

## Calculation method

DFT calculations were performed using the DMOL<sub>3</sub> module in Materials Studio 2017 software, employing the hyper generalized approximate gradient (m-GGA) with M60-L for all atoms [31]. The m-GGA density functional offered thermodynamic, kinetic, non-covalent interaction, bond length, reaction energy barrier, and vibrational frequency advantages. We adopted dual-value polarization basis set polarization function to consider electron polarization effects. All electronic calculations were performed on the complex domain with unrestricted system spin state, i.e., SCF =  $1.0 \times 10^{-5}$ , maximum SCF cycles = 800, and maximum iterations = 800.

We used a full LST/QST to search for transition states and hence determine the activation energy for a specific path. Only one imaginary frequency corresponds to the expected atomic motion in each transition structure. Convergence thresholds for energy, gradient, and displacement were  $2.0 \times 10^{-5}$  Ha, 0.004 Ha/Å, and 0.005 Å, respectively. Eyring [32] proposed the transition state theory for chemical reactions due to elementary reaction ( $E_a$ ) activation energy could be expressed as:

$$\Delta E = E(P) - EI \quad (1)$$

$$E_a = E(TS) - EI \quad (2)$$

Where EI, E(TS), and E(P) are electronic ground state energies for the reactant, transition, and product state, respectively. All energies were corrected by zero-point vibrational energy and Gibbs free energy.

## Material characterization

Analyses were performed using X-ray diffraction (XRD), Shimadzu Corporation XRD 6000, Using Cu target (K $\alpha$  ray,  $\lambda = 1.4518$  Å), Ni filter, working condition of 40 kV, working current of 30 mA, scanning within  $2\theta = 10^\circ \sim 80^\circ$ , and scanning speed of  $20^\circ/\text{min}$ ; Fourier Transform Infrared Spectroscopy (FT-IR), Thermo Corporation of America Nicolet-380, Using KBr as the background, according to the ratio of catalyst to KBr of 1:200, the tablet was pressed at a pressure of 1.75 Mpa for 1 min, and the sample was scanned after the tablet was pressed.; Temperature-programmed desorption

analysis of  $\text{NH}_3$  ( $\text{NH}_3$ -TPD), American Micromeritics Auto Chem II 2920, The samples were replaced in nitrogen at 200 °C for 1 h, and then  $\text{NH}_3$  was used for adsorption. Nitrogen gas was introduced into the reactor for 20 min, and then the TPD curve was recorded by increasing the temperature from 30 °C to 700 °C at a rate of 10 °C/min; Pyridine adsorption infrared spectroscopy (Py-IR), Germany Bruker Optics Tensor 27, The samples were pretreated at high temperature and high vacuum for 2 hours before pyridine adsorption, and then vacuum heated in situ; Scanning Electron Microscopy Analysis (SEM), Nippon Electronics Co., Ltd. JSM-7900F, The sample powders were modified by gold spraying and then characterized by scanning electron microscopy operating at 1.0 kV; Specific surface area and pore volume and pore size analysis (BET), American Micromeritics ASAP2020, The sample was first evacuated, and then high-purity nitrogen was used as the adsorbate, and the liquid nitrogen was adsorbed at low temperature to determine the specific surface area and pore volume of the sample; Contact angle (CA), German Dataphysics JY-82B Kruss DSA, The samples were compressed to a thickness of 2 mm and placed in a 1 cm disc (OD) and characterization determinations were made using optical contact angle measurements and ink droplet profiles; Thermogravimetric-Differential Thermal Analysis (TGA), Germany Netzsch STA 449C, Weigh 8 mg of sample, use high-purity nitrogen as protective gas, increase the temperature from 25 °C to 800 °C at a heating rate of 10 °C/min, and record the weight loss of the sample; X-ray photoelectron spectroscopy (XPS), Thermo Corporation of America Scientific K-Alpha to confirm successful acid treatment and OTS grafting and subsequent effects. We subsequently evaluated HCl-OTS-HZSM-5 effects for cyclohexene hydration under various conditions.

## Table information

Table. S1 Number of Mulliken electron layouts and distances between atoms before and after cyclohexene adsorption

Cyclohexene atomic distribution	Mulliken electron layout number (e)		Cyclohexene atomic distribution	Atomic distance (Å)	
	Before adsorption	After adsorption		Before adsorption	After adsorption
	C <sub>1</sub>	-0.132		-0.089	C <sub>1</sub> -C <sub>2</sub>
C <sub>2</sub>	-0.131	-0.293	C <sub>2</sub> -C <sub>3</sub>	1.494	1.504
C <sub>3</sub>	-0.385	-0.54	C <sub>3</sub> -C <sub>4</sub>	1.523	1.502
C <sub>4</sub>	-0.348	-0.453	C <sub>4</sub> -C <sub>5</sub>	1.520	1.523
C <sub>5</sub>	-0.347	-0.503	C <sub>5</sub> -C <sub>6</sub>	1.523	1.484
C <sub>6</sub>	-0.385	-0.528	C <sub>6</sub> -C <sub>1</sub>	1.494	1.333
H <sub>C1</sub>	0.158	0.220	C <sub>1</sub> -H	1.088	1.079
H <sub>C2</sub>	0.158	0.274	C <sub>2</sub> -H	1.088	1.099
H <sub>C31</sub>	0.181	0.234	C <sub>3</sub> -H	1.097	1.083
H <sub>C32</sub>	0.181	0.259	C <sub>4</sub> -H	1.098	1.090
H <sub>C41</sub>	0.172	0.213	C <sub>5</sub> -H	1.095	1.087
H <sub>C42</sub>	0.172	0.258	C <sub>6</sub> -H	1.101	1.079
H <sub>C51</sub>	0.172	0.239			
H <sub>C52</sub>	0.172	0.247			
H <sub>C61</sub>	0.181	0.247			
H <sub>C62</sub>	0.181	0.300			
SUM	0	0.085			

Table. S2 The number of Mulliken electron layouts and the distance between atoms before and after the adsorption of 34T-HZSM-5

34T-HZSM-5 atomic distribution	Mulliken electron layout number (e)		34T-HZSM- 5 atomic distribution	Atomic distance (Å)	
	Before adsorption	After adsorption		Before adsorption	After adsorption
	H	0.568		0.616	O <sub>A</sub> -H
O <sub>A</sub>	-1.192	-1.237	Al-O <sub>A</sub>	1.828	1.816
			Si-O <sub>A</sub>	1.673	1.670