

Supplemental information

Understanding the effect of H₂O on CO₂ adsorption capture :
Mechanism explanation, Quantitative approach and Application

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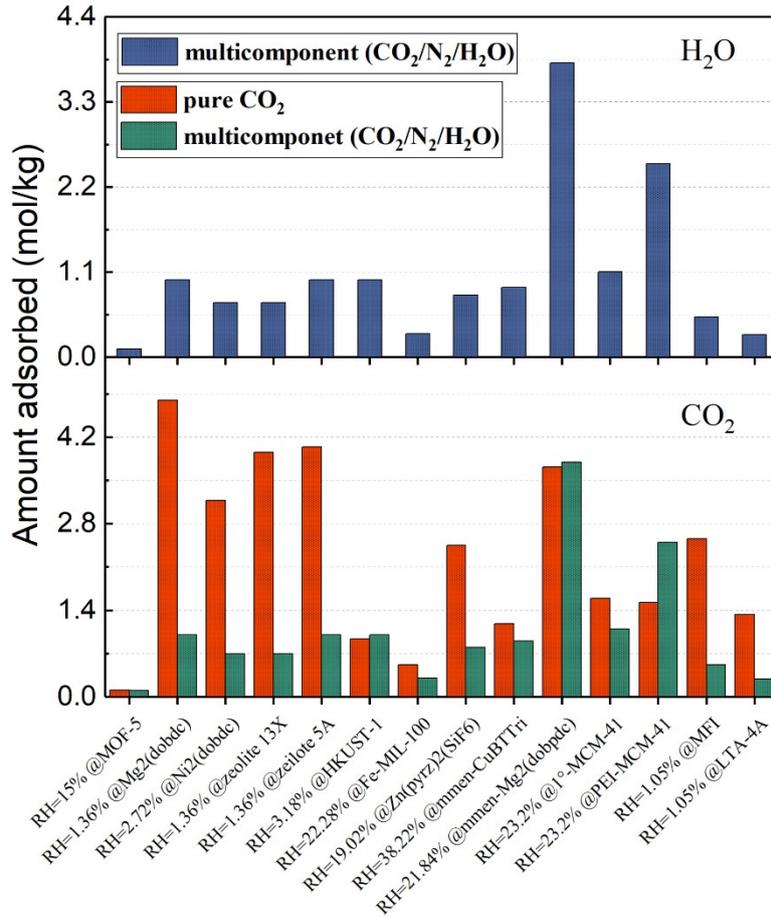


Fig.S1 A summary of multi-component adsorption measurements for CO₂, N₂ and H₂O multi-components, the adsorption experimental data from Jarad et al ^[9]. Equilibrium conditions represented by flue gas from coal-fired power plants. The blue bars represent the H₂O vapor adsorbed in the mixture. The red bars represent the amount of CO₂ adsorbed in the pure component. The green bars represent the amount of CO₂ adsorbed in the mixture at the same partial pressure as the pure component. The total pressure is 82.1-89 kPa. P_{CO₂} is 11.3-17.8 kPa, and the P_{H₂O} is 1-2.9 kPa. Adsorption temperature is 298-313 K. RH represents the relative humidity (P_{H₂O}/P_{sat, H₂O}).

1. adsorption entropy

To properly evaluate the adsorption entropy, it is important to remember that there are different degrees of freedom, each of which has its own contribution to the total entropy. An H₂O gas molecule has 3 translational, 3 rotational, and 3 vibrational degrees of freedom. An CO₂ molecule has 2 rotational and 4 vibrational degrees of freedom on top of 3 translations. After adsorption, the translational and rotational degrees of freedom of molecules are lost and replaced by the vibrational degrees of freedom, which essentially hinder the translational and rotational degrees of molecules. Therefore, the entropy change of adsorption phase is calculated by vibration entropy:

$$S_{vib} = Nk \left(\sum \frac{hv_i / kT}{e^{hv_i / kT} - 1} - \ln \left(1 - e^{-hv_i / kT} \right) \right)$$

2. Force field parameters used in this work.

Table S1 Force field parameters in this work.

	ϵ/k_b (K)	σ (Å)
C _{CO2} -C _{CO2}	29.933	2.745
C _{CO2} -O _{CO2}	56.640	2.880
O _{CO2} -C _{CO2}	85.617	3.017
C _{CO2} -O _{MFI}	37.595	3.511
O _{CO2} -O _{MFI}	78.980	3.237
O _{spce} -O _{spce}	78.197	3.1656
O _{spce} -O _{MFI}	85.152	3.723

Table S2 Charges

Atom	q (e-)
O _{CO2}	-0.32560
C _{CO2}	0.65120
Si	0.78598
Al	0.48598
O _{si}	-0.39299
O _{Al}	-0.41384

3. Adsorption isotherms for pure H₂O using SPC/E, TIP4P, TIP5P model.

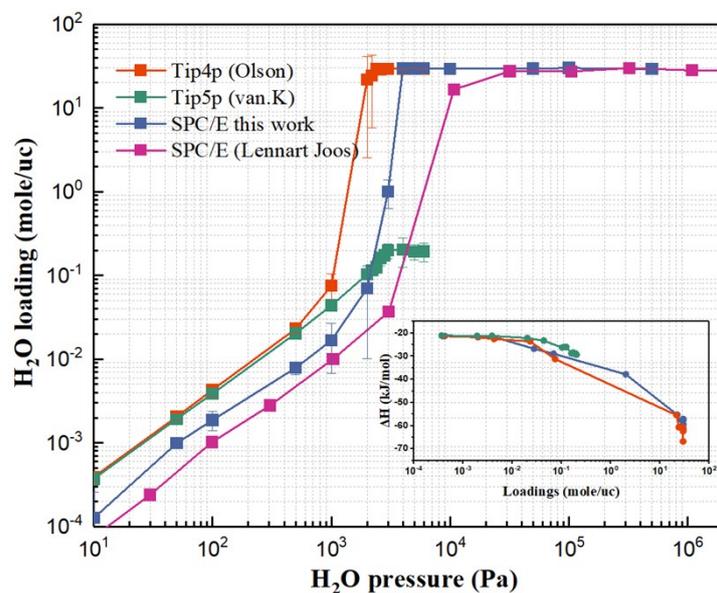


Fig. S2 Adsorption isotherm of H₂O under different water models

4. Fitting parameters for adsorption isotherms model in this work.

In order to obtain a working isotherm model for H₂O adsorption on MFI over a wide range of adsorbate pressures, the phenomena of monolayer, multilayer and capillary condensation should be considered carefully. The monolayer behavior is easy to account for by choosing an adsorption model that at low pressure reduces to the Langmuir isotherm. The prediction of multilayer behavior requires the model to have a built-in capability to account for the presence of successive adsorbate layers on top of each other. According to the current research on water adsorption, three common models were selected for fitting. It is found that the Sips model is more accurate to the water adsorption isotherm in all pressure ranges.

For H₂O:

1) Dual-sites Langmuir-Freundlich model (DSLFF)

$$N = A_1 \frac{B_1 \times P^{C_1}}{1 + B_1 \times P^{C_1}} + A_2 \frac{B_2 \times P^{C_2}}{1 + B_2 \times P^{C_2}}$$

N is molar loading of species i (mol/kg)

A is saturation capacity of species (mol/kg)

B is Langmuir constant (kPa⁻¹)

C is Freundlich constant

P is bulk gas phase pressure of species i (kPa)

Table S3

parameter	value		
	300 K	350 K	400 K
A ₁ (mol/kg)	5.04e-09	6.054e-09	7.487e-09
B ₁ (kPa ⁻¹)	0.03217	1.568e-10	4.769e-09
C ₁ (-)	1.078e-14	2.22e-14	4.525e-14
A ₂ (mol/kg)	5.14	4.99	4.913
B ₂ (kPa ⁻¹)	1.806e-14	3.783e-14	4.543e-14
C ₂ (-)	23.51	10.6	6.32
R ²	0.9933	0.9948	0.98
RMSE	0.2175	0.1684	0.3165

2) GAB:

$$\frac{q}{q_m} = \frac{C \cdot k \cdot p / p^{sat}}{(1 - k \cdot p / p^{sat}) \cdot (1 + (C - 1) \cdot k \cdot p / p^{sat})}$$

q_m is saturation capacity of species (mol/kg)

C, k is GAB constant

P_{sat} is the saturation pressure of species

Table S4

parameter	value		
	300 K	350 K	400 K
q _m (mol/kg)	1.9	1.89	1.7
C (-)	0.007218	0.05703	0.1013
k	1.52	1.808	1.478
R ²	0.996	0.986	0.9781
RMSE	0.1007	0.2082	0.1983

3) Sips:

$$f(p) = \frac{q_m (bp)^{1/n}}{1 + (bp)^{1/n}}$$

q_m is saturation capacity of species (mol/kg)

b, n is Sips constant

Table S5

parameter	value		
	300K	350K	400K
q_m (mol/kg)	5.147	4.99	4.68
B (1/kPa)	0.4681	0.0541	0.007742
n	0.0256	0.06242	0.06906
R ²	0.9998	0.9998	0.9984
RMSE	3.42%	3.78%	9.22%

For CO₂:

DSLFF:

Table S6

parameter	value		
	300K	350K	400K
A ₁ (mol/kg)	2.7	2.464	2.106
B ₁ (kPa ⁻¹)	0.04821	0.008799	0.001962
C ₁ (-)	0.8443	1.005	1.06
A ₂ (mol/kg)	0.3348	0.05879 mol/kg	0.2874 mol/kg
B ₂ (kPa ⁻¹)	0.003222	0.007554	0.008743
C ₂ (-)	2.404	0.5479	0.7071
R ²	0.9999	0.9992	0.9999
RMSE	0.89%	1.7%	0.26%

Reference

1. García-Sánchez, A.; Ania, C. O.; Parra, J. B.; Dubbeldam, D.; Vlugt, T. J. H.; Krishna, R.; Calero, S. Transferable Force Field for Carbon Dioxide Adsorption in Zeolites. *J. Phys. Chem. C* 2009, 113, 8814–8820.
2. Lennart Joos, Kurt Lejaeghere. Carbon capture turned upside down: high temperature adsorption & low-temperature desorption. *Energy and environmental science*. 2015, 8, 2480.