



Dataset Article

Dataset for CO₂ purification via a zeolite materialRuth Bello, Eleni A. Kyriakidou^{**}, Eric A. Walker^{*}

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY, 14260, USA

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ABSTRACT

In this work, data is collected on a series of impurities and carbon dioxide (CO₂) adsorbing on silver (Ag) ion-exchanged SSZ-13 zeolites. Density functional theory (DFT) calculations are used to obtain the adsorption energies of CO₂ and these impurities in the CO₂ stream. Pure CO₂ can be used in food and beverage production, enhanced oil recovery (EOR) and as feedstock for methanol or urea production. The impurities are oxygen (O₂), water (H₂O), dimethyl sulfide (DMS, C₂H₆S), hydrogen sulfide (H₂S), carbonyl sulfide (COS) and sulfur dioxide (SO₂). In order to design effective adsorbent materials, the fundamental hypothesis of adsorption on to Ag ion exchange sites in SSZ-13 zeolites is tested.

Specifications Table [Every section of this table is mandatory. Please enter information in the right-hand column and remove all the instructions]

Subject	4. Chemistry of deposition and growth 7. Surface engineering 11. Surface science applied to energy conversion and storage 12. Surface nanotechnology and devices 16. Theoretical calculation/modeling on surfaces and interfaces
Specific subject area	A candidate material for CO ₂ purification, Ag/SSZ-13 zeolite, is modelled for its adsorption properties in relation to a post-combustion CO ₂ flue gas stream. The purified CO ₂ is reuseable.
Type of data	Table Figure
How data were acquired	Kohn-Sham DFT calculations were performed using the Vienna ab initio simulation package (VASP) (Kresse and Furthmüller, 1996). The Perdew-Burke-Ernzerhof (PBE) functional, a generalized gradient approximation (GGA) functional, was the first used to obtain an optimized geometry and ground state energy (enthalpy) of the structures studied. A different functional was employed to get more accurate energy values. A hybrid DFT functional, Heyd-Scuseria-Ernzerhof (HSE06), was used to calculate the adsorption energy values. Adsorption energies are calculated as the change in free energy from the adsorbed states to the blank zeolite and gas molecule infinitely separated.
Data format	Analyzed

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Parameters for data collection	The calculated molecules are carbon dioxide (CO ₂), oxygen (O ₂), water (H ₂ O), dimethyl sulfide (DMS, C ₂ H ₆ S), hydrogen sulfide (H ₂ S), carbonyl sulfide (COS) and sulfur dioxide (SO ₂). The computational model of SSZ-13 zeolite used had a Si/Al ratio of 11. The zeolite lattice used for DFT calculations contained 73 oxygen atoms, 33 silicon atoms, and 3 aluminum atoms. The pore types were differentiated by size, with the structure containing both 8- membered rings and 6-membered rings. The exchanged Ag atoms were placed closest to Al but bound to the neighboring O's. The adsorbates were then placed in the largest volume pore close to the Ag atom. Zero-point energy (ZPE) corrections had to be made to the DFT calculated energy. Vibrational frequency calculations were done to obtain ZPE and the vibrational energy of the adsorbed molecules. Displacements of 0.001 Å were applied to every atom not a part of the zeolite lattice. The PBE optimized geometry zeolite structures were used in the HSE functional. The electronic convergence was 1×10^{-5} eV, and the plane wave cut-off was 400 eV. The ionic convergence was 0.01 eV/Å. For the k-points, a single gamma point was used.
Description of data collection	First, DFT-calculated adsorption energies are reported. To model the adsorption of the impurities over the zeolite, the Langmuir adsorption model and microkinetic model are used. Adsorption energies obtained from DFT calculations are passed to these models. A microkinetic model is also used to visualize adsorption and is used to focus on two components of the gas mixture, CO ₂ and SO ₂ . The microkinetic model is also run to equilibrium by setting

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* Corresponding author.

** Corresponding author.

E-mail addresses: elenikyr@buffalo.edu (E.A. Kyriakidou), ericwalk@buffalo.edu (E.A. Walker).

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	the run time to be very long, this ensures that the adsorption fractions do not change.
Data source location	Center for Computational Research, University at Buffalo, The State University of New York
Data accessibility	Repository name: zeolite_CO2 Direct URL to data: https://github.com/ericwalkwalke/299/zeolite_CO2 Instructions for accessing these data: The data is publicly available at the repository listed above.

1. Value of the data

- Carbon capture, utilization and storage (CCUS) is crucial to reducing CO₂ emissions from industrial sources (International Energy Agency, 2022; Dindi et al., 2019). Ag/SSZ-13 has been studied for its adsorption properties in the purification of CO₂ in flue gas (Ji et al., 2021).
- Zeolites' selective adsorption behavior makes them important for industrial gas separation. Knowing the adsorption affinity and molecular bonding site of the molecules of a post-combustion CO₂ flue gas stream to Ag ions is foundational for rationally designing a zeolite material for this CO₂ utilization application.

- The Si/Al ratio which in turn controls the number of Ag adsorption sites may be tuned based upon the adsorption findings. Furthermore, two adsorption models, Langmuir and microkinetic, are flexible for a vast condition space of temperature and concentrations for validation against experimental observations and compute quickly.
- Silver is hydrothermally stable and resistant to water, making it a good candidate for the adsorption material (Horvatits et al., 2020a).
- CO₂ has to be purified up to an allowable standard before use in applications like carbonating food or Enhanced Oil Recovery (EOR) (Abbas et al., 2013; Ghiaat and Al-Ansari, 2021; Lee et al., 2018).

1.1. Data description

The optimized adsorption geometries for multiple molecules for adsorption at the silver active site is shown in Fig. 1. The adsorption free energies for CO₂ and other impurities predicted by the HSE and PBE DFT functional are reported in Table 1. Table 2 reports the data of Langmuir adsorption for each molecule, using the DFT-computed adsorption energy as the input. Table 3 reports the data of the microkinetic model for adsorption CO₂ and SO₂ simultaneously.

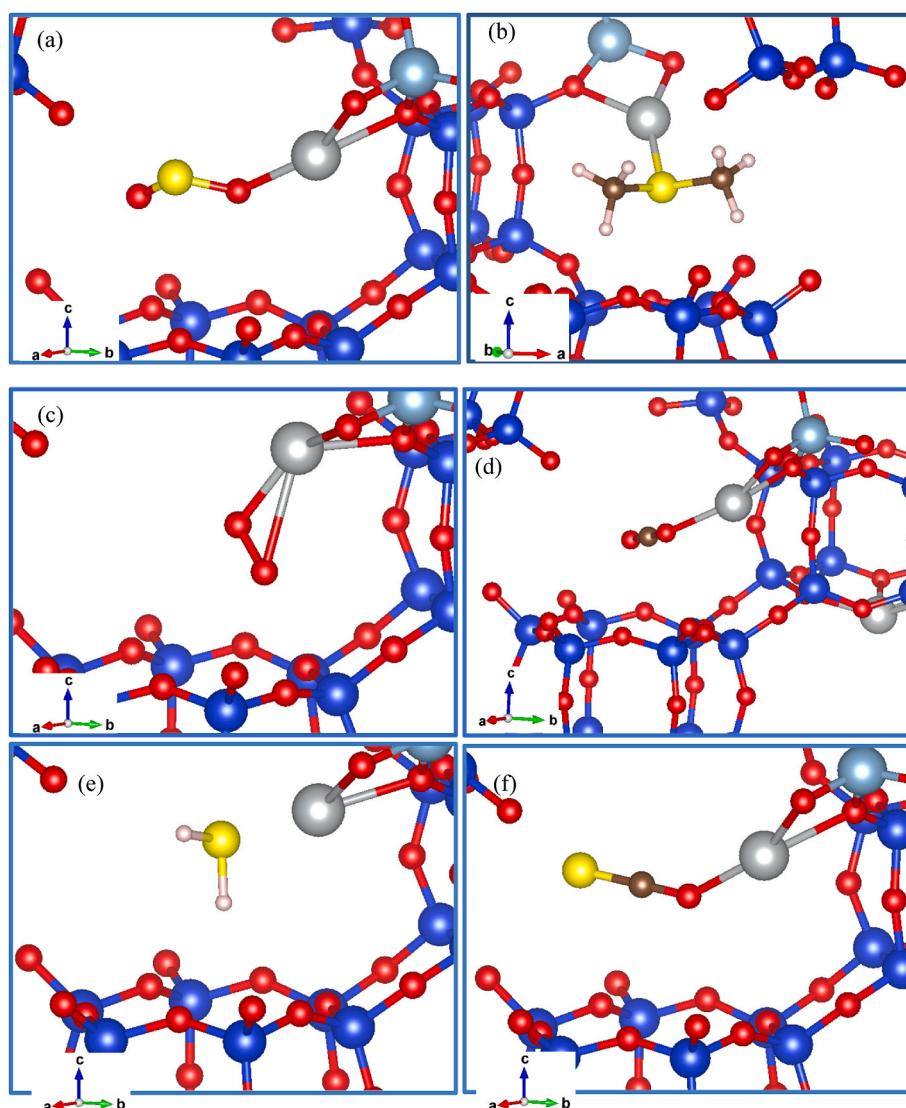


Fig. 1. Optimized functional structures of adsorbed molecules at Ag active sites. (a) SO₂ (b) Dimethyl Sulfide (DMS) (c) O₂ (d) CO₂ (e) H₂S (f) COS.

Table 1

Gibbs free energies (eV) calculated from the HSE and PBE functionals.

	CO ₂	O ₂	COS-S	COS-O	SO ₂ -S	SO ₂ -O	DMS	H ₂ S
HSE free energies of Adsorption, G (eV)	-0.4510	0.1213	-0.7561	-0.5724	-0.4044	-0.5704	-0.8319	-1.1473
PBE free energies of Adsorption, G (eV)	-0.2366	0.4590	-0.6501	-0.3856	-0.3669	-0.4290	-0.6559	-1.0614

Table 2

Adsorption fractions according to Langmuir model.

	CO ₂	O ₂	COS	SO ₂	DMS	H ₂ S	Vacant
Gas Fractions	0.75	0.05	0.05	0.05	0.05	0.05	–
Adsorption Fractions	2.55×10^{-11}	3.59×10^{-22}	2.44×10^{-07}	1.77×10^{-10}	4.66×10^{-06}	0.99	8.07×10^{-17}

Table 3Adsorption fractions of CO₂ and SO₂ according to Microkinetic model.

	CO ₂	SO ₂	Vacant
Gas Fractions	0.95	0.05	–
Adsorption Fractions	0.15	0.85	3.85×10^{-7}

2. Experimental design, materials and methods

The DFT calculation methods are detailed above. DFT provides an energy, but a free energy that includes temperature-dependence and is zero-point energy corrected is desired and provided in the data. The zero-point energy correction is obtained by the equation,

$$E_{ZPE} = \frac{1}{2} \sum_i h\omega_i \quad (1)$$

where Planck's constant, $h = 4.1357 \times 10^{-15}$ (eV s). The wavenumber ω (s⁻¹) which is gotten from the frequency job is converted to frequency by multiplying by the speed of light, $c = 2.998 \times 10^{10}$ (cm⁻¹). The vibrational entropy is calculated by the equation,

$$S_{vib} = k_B T \ln \left(\sum_i \frac{1}{1 - \exp\left(-\frac{h\omega_i}{k_B T}\right)} \right) \quad (2)$$

with T (K) given at $T = 298$ K. Boltzmann's constant is k_B . The free energy of the adsorbed molecules is finally given by combining the energy gotten from the DFT calculations, zero-point energy corrections and then subtracting the vibrational entropy. The total free energy is then,

$$G = E_{HSE06} + E_{ZPE} - k_B T \ln \left(\sum_i \frac{1}{1 - \exp\left(-\frac{h\omega_i}{k_B T}\right)} \right) \quad (3)$$

The Langmuir model is widely used for modeling adsorption equilibrium data (Guo and Wang, 2019; Azizian et al., 2018). In this model, a maximum of one molecule may adsorb per active site. The surface coverage of each species can be calculated by the following equations:

$$\theta_i = \frac{K_i P_i}{1 + \sum_{i=1}^{n=6} K_i P_i} \quad (4)$$

$$\theta^* = \frac{1}{1 + \sum_{i=1}^{n=6} K_i P_i} \quad (5)$$

where θ_i is the surface fraction for component i , and i represents each component of the gas mixture. K is the adsorption equilibrium constant over the Ag-exchanged zeolite, it is calculated by the following equation,

where G is the Gibb's free energy of the reaction.

$$K = \exp \left[\frac{G}{k_B T} \right] \quad (6)$$

P is the gas phase partial pressure which is equivalent to the gas phase concentration. θ^* represents the vacant space on the surface of the zeolite. Being normalized, the sum of all theta's equal 1.

The microkinetic model is also used to visualize adsorption and is used to focus on two components of the gas mixture, CO₂ and SO₂ (Horvath et al., 2020b). The microkinetic model is also run to equilibrium by setting the run time to be very long, this ensures that the adsorption fractions do not change. Rate limitations due to diffusion are also ignored due to the reaction being run to steady state and diffusion rate limitations being negligible at temperatures below 200 °C (Metkar et al., 2011).

Forward and reverse reactions are used in the model to reflect the fact that individual molecules continue to react to reach equilibrium. The microkinetic model equations are

$$r_{rxn,CO_2} = p_{CO_2, gas} k_f, CO_2 \theta^* - k_r, CO_2 \theta_{CO_2} \quad (7)$$

$$r_{rxn,SO_2} = p_{SO_2, gas} k_f, SO_2 \theta^* - k_r, SO_2 \theta_{SO_2} \quad (8)$$

The rate constants, k , are calculated based on collision theory and the relation to the calculated equilibrium constant, K , by the equation, [16]

$$K = \frac{k_f}{k_r} \quad (9)$$

The following ordinary differential equations are used to model the time evolution of the adsorption fractions complete the model:

$$\frac{d\theta_{CO_2}}{dt} = r_{rxn,CO_2} \quad (10)$$

$$\frac{d\theta_{CO_2}}{dt} = r_{rxn,SO_2} \quad (11)$$

CRediT authorship contribution statement

Ruth Bello: Data curation, Investigation, Software, Formal analysis, Methodology, Visualization, Writing – original draft. **Eleni A. Kyriakidou:** Investigation, Project administration, Resources, Supervision. **Eric A. Walker:** Supervision, Writing – review & editing, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is available on github.

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