

Supporting Information

Towards computational design of zeolite catalysts for CO₂ reduction

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Inverse-Ideal Adsorbed Solution Theory (I-IAST)

IAST is widely used for predicting the adsorbed concentration of multiple components given a feed (or gas phase) composition^{1,2}. In this work, the inverse is of interest, i.e. the prediction of the feed composition required to achieve a desired adsorbed composition. Beginning with Raoult's law for vapor-liquid equilibrium,

$$Py_i = P_i^o(\pi_i)x_i \quad i = 1, \dots, N$$

where P is the total feed equilibrium pressure, x_i is the adsorbed composition of component i , y_i is the feed composition of component i , π_i is the spreading pressure of component i in the mixture and P_i^o is the hypothetical pure component pressure of component i that yields the same spreading pressure found in the mixture. According to the Gibbs adsorption isotherm, the spreading is defined as follows,

$$\frac{\pi_i}{RT} = \int_0^{P_i^o} \frac{n_i^o(P)}{P} dP \quad i = 1, \dots, N$$

where R is the universal gas constant, T is the temperature and n_i^o is the pure component capacity at pressure P . At the temperature and pressure ranges of interest, the pure component isotherms are satisfactorily modelled with the dual-site Henry and Langmuir model,

$$n_i^o(P) = k_{H,i}P + C_i \frac{k_{L,i}P}{1 + k_{L,i}P} \quad i = 1, \dots, N$$

where $k_{H,i}$ is the Henry coefficient, $k_{L,i}$ is the Langmuir coefficient and C_i is the saturation capacity of Langmuir sites for component i . The form of the isotherm model is not important, however there must be a good fit with the simulated data, see Figure S3 that demonstrates a good fit. These variables are fitted to the isotherm data. For a 2-component system this leaves six remaining variables. Given the target adsorbed compositions, x_1 and x_2 , there are four variables to be determined, namely y_1, y_2, P_1^o and P_2^o . At equilibrium the spreading pressures for each component must be identical. Therefore the four remaining variables may be solved numerically given the following four constraints,

$$\pi_1 = \pi_2$$

$$Py_1 = P_1^o x_1$$

$$Py_2 = P_2^o x_2$$

$$y_1 + y_2 = 1$$

Finally, the total loading in the adsorbed phase is calculated as,

$$n_t = \left[\sum_{i=1}^N \frac{x_i}{n_i^o(P_i^o)} \right]^{-1}$$

Assuming complete conversion of adsorbed species, n_t is used to predict the quantity of product formation.

Table S1. Lennard-Jones parameters

adsorbate/adsorbent	ϵ/k_B (K)	σ (Å)
<i>Deeg et al.</i> ³		
H ₂ - H ₂	36.733	2.958
H ₂ - Si	28.256	1.854
H ₂ - O _{zeo}	66.055	2.890
<i>García-Pérez et al.</i> ⁴		
C _{CO2} - C _{CO2}	28.129	2.76
C _{CO2} - O _{zeo}	50.2	2.7815
O _{CO2} - O _{CO2}	80.507	3.033
O _{CO2} - O _{zeo}	84.93	2.9195

Table S2. Coulombic charges

adsorbate/adsorbent	q (K)
<i>García-Pérez et al.</i> ⁴	
C _{CO2}	+0.6512
O _{CO2}	-0.3256
Si	+2.05
O _{zeo}	-1.025

Table S3. Top candidates with the strongest dual-adsorption properties in preparation for each product formation at 300 K and 1 bar.

Product	Top 5 Structure Names	Product Quantity (mol/m ³)	Change in Free Energy (kJ/mol)	Required H ₂ Feed Concentration (%)	Required CO ₂ Feed Concentration (%)
Formic Acid (H ₂ :CO ₂ = 1:1)	h8287217	41.56	-13.70	98.35	1.65
	STW	34.61	-15.63	99.41	0.59
	FER	28.16	-16.39	99.38	0.62
	OFF	30.06	-15.15	99.11	0.89
	STI	29.89	-14.97	99.32	0.68
Formaldehyde (H ₂ :CO ₂ = 2:1)	h8287217	21.00	-15.12	99.17	0.83
	STW	17.40	-17.20	99.70	0.30
	h8123219	17.20	-15.34	99.82	0.18
	FER	14.16	-18.15	99.69	0.31
	SOF	16.67	-15.30	99.36	0.64
Methanol (H ₂ :CO ₂ = 3:1)	STW	11.62	-18.77	99.80	0.20
	h8123219	11.50	-17.32	99.88	0.12
	OSO	11.08	-17.45	99.69	0.31
	FER	9.46	-19.91	99.79	0.21
	OFF	10.12	-18.22	99.70	0.30
Methane (H ₂ :CO ₂ = 4:1)	h8315435	7.60	-26.61	99.9996	0.0004
	h8287217	10.56	-17.93	99.58	0.42
	PUN	8.80	-21.08	99.69	0.31
	STW	8.72	-20.34	99.85	0.15
	h8123219	8.64	-19.30	99.91	0.09

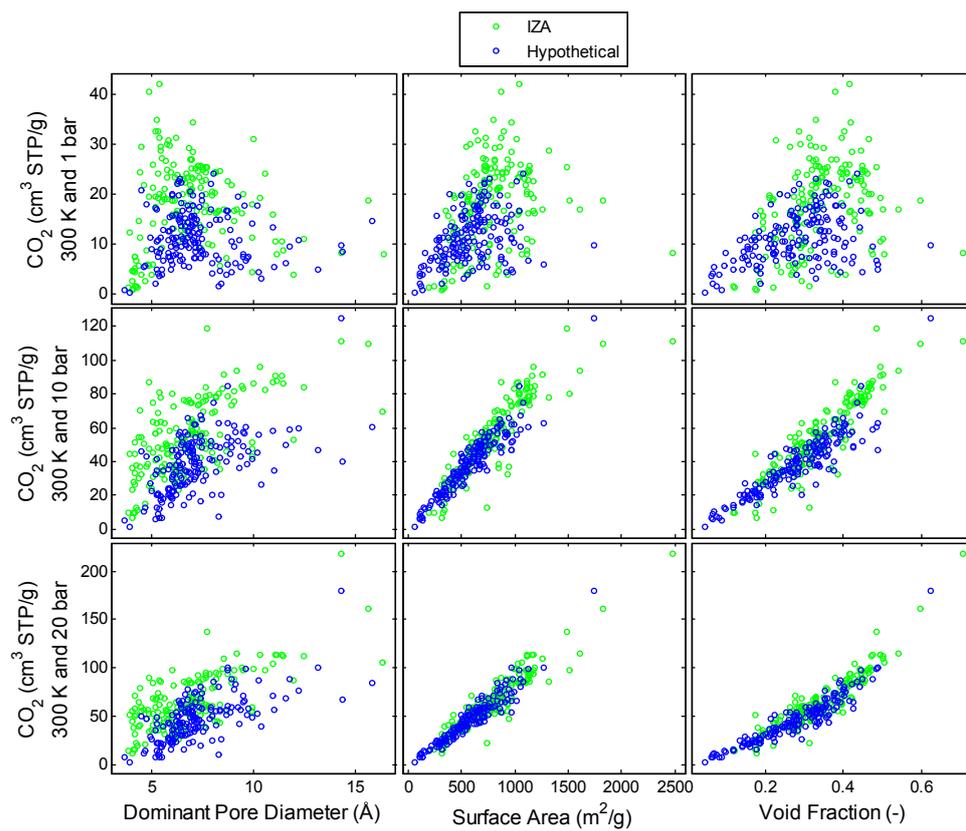


Figure S1: Gravimetric CO₂ uptake versus structural properties.

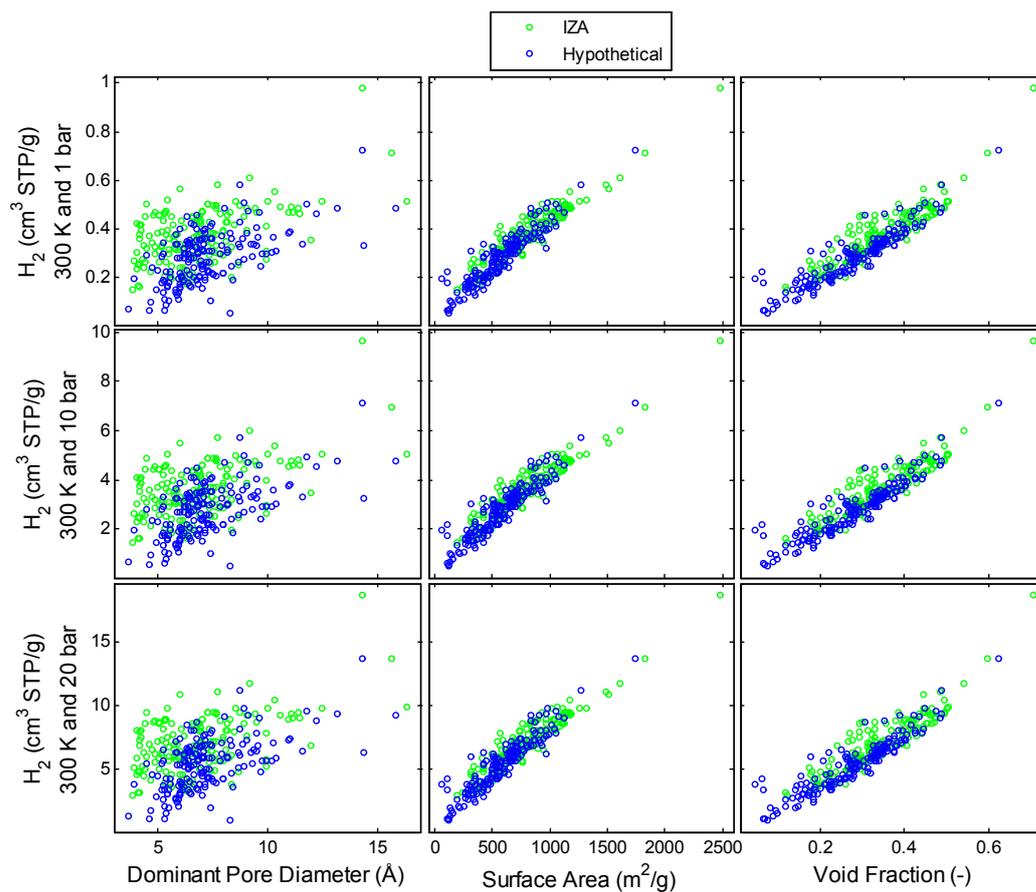


Figure S2: Gravimetric H₂ uptake versus structural properties.

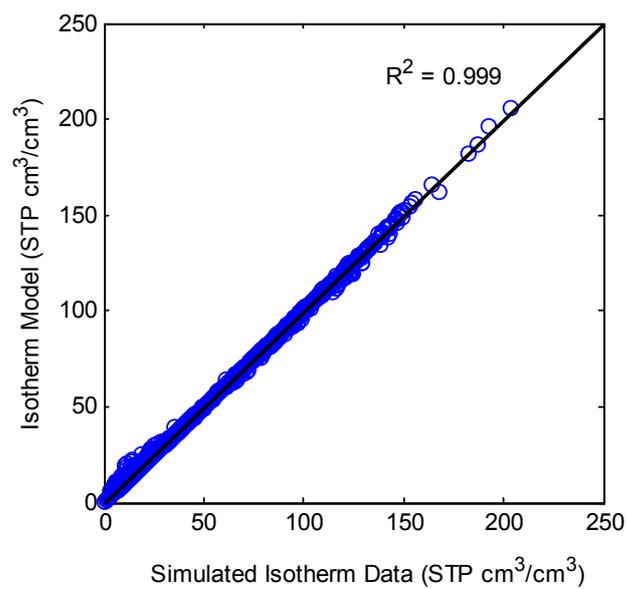


Figure S3: Fitted isotherm data using dual-site Henry and Langmuir model for CO₂ and H₂ up to 20 bar within both IZA and hypothetical zeolite sets.

References

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- (3) Deeg, K. S.; Gutiérrez-Sevillano, J. J.; Bueno-Pérez, R.; Parra, J. B.; Ania, C. O.; Doblaré, M.; Calero, S., Insights on the Molecular Mechanisms of Hydrogen Adsorption in Zeolites. *J. Phys. Chem. C* **2013**, *117* (27), 14374-14380.
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