Supporting Information

Alkyl-Chain Grafted 13X Zeolite for Steady CO_2 Capture from Humid Flue Gas

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Experimental

Materials

Trimethoxy(propyl)silane ($C_6H_{16}O_3Si$,CAS: 1067-25-0, 98%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Hexyltrimethoxysilane ($C_9H_{22}O_3Si$,CAS: 3069-19-0, 98%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Dodecyltrimethoxysilane($C_{15}H_{34}O_3Si$,CAS: 221-332-4, 97%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Toluene(C_7H_8 ,CAS: 108-88-3, specification: pharmaceutical grade, 99.5%) was purchased from Sinopharm Chemical Reagent Co.,Ltd. Commercial 13X zeolite(Si/Al = 1.24) purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Ethanol(C_2H_6O ,CAS: 64-17-5, specification: pharmaceutical grade, 99.5%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd.

Synthesis

1. Preparation of 13X-3C

Commercial 13X zeolite was dried in a tube furnace at 300°C under vacuum for 6 hours. Then, 2 g of the dried 13X zeolite was added to 100 ml of toluene solution and ultrasonically dispersed for 30 minutes. Subsequently, 0.838 g of trimethoxy(propyl)silane was added and stirred at room temperature under a sealed condition for 12 hours. After the reaction, the product was separated by centrifugation and washed alternately with anhydrous ethanol for 4 times. Finally, the product was dried at 80°C overnight.

2. Preparation of 13X-6C

Commercial 13X zeolite was dried in a tube furnace at 300°C under vacuum for 6 hours. Then, 2 g of the dried 13X zeolite was added to 100 ml of toluene solution and ultrasonically dispersed for 30 minutes. Subsequently, 1.053 g of hexyltrimethoxysilane was added and stirred at room temperature under a sealed condition for 12 hours. After the reaction, the product was separated by centrifugation and washed alternately with anhydrous ethanol for 4 times.

3. Preparation of 13X-12C

Commercial 13X zeolite was dried in a tube furnace at 300°C under vacuum for 6 hours. Then, 2 g of the dried 13X zeolite was added to 100 ml of toluene solution and ultrasonically dispersed for 30 minutes. Subsequently, 1.768 g of dodecyltrimethoxysilane was added and stirred at room temperature under a sealed condition for 12 hours. After the reaction, the product was separated by centrifugation and washed alternately with anhydrous ethanol for 4 times

Materials characterization

X-ray diffraction (XRD) were performed in a Bruker D8 Advance model X-ray diffractometer measurement with CuKα (λ=1.5406 Å)radiations. Scanning electron microscopy (SEM) images were employed with Hitachi JSM-7001F electron microscopes. Solid-state 13C NMR spectra were acquired using a AVANCE IIITM 600 MHz instrument. Surface area measurement was conducted in instrument ASAP2020C. The volume and surface area of the micropores were derived from the adsorption isotherms using the BJH method. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. The contact angle of water droplets on the solid surface were measured on an Optical Contact Angle Meter (SL200KB).

Adsorption measurements

Simulation test of industrial flue gas adsorption

The evaluation device is shown in Fig. S1. The test conditions are as follows: the temperature is 41℃, the composition of the mixed gas is 7.2% H_2O, 13.92% CO_2, and 78.88% N_2, and the total gas velocity is 30 sccm. The adsorbent is filled in a quartz tube with a volume of 3 mm in radius and 20 mm in height, with a filling height of 7 mm. The size of the adsorbent particles is 40 to 60 mesh. The activation conditions before the test are 250℃ and vacuum for 6 hours.

Humidity regulation test

The composition of the mixed gas is H_2O:CO_2:N_2 = x:0.15(100-x):0.85(100-x), with x ranging from 0 to 7.2. The test temperature is 41℃, and the total gas velocity is 30 sccm. The water content in the mixed gas is controlled by adjusting the flow rates of the two nitrogen branches. The activation conditions before the test are 250℃ and vacuum for 6 hours.

Static water vapor adsorption

The test results are shown in Figure Fig.S12. The test conditions are as follows: temperature 41℃, 100% humidity; pressure changes gradually from 50 pa to 7700 pa.

Cyclic stability test

The test temperature was set at 41℃. The composition of the mixed gas was 7.2% H_2O, 13.92% CO_2 and 78.88% N_2. The total gas velocity was 30 sccm. The activation conditions for the cyclic test were 200℃ and vacuum for 1 hour.

Formula for calculating adsorption capacity

$$Q_{CO_2 Adsorption} = q \times C_{CO_2} \times \Delta T - \int_0^t q \times C_t dt$$

q :Total gas flow rate (sccm)

C_{CO_2} : CO_2 inflow concentration (%)

C_t : CO_2 effluent concentration at time t (%)

ΔT :Adsorption test time (s)

Water vapor adsorption kinetics test

The test temperature is 41℃ and the radial diffusion model with constant diffusion coefficient[1] is adopted.

By Fick's second law $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_{eff}\frac{\partial C}{\partial x}\right) = D_{eff}\nabla^2 C$ * MERGEFORMAT (1.1)In spherical coordinates

$$\nabla^2 = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad \text{* MERGEFORMAT (1.2)}$$

Radial diffusion C is independent of θ and ϕ

$$\frac{\partial C}{\partial t} = D_{eff}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = D_{eff}\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \text{* MERGEFORMAT (1.3)}$$

On putting u=Cr, $\frac{\partial u}{\partial t} = D_{eff}\frac{\partial^2 u}{\partial r^2}$ * MERGEFORMAT (1.4)

Laplace transforms at both ends $D_{eff}\frac{\partial^2 \bar{u}}{\partial r^2} = p\bar{u} - rC_1$ * MERGEFORMAT (1.5)

Apply boundary conditions $\bar{u} = a\left(C_0 - C_1\right)\frac{\sinh qr}{p\sinh qa} + \frac{rC_1}{p}$ * MERGEFORMAT (1.6)

Two representations of the Laplace inverse transform

$$L^{-1}\left\{\frac{\sinh qr}{p\sinh qa}\right\} = \frac{r}{a} + \frac{2}{\pi}\sum_{n=1}\frac{(-1)^n}{n}\sin\frac{n\pi r}{a}\exp\left(-\frac{D_{eff}\pi n^2 t}{a^2}\right) \quad \text{* MERGEFORMAT (1.7)}$$

and $$L^{-1}\{\frac{\sinh qr}{p\sinh qa}\}=\sum_{0}^{\infty}erfc(\frac{a(2n+1)-r}{2\sqrt{D_{eff}t}})-\sum_{0}^{\infty}erfc(\frac{a(2n+1)+r}{2\sqrt{D_{eff}t}})$$ * *MERGEFORMAT (1.8)*

Trigonometric function solution $$\frac{M_t}{M_\infty}=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D_{eff}\pi n^2 t}{a^2}\right)$$ * *MERGEFORMAT (1.9)*

Error function solution $$\frac{M_t}{M_\infty}=\frac{6\sqrt{D_{eff}t}}{a\sqrt{\pi}}+\frac{12}{a}\sqrt{D_{eff}t}\sum_{1}^{\infty}ierfc(\frac{an}{\sqrt{D_{eff}t}})-\frac{3Dt}{a^2}$$ * *MERGEFORMAT (1.10)*

The two forms of solutions mentioned above yield the same numerical results in the case of high n, and the sampling limitations also decrease. The above-mentioned diffusion model(1.10) was fitted using the trust region reflection method from the SciPy library (Python3.7). Using the constraints that n is less than 10,000 or the sum of consecutive terms is less than 1×e-10 to construct the n-th order consecutive sum terms in the model; attempt to fit the parameters M_∞ and D after normalization.

$$M_t=k_w t^{1/2}+b$$ * *MERGEFORMAT (1.11)*

The intraparticle diffusion model [2] is adopted to describe the adsorption kinetics in the later stage of adsorption, and the parameters k_w (mg/(g·s$^{1/2}$))and b (mg/g) are linearly fitted using the least squares method.

Models and methods of simulation

13X is a common zeolite of faujasite(FAU) with a silicon-aluminum ratio of 1.1 to 1.5. In this simulation, the faujasite structure proposed by Olson was adopted[3]. In the FAU structure with alternating silicon and aluminum, 10 silicon atoms randomly replace the positions of aluminum to meet the Si/Al requirement of 13X and Lowenstein's rule. The Na^+ was subsequently inserted in the subsequent molecular simulation. The unit cell of FAU is a cube with lattice parameter of 25.028 Å, and its chemical formula is $Na_{86}Al_{86}Si_{106}O_{384}$.

The interaction between the adsorbent and the adsorbate is described as the combined effect of the Lennard-Jones potential and the Coulomb electrostatic interaction. The L-J potential parameters and atomic charges of the FAU structure are acquired from Sofia's work. [4] Research has shown that the parameters of Sofia can better predict the diffusion of water in FAU. [5] The substituent alkyl groups in the pores are was represented by the TraPPE force field [6] and the water molecule was described by the TIP5P-Ew model[7]. The Lorentz-

Berthelot combining rules ere employed to calculate the cross interactions. All the potentials are truncated at 12Å and tail correction is applied; The Ewald method is used to calculate the electrostatic contributions, with the calculation accuracy set at 1E-6.

The alkyl-modified 13X-healy was optimized by the CASTEP module of Material Studio software. After optimization, the position of the alkyl group was fixed. The structure in primitive unit cell is shown in the figure.

The adsorption and equilibrium diffusion of water vapor through 13X and 13X-heaxly were simulated by grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) methods. The framework was assumed to be rigid, and all GCMC and MD simulations used the RASPA package.[8] The final configuration obtained by GCMC simulation was used as the initial configuration for NVT-MD simulation to investigate gas diffusion. The MD simulation was run for 250,000 cycles. The first 50,000 cycles were used for cycle balance, and the last 200,000 cycles were used for overall averaging (1ns). Each cycle included n trials of molecular movement (n: the number of adsorbed molecules), including translation, rotation and regrowth.

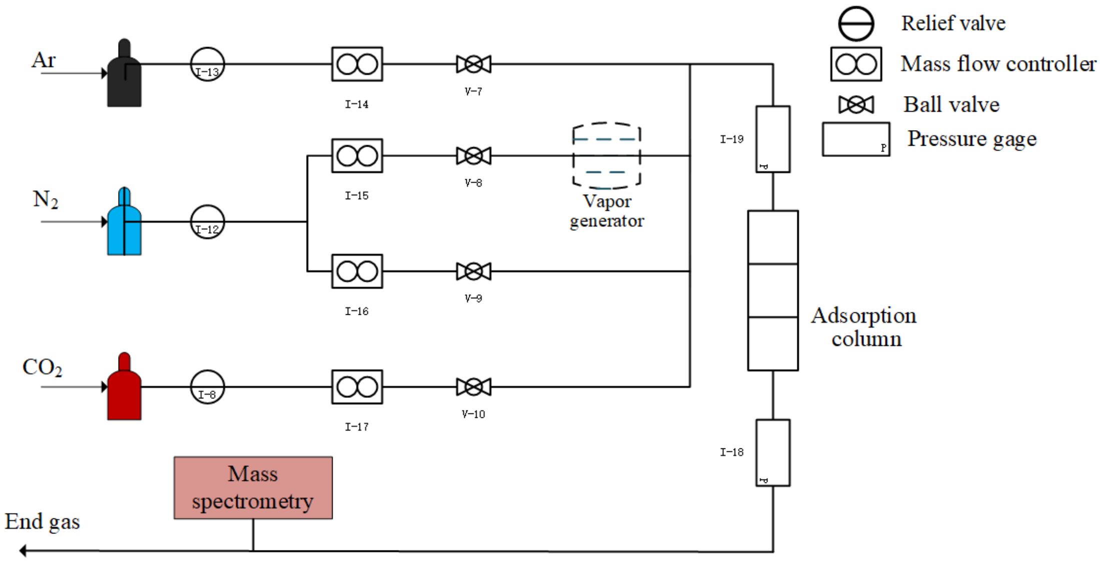

Fig.S 1 Diagram of adsorption evaluation device

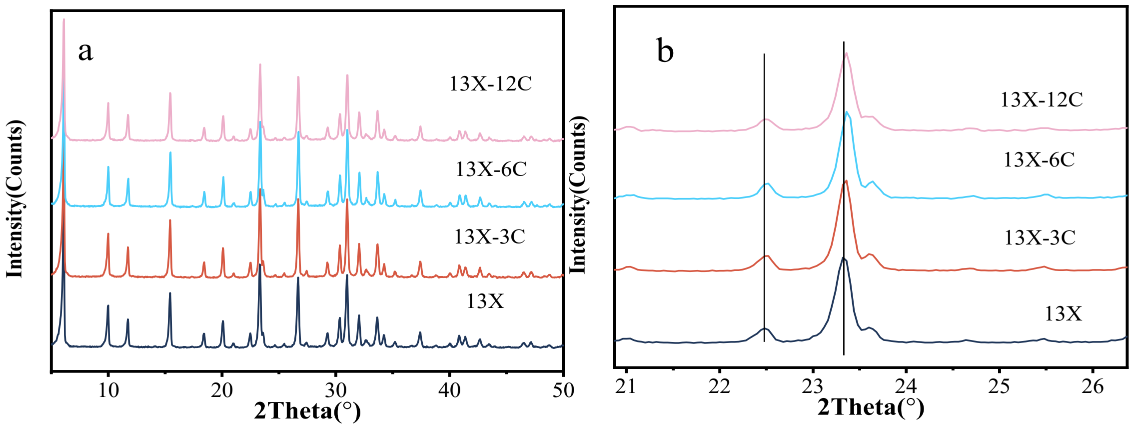

Fig.S 2 XRD patterns All the ample have typical peaks assigned to the FAU zeolite structure.

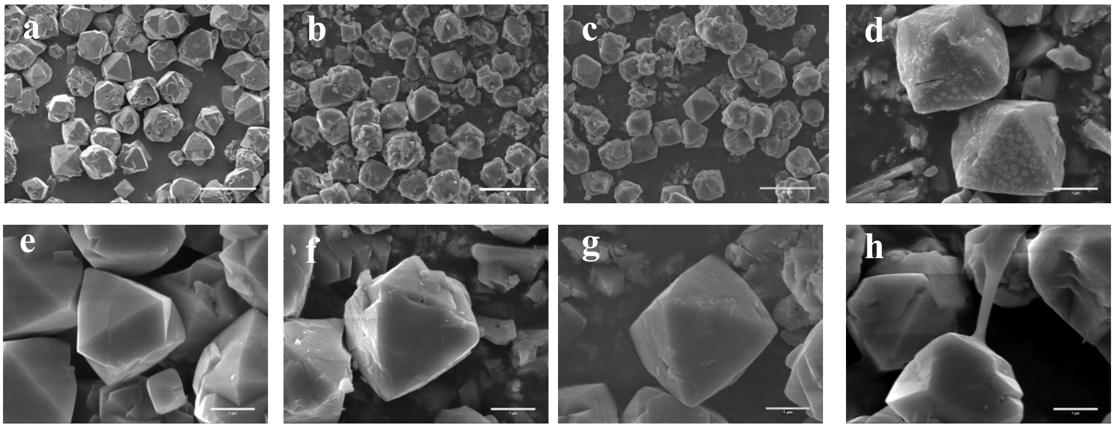

Fig.S 3 SEM image a,e)13X. b,f) 13X-3C. c,g) 13X-6C. d,h) 13X-12C.

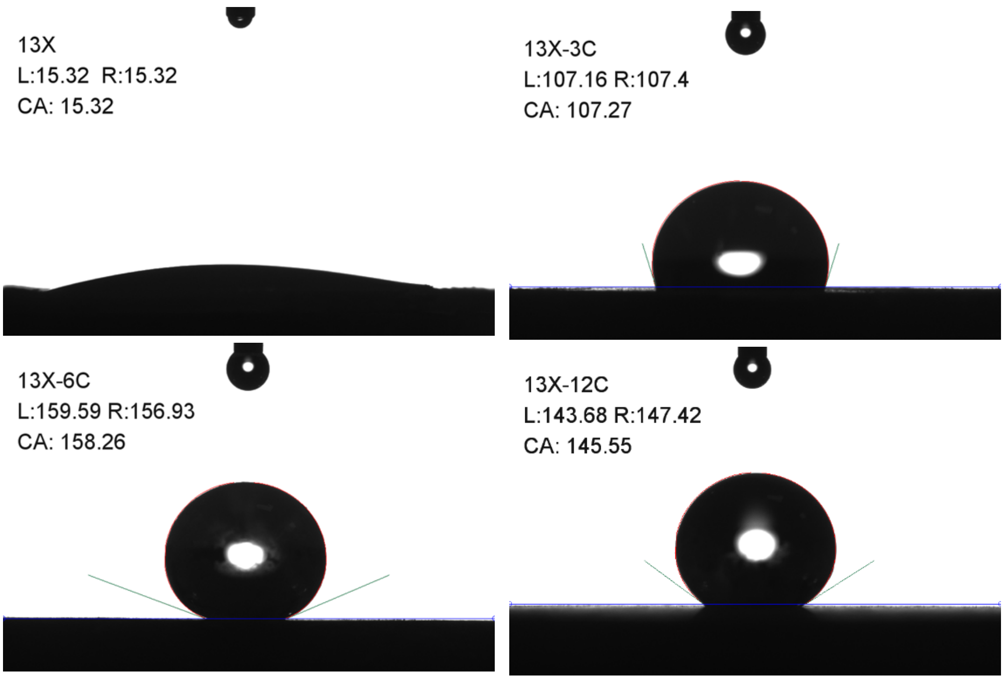

Fig.S 4 Contact Angle of sample-

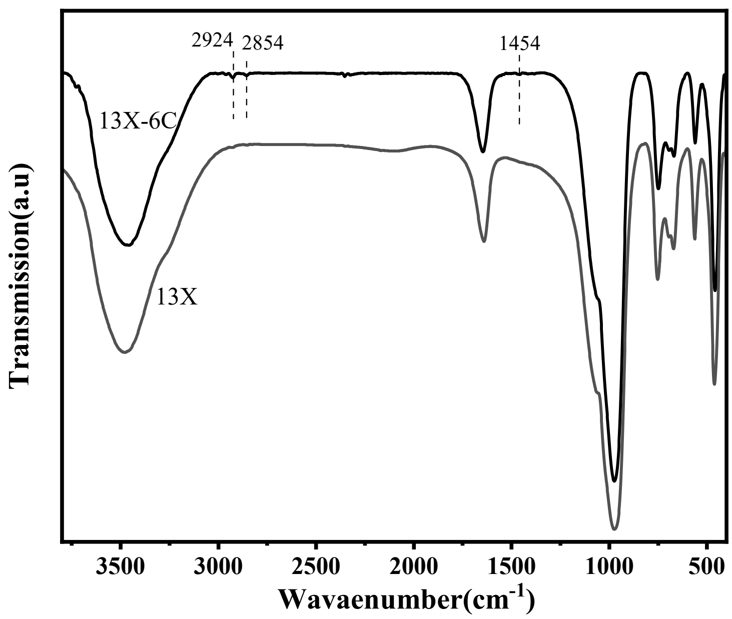

Fig.S 5 FT-TR spectra of 13X and 13X-6C

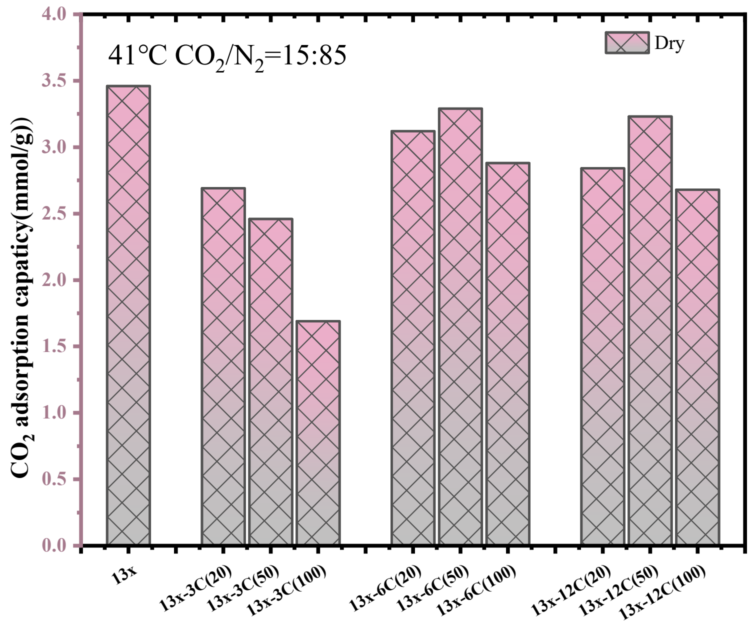

Fig.S 6 The influence of silicon oxide addition amount on the adsorption performance of 13X; (x) indicates that the concentration of the grafting agent during the reaction process is x mmol/L.

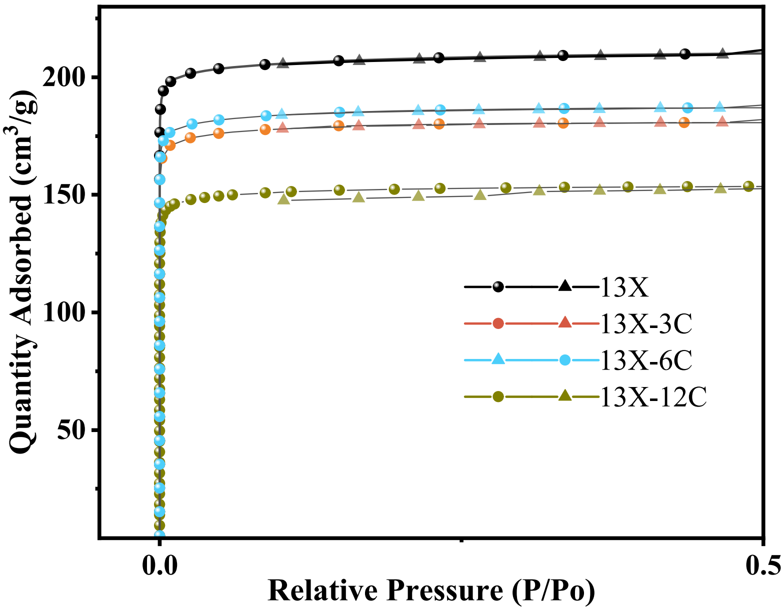

Fig.S 7 N_2 sorption isotherms of 13X zeolite and grafting zeolite(77K)

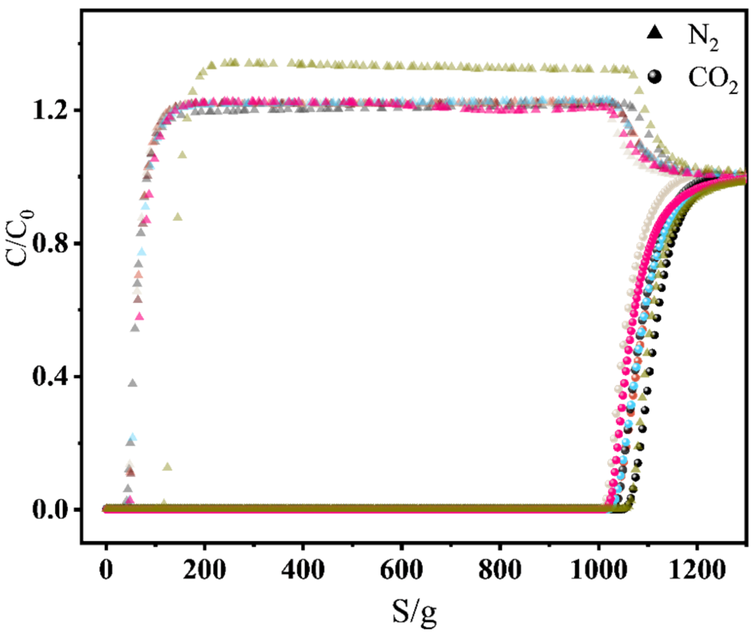

Fig.S 8 Recyclability under $CO_2/N_2/H_2O$(13.89/78.88/7.2, v/v/v) column breakthrough tests over the 13X-6C.

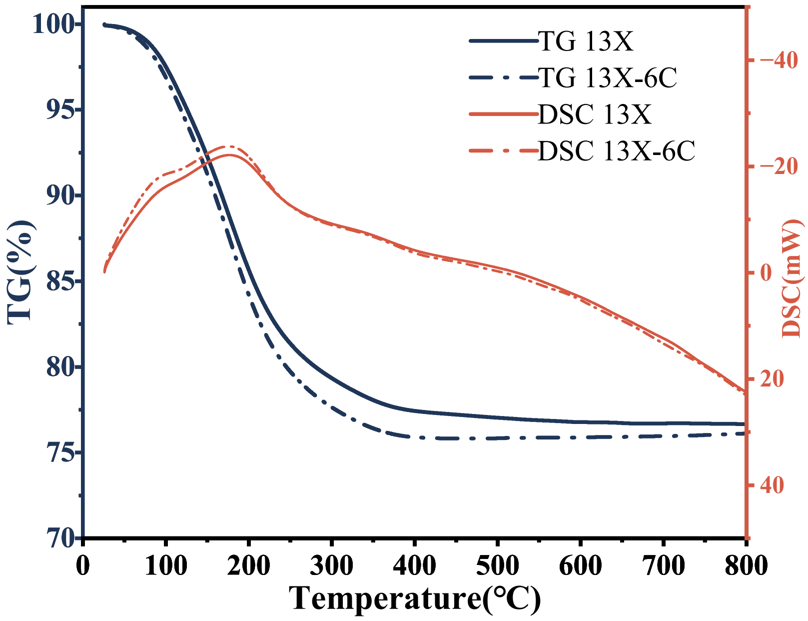

Fig.S 9 TG-DSC of 13X and 13X-6C under Ar atmosphere

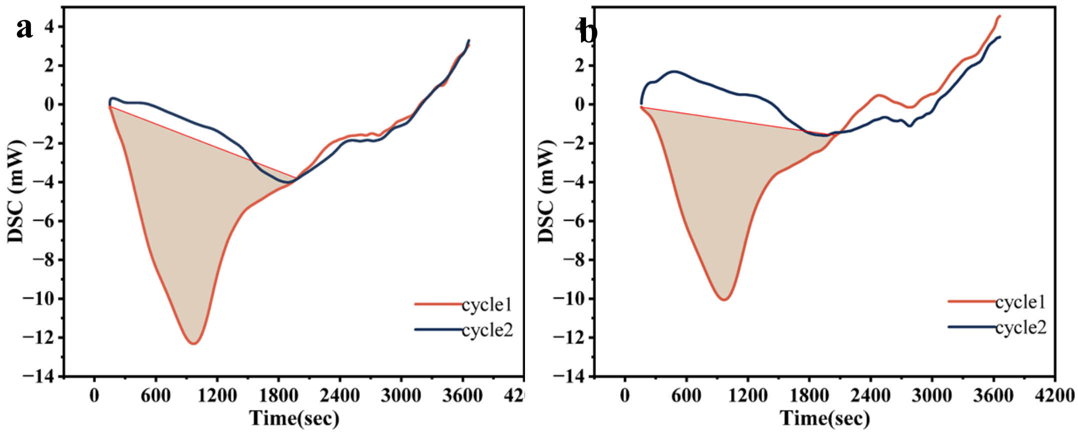

Fig.S 10 DSC thermograms of the heating segments for a) 13X and b)13X-6C over two cycles . Prior to cycle 1, the sample was saturated with adsorbed H_2O in a 7.7% aqueous atmosphere. The Q desorption heat of water is divided by the integral area of DSC by the mass of dehydration weight in the temperature program of 10℃/min. The Q desorption heat of 13X and 13X-hexyl are 62.05kJ/mol and 60.427kJ/mol, respectively.

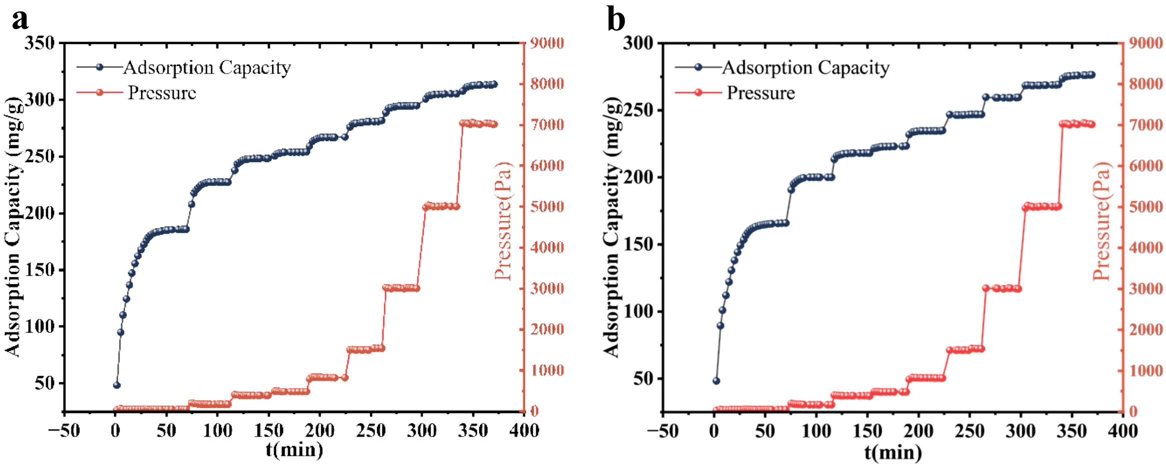

Fig.S 11 Kinetic sorption of H_2O at 298 K on a) 13X and b) 13X-6C.

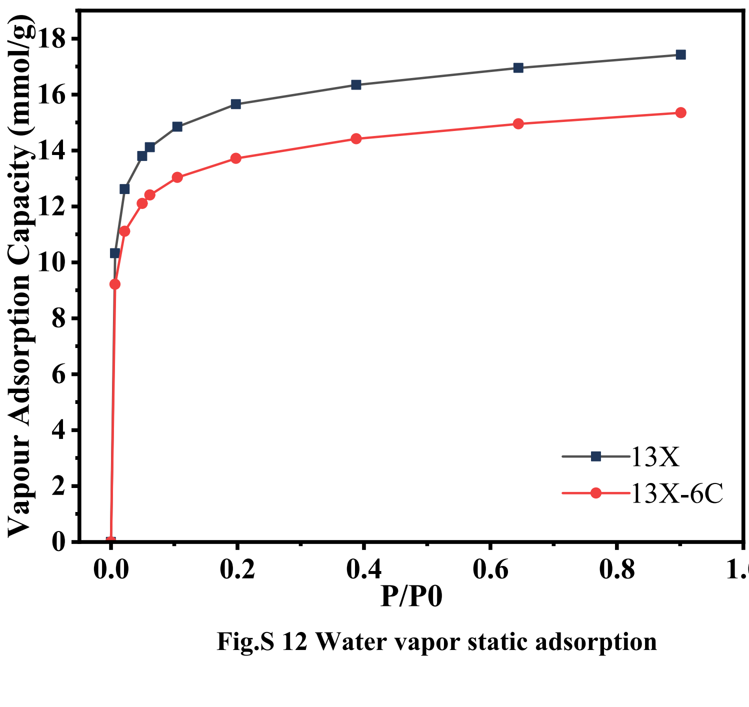

Fig.S 12 Water vapor static adsorption

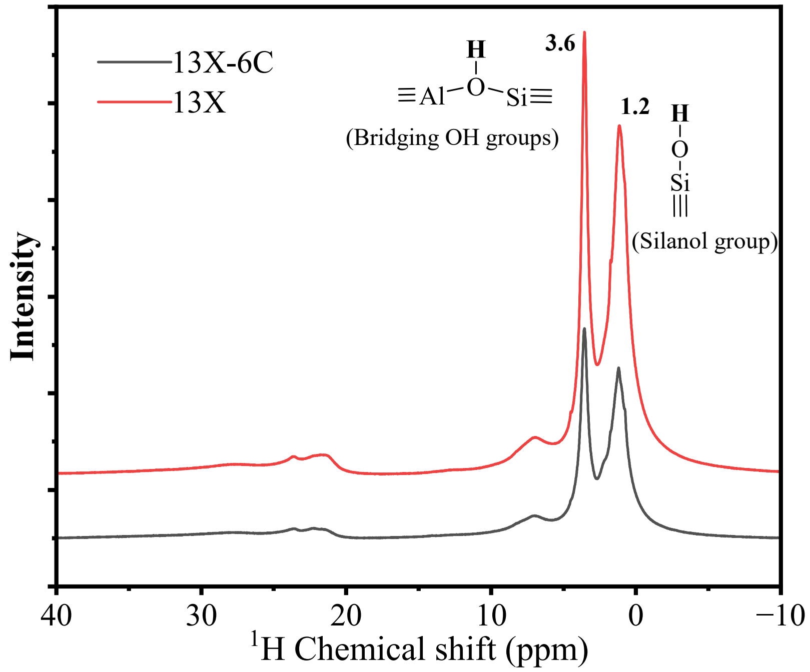

Fig.S 13 The solid-state 1H NMR spectra of 13X and 13X-6C

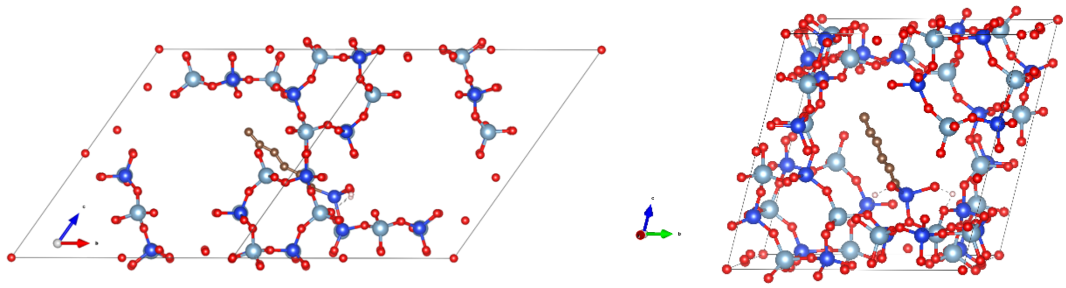

Fig.S 14 Structural optimization of the modified hexyl groups in the 13X primitive cell (two interconnected FAU zeolite cages). Blue: Si; Grey-blue: Al; Red: O; Brown: C; Pink: H

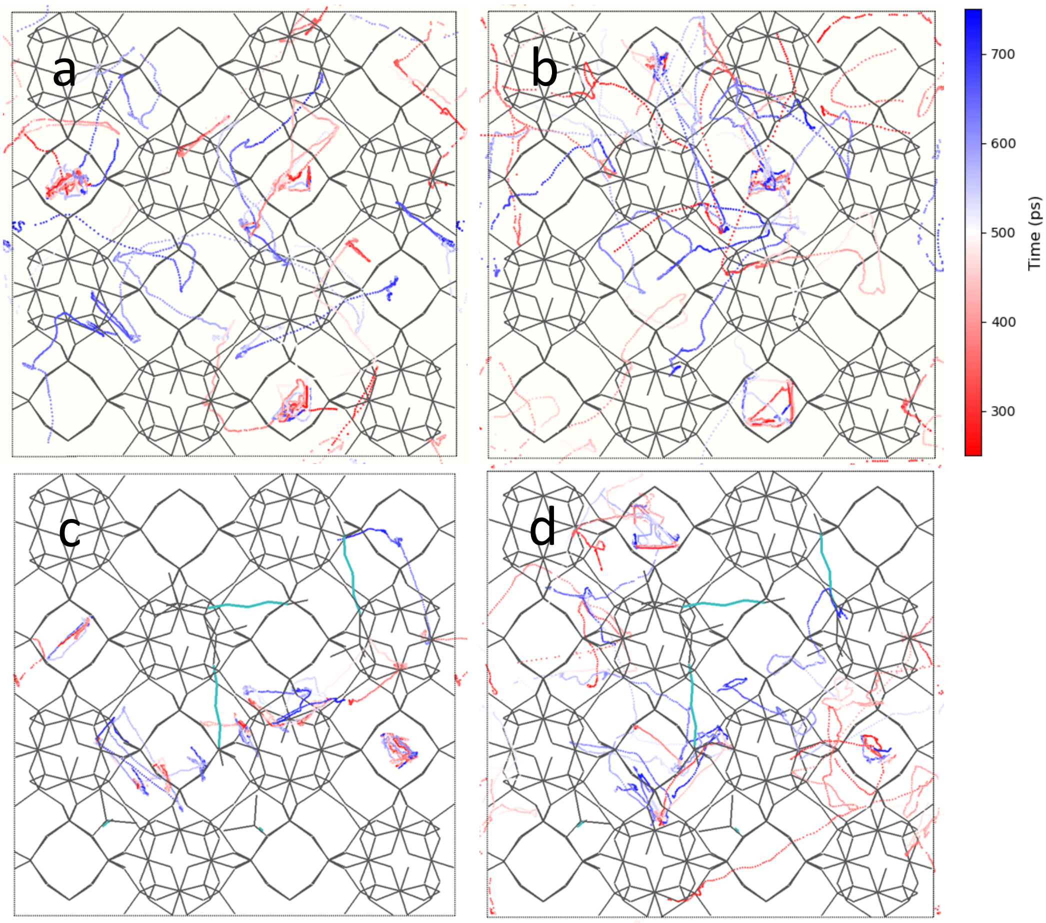

Fig.S 15 MD molecular simulation of water diffusion in 13X(a,b) and 13X-6C(c,d) under low pressure(a,c) and high pressure(b,d). The blue and red gradient lines represent the movement trajectories of water molecules in the randomly selected area; Grey: Zeolite framework; Blue-green: Modified alkyl groups

Tab 1 Mutual diffusion and self-diffusion of water molecules

	Mutual diffusion		Self-diffusion	
	0→50.7Pa	384.5→480Pa	50Pa	500Pa
13X cm^2/s	6.6339×10^{-13}	19.366×10^{-13}	6.022×10^{-9}	1.528×10^{-8}
13X-6Ccm^2/s	1.2771×10^{-13}	20.191×10^{-13}	2.840×10^{-9}	7.388×10^{-9}

Tab 2 Model fitting parameters

			0→50.7Pa			
	D($10^{-13}cm^2/s$)	M(mg/g)	R^2	K(mg/(g·$s^{1/2}$))	b(mg/g)	R^2
13X	6.6339	217.93	0.9965	0.15206	176.41	0.9158
13X-6C	1.2771	249.54	0.9956	0.13488	109.39	0.2155
			384.5→480Pa			
	D($10^{-13}cm^2/s$)	M(mg/g)	R^2	K(mg/(g·$s^{1/2}$))	b(mg/g)	R^2
13X	19.366	5.96	0.9995			
13X-6C	20.191	2.608	0.9962			

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