZSM-5(NCOOH-CTAB) + Supernatant: The product after high temperature crystallization was directly stirred at room temperature without separating supernatant, and then was acidified by adding concentrated hydrochloric acid (HCl) until pH=1. Then the acidified suspension was stirred under 80 °C to evaporate the solvent, followed by further drying under vacuum at 80 °C. So the obtained solid contains the –COOH group both anchored on the zeolite and existing in the supernatant.

ZSM-5 (NCOOH-CTAB): The zeolite after high temperature crystallization was

stirred at room temperature without separating supernatant, and was acidified by adding concentrated hydrochloric acid (HCl) until pH=1. The acidified zeolite was collected by centrifugation, followed by repeated washing with 0.1 mol/L HCl solution. Then the solid was further dried under vacuum at 80 °C. So the obtained solid contains the –COOH group only anchored on the zeolite.

Characterization

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max2550V diffractometer, with CuK α Radiation at 40 kV and 100 mA. The XRD patterns were collected in the range of 5–50° in $2\theta / \theta$ scanning mode with a 0.02° step and scanning speed of 12 degree/min. Nitrogen adsorption–desorption isotherms were measured at 77 K on an ASAP 2010 (Micromeritics, USA) analyzer. Specific surface area was calculated by the BET (Brunauer-Emmett-Teller) method based on the adsorption data at P/P_0 of 0.05-0.25. The poresize distribution was calculated from the adsorption branch using the BJH (Barrett-Joyner-Halenda) method, and total pore volume was obtained from the adsorption at $P/P_0 = 0.995$. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-3400N Electron Microscope at an acceleration voltage of 15 kV. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 instrument operated at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on copper grids. Solid state ^{29}Si MAS NMR spectra were recorded with an AVANCE 500 NMR spectrometer at a spinning frequency of 99.36 MHz. ^{29}Si chemical shifts were obtained with reference to tetramethylsilane (TMS) as an external standard (δ_{TMS}

= 0 ppm). The Fourier transform infrared spectra (Nicolet 6700 FTIR) of the sample were recorded in the range of 400~4000 cm^{-1} with a resolution of 2 cm^{-1} . The solid samples were pressed into KBr pellets; the liquid sample (ester form of the IDAA silane) was analyzed by casting a film on KRS-5 plate. Thermogravimetric (TGA) analyses were performed using a Perkin-Elmer Pyris 1 TGA instrument at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in air.

Table S1 Textural properties obtained by nitrogen physisorption experiments.

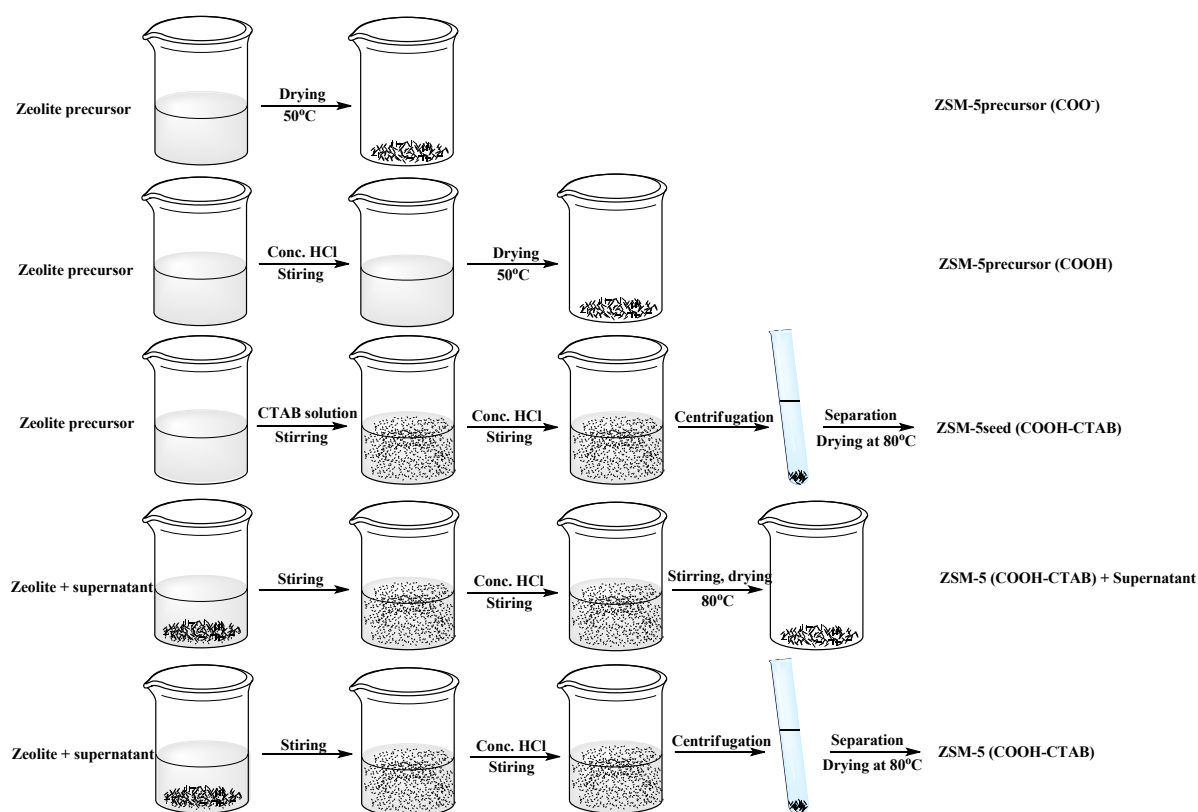
Sample	S_{BET} (m^2g^{-1}) ^a	V_{micro} (cm^3g^{-1}) ^b	V_{total} (cm^3g^{-1}) ^c	V_{meso} (cm^3g^{-1}) ^d
ZSM-5(NCOO-CTAB)	441	0.11	0.36	0.25
ZSM-5(CTAB)	475	0.09	0.43	0.34
ZSM-5(NH ₂ -CTAB)	339	0.11	0.25	0.14

^a Surface areas were obtained by the BET method using adsorption data in P/P_0 range from 0.05 to 0.25.

^b Measured by t-plot method.

^c Total pore volumes were estimated from the adsorbed amount at $P/P_0=0.995$.

^d $V_{\text{meso}}=V_{\text{ads, } P/P_0=0.99} - V_{\text{micro}}$.



Scheme S1. Schematic diagram of the sample preparation procedures for FT-IR measurement.

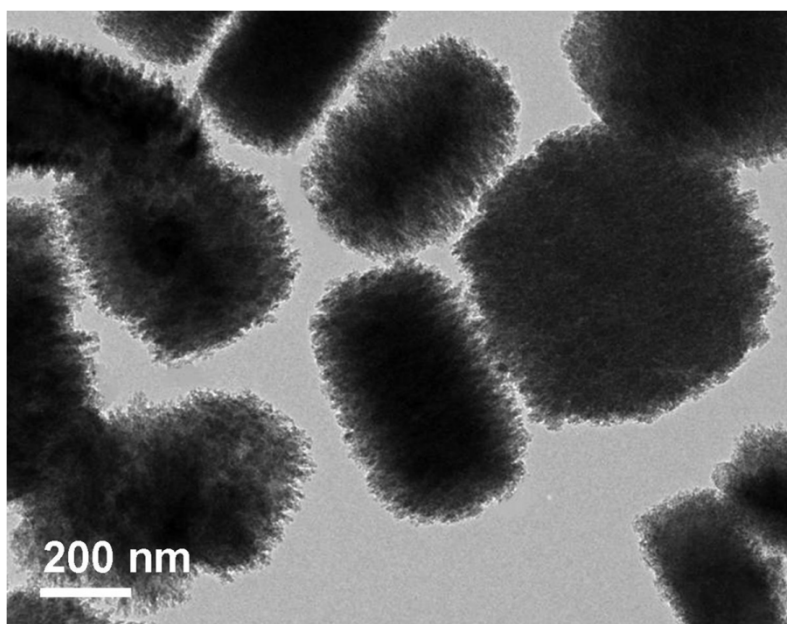


Figure S1. TEM image of ZSM-5 (NCOO-CTAB).

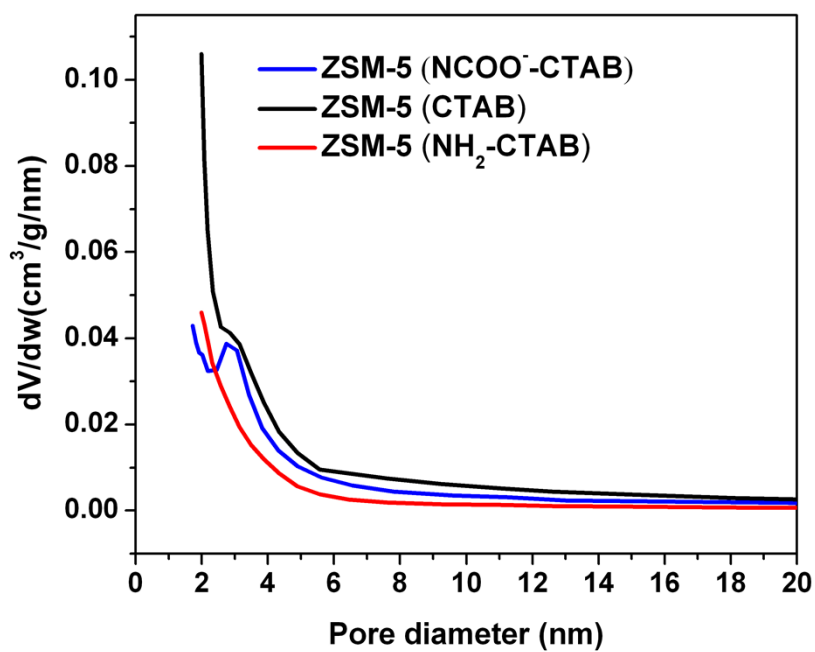


Figure S2 BJH pore size distributions of ZSM-5 (NCOO⁻-CTAB), ZSM-5 (CTAB) and ZSM-5 (NH₂-CTAB).

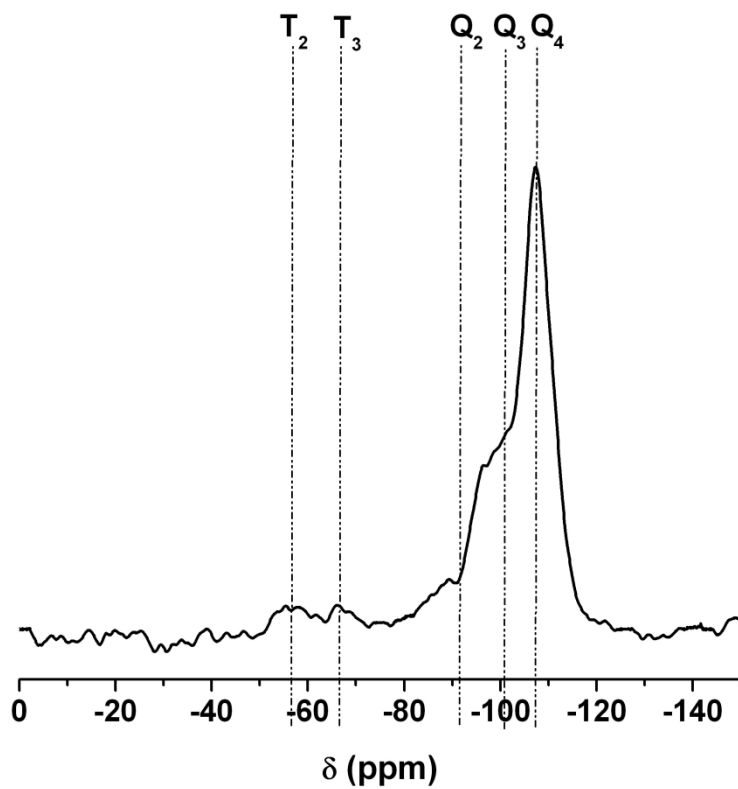


Figure S3 ^{29}Si MAS NMR spectrum of as-synthesized ZSM-5 (NCOO-CTAB).

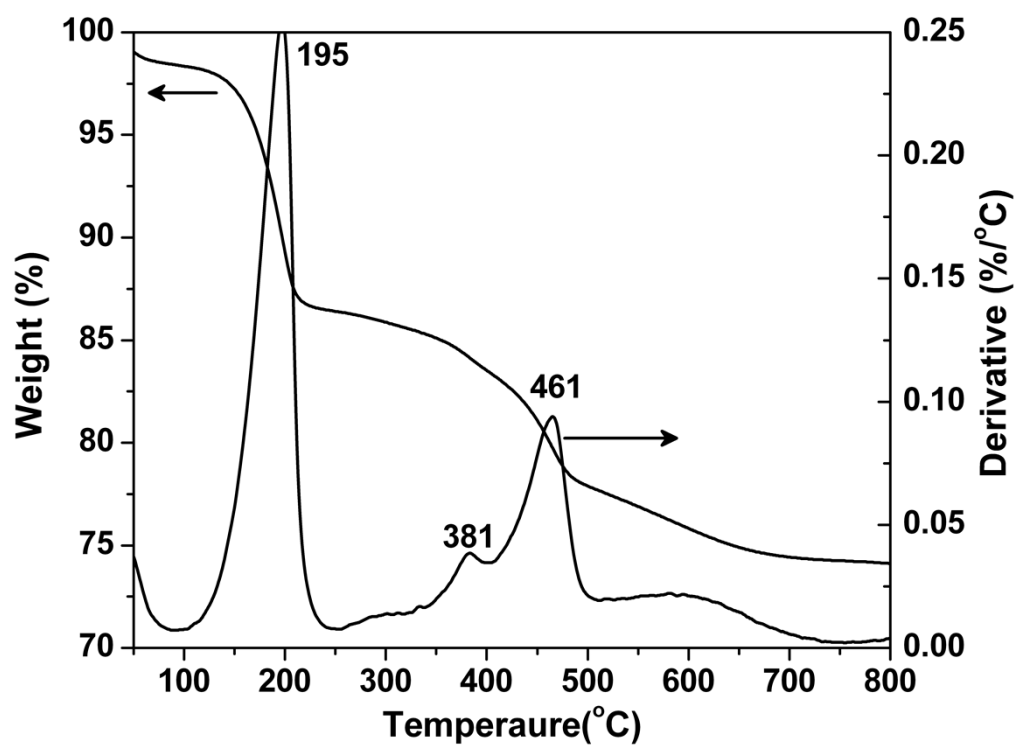


Figure S4 TG and DTG of as-synthesized ZSM-5 (NCOO-CTAB). The weight losses within 130-340 °C and 340-410 °C are due to the decomposition of CTAB and organic moiety of IDAA silane, which are estimated to be 12.7% and 1.8%, respectively. The weight loss within 410-510 °C is due to the TPA^+ strongly retained in the zeolite micropores, and that within 510-800 °C is due to the complete combustion of all the remaining organics.

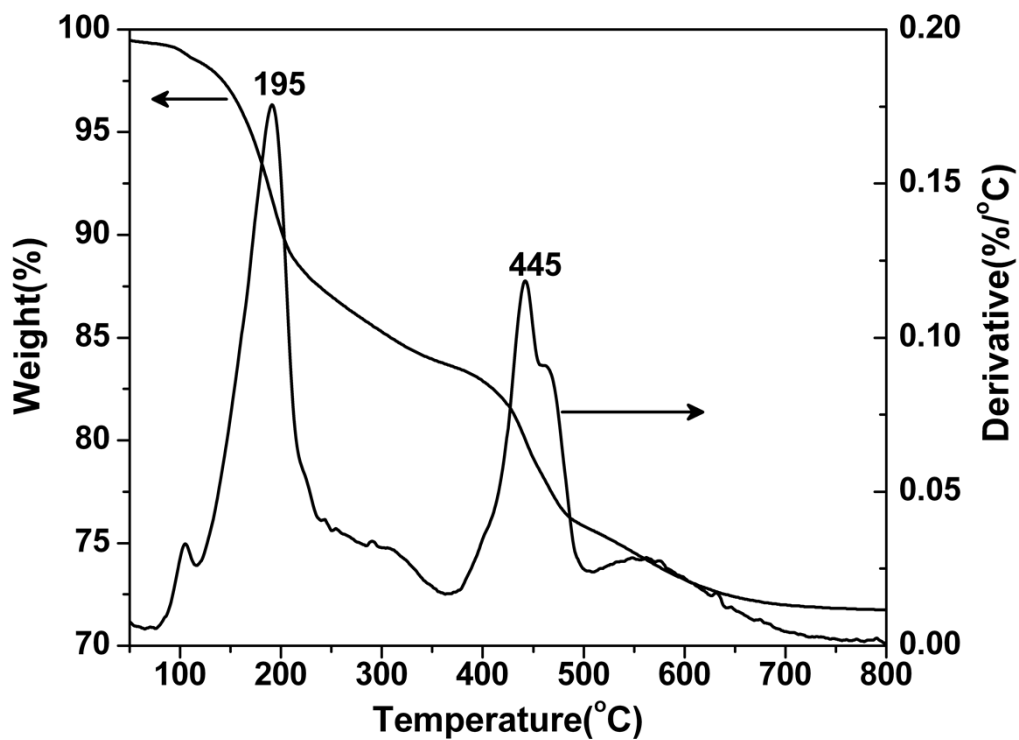


Figure S5 TG and DTG of as-synthesized ZSM-5 (CTAB). The weight loss within 120-340 °C is due to the decomposition of CTAB, which is estimated to be 14.2%. The weight loss within 420-510 °C is due to the TPA⁺ strongly retained in the zeolite micropores, and that within 510-800 °C is due to the complete combustion of all the remaining organics.

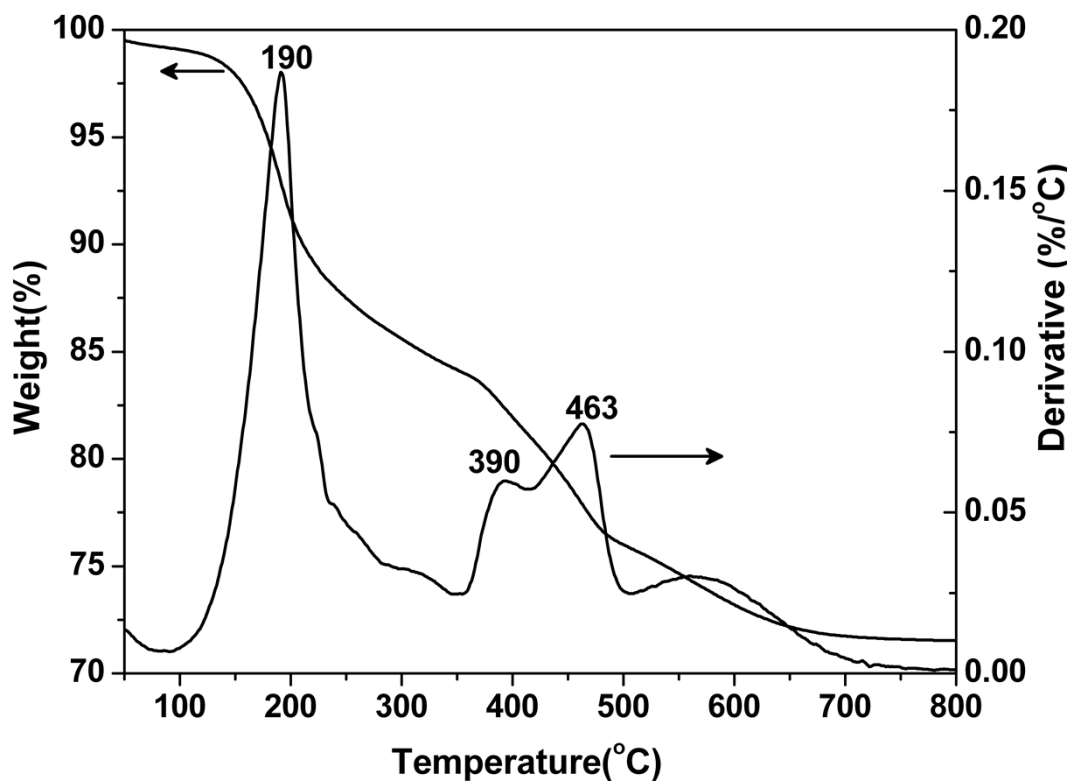


Figure S6 TG and DTG of as-synthesized ZSM-5 (NH₂-CTAB). The weight losses within 130-350 °C and 350-420 °C are due to the decomposition of CTAB and organic moiety of APTES, which are estimated to be 14.9% and 2.6%, respectively. The weight loss within 420-510 °C is due to the TPA⁺ strongly retained in the zeolite micropores, and that within 510-800 °C is due to the complete combustion of all the remaining organics.

References

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- (2) D. P. Serrano, J. Aguado, J. M. Escola, J. M. Rodríguez and Á. Peral, *Chem.*

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