Appendix A Supplementary data

Preparation of Green Hydrophobic ZSM-5 Zeolite and Its Toluene Adsorption Performance under High Humidity Conditions

Material characterization methods

X-ray diffraction (XRD) was performed using a D8 ADVANCE diffractometer (Bruker, Germany) to analyze the crystal structure of the prepared samples, with a Cu-Kα radiation source (λ=1.5406 Å), operating voltage of 40 kV, operating current of 40 mA, scanning speed of 10 °/min, and a scattering angle of 2θ, with data collection ranging from 4° to 60°.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted using a Nicolet-6700 Fourier Transform Infrared Spectrometer to characterize the surface chemical functional groups, elemental composition, and molecular structural information of the prepared samples, obtaining infrared spectra. Test conditions included drying the adsorbent material, mixing it with potassium bromide at a mass ratio of 1:150 (3 mg adsorbent: 450 mg potassium bromide), grinding thoroughly, and pressing into pellets. The scan range was set from 4000 to 400 cm^{-1}, with a resolution of 1.93 cm^{-1} and 64 scans.

N_2 adsorption-desorption isotherms and pore size distribution tests (BET) were performed using an ASAP 2020 M fully automatic specific surface area analyzer (Micromeritics, USA) to characterize the specific surface area and pore structure of the adsorbent materials, obtaining a series of data including the nitrogen adsorption-desorption isotherm. Test conditions involved adsorption and desorption of nitrogen at 77 K for total pore/mesopore testing. The specific surface area was calculated using the BET method, and the micropore specific surface area and micropore volume of the sample were determined using the t-Plot method. Pore size distribution was analyzed using the DFT method based on nitrogen desorption data, with the desorption line of the adsorption-desorption isotherm as the reference. Sample pretreatment involved vacuum degassing at 180 °C for 8 hours to remove physically adsorbed impurities, such as water vapor.

The contact angle of water (Contact Angle) was measured using the JC2000D optical contact angle meter from Shanghai Zhongchen Company, employing the external shape image analysis method. A sufficient amount of molecular sieve sample was dispersed in ethanol to form a uniform suspension, which was then dropped onto a slide to form an even film and dried at 100 °C for 30 minutes. Test conditions included a minimum of 0.5 mL of molecular sieve sample powder, a water droplet volume of 3 μL, an injection speed of 1 $\mu L \cdot s^{-1}$, an accuracy of ±0.1° circle fitting method, and a contact angle test range of $0° < \theta < 180°$.

Thermogravimetric analysis (TGA) was conducted using a thermogravimetric-differential thermal analyzer (NETZSCH STA 449 F5/F3 Jupiter) to analyze the thermal stability of the adsorbents. The adsorbent samples were heated at a rate of 10 $°C \cdot min^{-1}$ from room temperature to 800 °C in an air atmosphere, recording the corresponding data.

In-situ infrared (In-situ DRIFTs) spectroscopy was used to study the adsorption of the adsorbent samples. Infrared spectra were recorded using a Nicolet iS50R (in-situ DRIFT, USA) spectrometer and MCT detector, with an extended KBr beam splitter. Spectra were recorded in the range of 700-3200 cm^{-1}, with a resolution of 4 cm^{-1}, and 32 scans were collected for each spectrum. The specific steps were: (1) The adsorbent sample was placed in the in-situ reaction cell, heated to 300 °C, and purged with nitrogen for 3 hours to remove physically adsorbed water and other impurities. (2) After cooling to 30 °C, infrared spectral data collection began, while 50 ml/min of 500 ppm toluene was introduced into the in-situ reaction cell for 1 hour.

Density Functional Theory (DFT) calculations

Density Functional Theory (DFT) calculations were conducted to assess the adsorption energies of water and toluene on molecular sieves. The Sorption and Forcite modules within the Material Studio (MS) software suite were utilized for

Monte Carlo (MC) simulations. The DFT calculations were performed using the Vienna Abinitio Simulation Package (VASP). These computations were executed within the generalized gradient approximation (GGA) framework, employing the Perdew-Burke-Ernzerhof (PBE) functional. The Projector Augmented Wave (PAW) potential was selected to represent the ionic cores, while the valence electrons were treated with a plane wave basis set, with a kinetic energy cutoff of 520 eV. The Gaussian smearing method was applied, with a width of 0.05 eV, permitting partial occupation of the Kohn-Sham states. Self-consistency in the electron energy was achieved when the energy change was below 10^{-5} eV. Geometric optimization was deemed complete when the energy change was less than 0.05 $eV\cdot Å^{-1}$. The integration over the Brillouin zone was carried out using a 2×2×1 Monkhorst-Pack k-point mesh. The adsorption energy (Eads) was determined using the formula Eads= Ead/sub-Ead-Esub, where Ead/sub is the total energy of the optimized adsorbent/substrate system, Ead is the energy of the adsorbent within the system, and Esub is the energy of the pristine substrate.

X-ray fluorescence spectroscopy (XRD)

Fig. S1 illustrated the X-ray diffraction (XRD) patterns of ZSM-5 molecular sieve both before and after liquid-phase silanization modification. The XRD patterns revealed that the diffraction peaks of the pristine ZSM-5 and its modified counterpart were essentially identical, with no discernible impurity peaks present. The principal diffraction peaks were positioned at 2θ values of 7.81°, 8.82°, 23.03°, 23.78°, and 24.31°, which corresponded to the (101), (200), (501), (151), and (303) crystallographic planes, respectively. This consistency in peak positions suggested that the liquid-phase silanization process did not alter the molecular sieve's crystal structure. It could be inferred that the modification preserved the integrity of the molecular sieve's fundamental framework and that there was no significant alteration in the interlayer spacing of the sieve's structure.

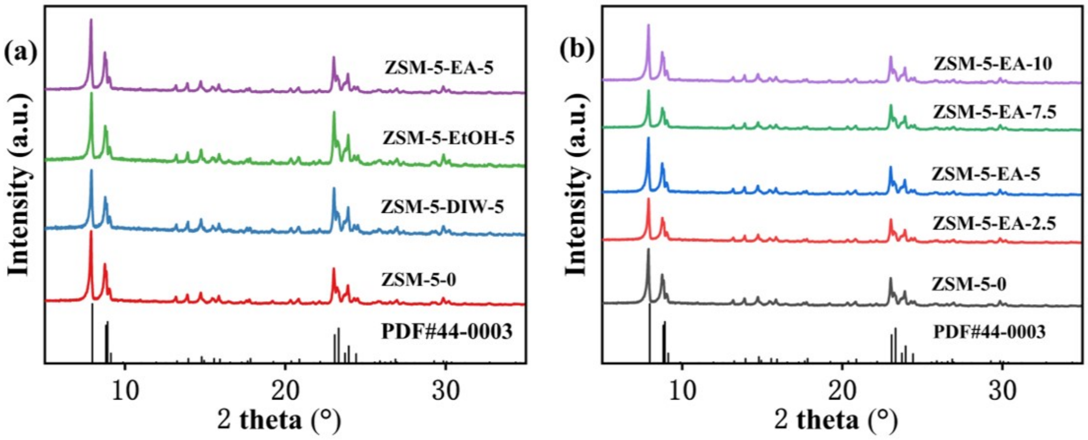

Fig. S1 XRD pattern of ZSM-5 molecular sieve before and after silanization

Fourier Transform Infrared Spectroscopy (FTIR)

All samples exhibited strong absorption at 450 cm^{-1}, 550 cm^{-1}, 790 cm^{-1}, 1095 cm^{-1}, and 1220 cm^{-1}. The emergence of these characteristic peaks confirmed that the samples synthesized in this study were ZSM-5 molecular sieves with an MFI structure. The vibrational absorption peak at 450 cm^{-1} was associated with the bending vibration of T-O (T = Si, Al) in the framework. The peaks at 790 cm^{-1} and 1095 cm^{-1} were due to the asymmetric stretching vibration of Si-O-Si, a typical feature of silicate materials. The peak at 550 cm^{-1} was a characteristic vibrational absorption peak of the double five-membered rings in the MFI structure. The peak at 1220 cm^{-1} was caused by the asymmetric stretching vibration of the Si-O tetrahedra, a feature often found in ZSM-5 zeolites or mordenite materials with a high silicon content. Additionally, the absorption peak at 1640 cm^{-1} was due to the free -OH peaks of lattice water and adsorbed water, with the peak width primarily influenced by intermolecular hydrogen bonding interactions.

Thermal stability (TG-DTG)

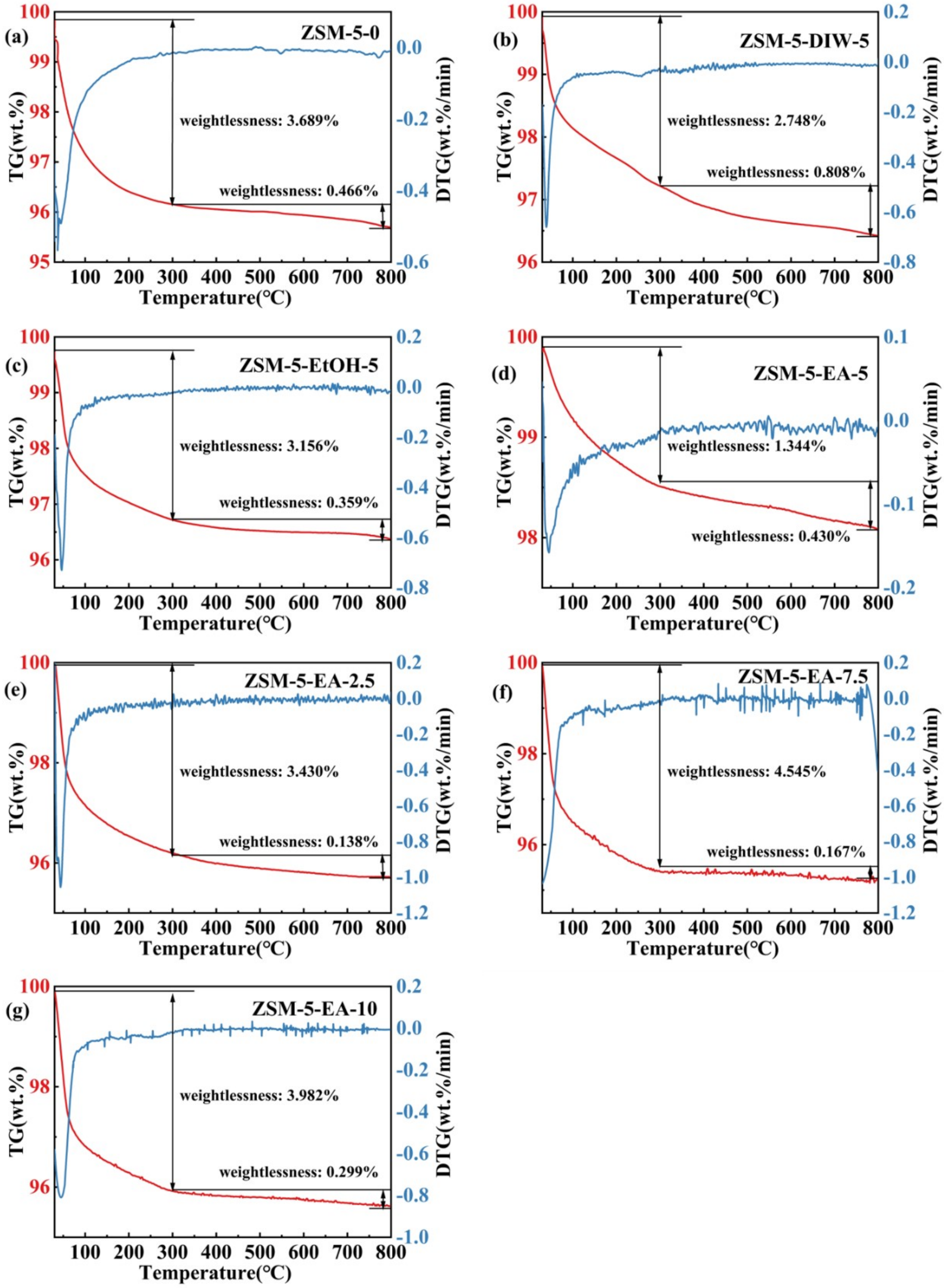

Fig. S2 Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis of ZSM-5 zeolite before and after modification

DFT calculation

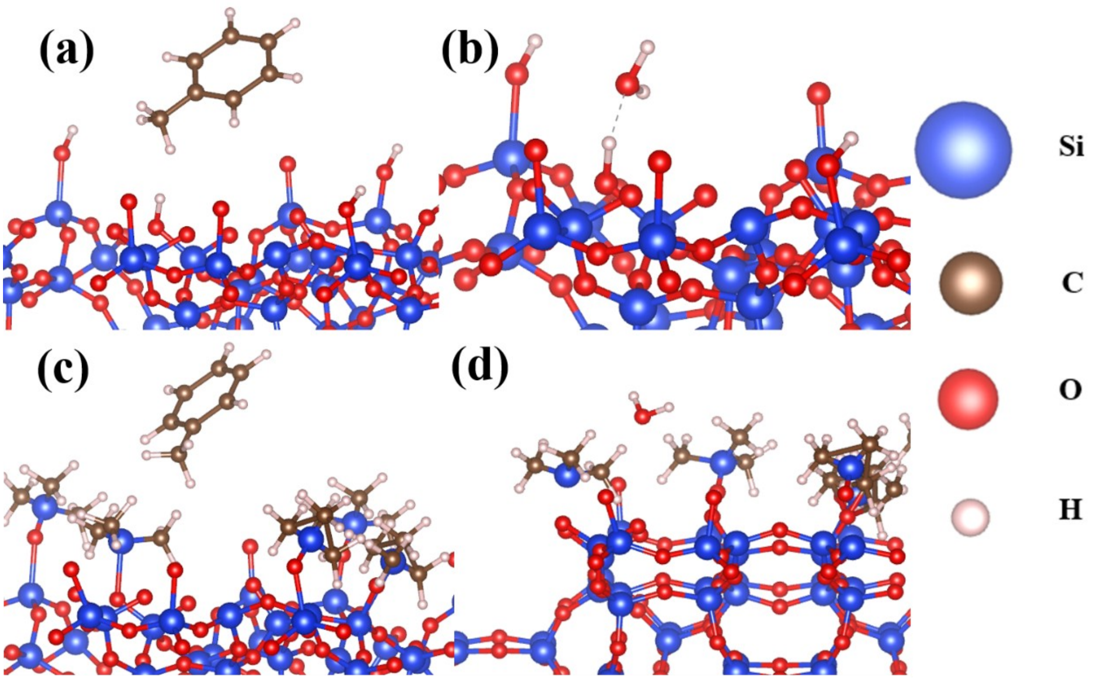

Fig. S3 Adsorption configuration of ZSM-5 zeolite for toluene and water before and after modification

(a) Adsorption configuration of ZSM-5-0 toluene, (b) Adsorption configuration of ZSM-5 H_2O, (c) Adsorption configuration of ZSM-5-EA-5 toluene, (d) Adsorption configuration of ZSM-5-EA-5 H_2O