Zeolite screening for the separation of gas mixtures containing SO₂, CO₂ and CO

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We used a combination of experiments and molecular simulations to investigate at molecular level the effects of zeolite structure on the adsorption and diffusion of sulfur dioxide, carbon dioxide and carbon monoxide as well as separation processes of their mixtures. Our study involved different zeolite topologies and revealed numerous structure-property trends depending on the temperature and pressure conditions. Sulfur dioxide, which has the strongest interactions with zeolites due to its size and polarity, showed the largest adsorption across investigated temperatures and pressures. Our results indicate that structures with channel-type pore topology and low pore volume are the most promising for selective adsorption of sulfur dioxide over carbon dioxide and carbon monoxide at room conditions, while structures with higher pore volume exhibit better storage capacity at higher pressure. Our results emphasize the need for considering both adsorption and diffusion processes in the selection of the optimal structure for a given separation process. Our findings help to identify the best materials for effective separation processes at realistic operating conditions.

1. Introduction

Sulfur dioxide (SO₂) is an ubiquitous component of fuel combustion exhausts and a gas of relevant environmental impact which control remains a challenging issue¹. Aside the toxicity of sulfur dioxide itself, SO₂ emissions also affect the efficiency of carbon dioxide capture processes^{2, 3} where investigations have been particularly intense over the last years to fight the global warming and reduce greenhouse gas emissions. The trace amounts of SO₂ in the flue gas from coal fired plants (typical composition contains 10-15% CO₂, and many other contaminants as O₂, H₂O, SO₂, NO_x, H₂ at different levels of concentration) is known to undergo parasitic reactions with current methods for CO₂ capture (namely amines and calcium sorbents). For instance, in the separation of CO₂ by adsorption in amines it is necessary to lower the SO₂ concentration in the gas influent below 10 ppm to minimize the loss of the solvent associated to thermally stable salts of the amine with SO₂^{4, 5}. The sulfation of calcium based sorbents is also a competing process that affects the regeneration

temperature of CaO, decreasing the regenerative capacity of the sorbent over subsequent cycles^{6, 7}. Whereas research on the simultaneous removal of SO₂/CO₂ mixtures is still under development⁸, separation of these gases is crucial to achieve high carbon capture efficiencies.

Over the past decades, a number of technologies have been developed to prevent the generation and release of SO₂ during combustion processes. They are based on different approaches: before (fuel desulfurization before combustion), during (fluidized bed combustion coupled to integrated gasification combined cycle (IGCC) systems) or post-combustion (flue gas desulfurization)^{9, 10}. Sulfur dioxide removal via scrubbing is the most widely applied approach for post-combustion process due to the availability of efficient scrubber systems and their relatively low cost. However, this process still generates large amounts of solid wastes and off-gas streams, further management and disposal of which entail an important cornerstone of this technology. For instance, the catalytic reduction of SO₂ to elemental sulfur by CO ($2\text{CO} + \text{SO}_2 \rightarrow \frac{1}{2}\text{S}_2 + 2\text{CO}_2$)¹¹⁻¹³ is used to process the off-gas stream generated in

flue gas desulfurization systems, to obtain high added value by-products such as elemental sulfur or sulfuric acid. Adsorption of SO₂ in nanoporous materials is a potential alternative technology to reduce or eliminate the emissions of SO₂ and other pollutants, as well as reducing the generation of solids in flue gas desulfurization systems. This would avoid the management and disposal of solid wastes, therefore decreasing the cost and accelerating the implementation of this technology.

In the present work, the separation efficiency SO₂-containing binary and ternary mixtures (CO₂-SO₂, CO-SO₂, CO-CO₂-SO₂) was studied through experimental measurements and molecular simulation calculations. We focus on systems containing SO₂ for which available data in the literature is rather scarce^{14, 15}.

Among nanoporous sorbents, zeolites are promising candidates for this application as molecular sieves¹⁶⁻¹⁹. Zeolites are crystalline aluminosilicates consisting of tetrahedral units with four oxygen atoms (O atoms) bonded to one atom of silicon, aluminium, or other four-fold coordinated metal (T atoms). Each aluminium that replaces an atom of silicon generates a negative net charge in the structure that can be balanced by the addition of protons and cations in the system^{20, 21}. Tetrahedra are connected via oxygen atoms, generating 3D structures with cages and/or channels. The shape and size of these channels and cages, as well as the silicon/aluminium ratio, and the presence of cations are very important because they influence the adsorption, diffusion, and separation properties²²⁻²⁸. Highly ordered zeolite structure have many desirable properties^{20, 29, 30}, such as high surface area or thermal stability, that make them promising materials for the storage, separation, and purification of gas mixtures³¹⁻³³.

The large amount of available zeolitic structures (about 200 unique topologies) and the corrosive nature of sulfur dioxide – hindering their handling – pose a challenge to experimentally screen many structures to identify the most adequate material(s) for the selective separation of sulfur dioxide from post-combustion streams containing carbon dioxide and carbon monoxide. In this study, we aim to guide experimental work by performing a molecular simulation screening of different zeolite, and predict their SO₂ adsorption and separation potential. We provide the molecular level understanding of the effect of the structural features of zeolites, such as the pore topology or accessible pore volume, on the adsorption, diffusion, and separation of sulfur dioxide from carbon dioxide and carbon monoxide. Our study focused on a set of zeolites with a diverse porosity (in terms of pore size, shape and topology) selected from 194 all silica zeolite structures from the IZA database³⁴. For these selected structures we have computed adsorption properties and diffusion coefficients of the three gasses under study, and we have compared our simulations with the experimental data available from the literature. We describe the models for zeolites and adsorbates as well as the simulation techniques in Section 2. The obtained results are discussed in

Section 3 and we summarize the most relevant conclusions in Section 4.

2. Methodology

2.1. Computational details

Adsorption isotherms were computed using Monte Carlo simulations in the Grand Canonical ensemble (GCMC), where the temperature, the volume, and the chemical potential remain fixed. Chemical potential is associated to the fugacity, and fugacity is directly related to pressure with the fugacity coefficient. Based on the type of gas and on the operating conditions, in this work we equate pressure with fugacity, i.e. the fugacity coefficient is 1. To compare simulated and experimental isotherms, absolute adsorption is converted to excess adsorption^{35, 36}. Simulations were performed using our in-house code RASPA³⁷. This code has been extensively tested and validated with a large number of experimental and simulation data^{17, 38-41}. Isothermic heats of adsorption and Henry coefficients were computed using the Widom test particle Method⁴². Self-diffusion coefficients were computed from the mean square displacements of the adsorbates calculated from Molecular Dynamic simulations in the canonical ensemble. We started from equilibrium conditions previously achieved in GCMC simulations for ternary mixture and successive configurations of the system were generated by integrating Newton's laws of motion using the Verlet algorithm. We use Nosé-Hoover thermostat. The self-diffusion coefficients were computed from the slope of the mean-square displacement at long times. Simulations have been run for 1000–10000 ps using an integration time step of $\tau = 5 \times 10^{-4}$ ps. Other properties of the structures such as surface area and pore volume were also computed for later analysis.

Atomic interactions were described by Lennard-Jones and Coulomb potentials. We use a cutoff distance of 12 Å, and Ewald summation to calculate Coulombic interactions. We used previously published models for carbon dioxide and carbon monoxide^{38, 40}. Sulfur dioxide molecules are modeled rigid with S-O bond length of 1.431 Å and O-S-O bond angle of 119°. To mimic the dipole moment of the molecule (1.62 Debye)⁴³ we assigned point charges to the sulfur atom (0.402 e-) and to the oxygen atoms (-0.201 e-). The Lennard-Jones parameters for sulfur dioxide were obtained by fitting to the vapour-liquid equilibrium curve⁴⁴ (Figure S1 in the Electronic Supporting Information). To compute this curve we used Gibbs-ensemble Monte Carlo simulations⁴². Interactions between adsorbates are computed using Lorentz-Berthelot mixing rules^{45, 46}. Since zeolites not always obey the Lorentz-Berthelot mixing rules^{17, 38} for the adsorbate-adsorbent interactions Lennard-Jones parameters have to be adjusted independently to reproduce the experimental data^{17, 38}. We define the adsorbate-adsorbent interactions by those of the oxygen atoms of the framework (Ozeo) with all the atoms from the adsorbed molecules. We use the Lennard-Jones parameters proposed by *García-Sánchez et*

*al.*³⁸ to reproduce the interactions with carbon dioxide. The Lennard-Jones parameters to reproduce the interactions between the other two adsorbates (sulfur dioxide and carbon monoxide) and the zeolites were developed in this work. Lennard-Jones parameters and partial charges of the molecules are summarized in Table 1.

Table 1. Lennard-Jones parameters and partial charges of the adsorbates and the structure.

Atom 1	Atom 2	ϵ/k_B (K)	σ (Å)	Charge (e-)
Adsorbed Molecules				
C(CO ₂)	C(CO ₂)	29.933	2.745	0.651
O(CO ₂)	O(CO ₂)	85.671	3.017	-0.326
C(CO)	C(CO)	16.141	3.658	-0.242
O(CO)	O(CO)	98.014	2.979	-0.274
Dum(CO)	Dum(CO)	-	-	0.517
S(SO ₂)	S(SO ₂)	189.353	3.41	0.402
O(SO ₂)	O(SO ₂)	58.725	3.198	-0.201
Zeolite				
O(zeo)	O(zeo)	-	-	-0.393
Si(zeo)	Si(zeo)	-	-	0.786
Zeolite - Adsorbed Molecules				
C(CO ₂)	O(zeo)	37.595	3.511	-
O(CO ₂)	O(zeo)	78.98	3.237	-
C(CO)	O(zeo)	40.109	3.379	-
O(CO)	O(zeo)	98.839	3.057	-
Dum(CO)	O(zeo)	-	-	-
S(SO ₂)	O(zeo)	138.555	3.168	-
O(SO ₂)	O(zeo)	77.161	3.066	-

A set of 194 all silica zeolite structures from the International Zeolite Association (IZA)³⁴ was characterized in terms of pore geometry and topology using Zeo++ software^{47, 48}. Zeo++ performs segmentation of the void space to identify pore systems accessible to a given probe. For each pore system Zeo++ calculates dimensionality of the pore system, the diameter of the largest included sphere (D_i), the largest free sphere (D_f), and the largest included sphere along the free sphere path (D_{if}). D_i measures the largest opening in the structure while D_f measures the restriction along the diffusion pathway of the largest spherical probe. All calculations performed with Zeo++ involve hard sphere approximation for atoms. Radius of 1.35 Å was assumed for both O and Si atoms⁴⁹ while a probe radius of 1.4 Å was used for the void space segmentation to detect pore systems. Additionally, each characterized material is classified as either channel or interconnected cage system based on the ratio of D_{if} and D_f , where channel is recognized for structures with $D_{if}/D_f < 1.5$, and interconnected cage system otherwise. Among the structures collected in the IZA we have selected 194. The results of the above characterization for the selected zeolites are

collected in Tables S1-S6 in the Electronic Supporting Information (ESI). Thus, the structures were classified according to their channel or interconnected cage character, and the corresponding directionality, 1-3, of the pore space. We selected structures within each of these six classes to obtain representative sets: 1D channels (ASV, DON, ITW, JRY, LAU, LTL, MOR, NAT, PON), 2D channels (AFR, FER, IWV, NES, SFO, SFG, TER), 3D channels (AFY, BEC, BOG, MEL, MFI, ITR, SBT, STW, SZR), 1D interconnected cages (ITE, MTF, SAS), 2D interconnected cages (DDR, LEV, MWW), 3D interconnected cages (CHA, ERI, FAU, LTA, KFI, PAU, RHO, SBE). The pore landscapes of representative structures of each group are shown in Figure 1. The pore landscapes for all the selected structures are shown in Figures S2-4 in ESI.

Figure 1. Pore landscapes of representative zeolites used in this work. Channels: 1D, 2D and 3D – ASV, FER and BOG, respectively; interconnected cages: 1D, 2D and 3D – MTF, DDR and SBE, respectively. The inner surface of the pores is highlighted in yellow. The color codes for atoms are red and beige for oxygen and silicon, respectively.

We considered all zeolites under study as all silica, rigid models^{34, 50-67}. The set of charges of the frameworks are taken from *García-Sánchez et al.*³⁸. A summary of some characteristics of the different zeolites, as their unit cell lengths, angles, computed pore volume, and computed surface areas can be found in Table S7 in ESI.

2.2. Experimental details

All silica (Si/Al $\approx \infty$) MFI was kindly supplied by the Instituto de Tecnología Química (ITQ) belonging to the Consejo Superior de Investigaciones Científicas (CSIC). Experimental adsorption isotherms of CO at temperatures near ambient conditions were performed in a volumetric analyzer (ASAP 2020, Micromeritics) in the pressure range from 10^{-2} up to 120 kPa; the instrument was equipped with a turbo molecular vacuum pump and three pressure transducers (0.13, 1.33, and 133 kPa, uncertainty within 0.15% of each reading) to enhance the sensitivity in the low pressure range. Prior to the adsorption measurements, the zeolite was in situ outgassed under vacuum (ca. 10^{-3} kPa) at 673 K overnight. All of the isotherms were done in triplicate, and the data is reproducible with an error

below 0.1%. The temperature of the isotherms was controlled using a thermostatic circulating oil bath. Ultrahigh purity CO (i.e., 99.995%) was supplied by Air Products.

3. Results and Discussion

The adsorption loadings computed for sulfur dioxide, carbon dioxide, and carbon monoxide, as pure components, as well as for the 20:40:40 ternary mixture ($\text{SO}_2/\text{CO}_2/\text{CO}$), and the CO_2/CO equimolar binary mixture were obtained at a pressure span from 10^{-1} to 10^4 kPa. Self-diffusion coefficients were obtained from the adsorption isotherms of ternary mixtures at ambient conditions. The adsorption properties in the low coverage regime (Isosteric heats of adsorption and Henry coefficients) were computed for the three adsorbates in all the zeolites under study. In case of mixtures we studied (a) the selective adsorption and diffusion behavior of the ternary mixture at atmospheric pressure and room temperature, and (b) the selective adsorption behavior of the CO_2/CO binary equimolar mixture. Based on our findings we have discussed separation performance in terms of both pore volume and permselectivity.

3.1. Adsorption of pure components for forcefield validation

Pure component gas adsorption isotherms were computed and compared to available experimental data to validate the forcefield parameters developed in this work for CO and SO_2 accounting for the gas-adsorbent interactions. The parameters describing CO_2 -zeolite interactions have been validated in a previous work³⁸. Simulated and experimental adsorption isotherms of SO_2 and CO as pure components on MFI are shown in Figure 2. It should be mentioned that available experimental data on SO_2 adsorption on nanoporous materials is rather scarce, due to the corrosive nature of this gas that difficult its handling. Anyhow, Figure 2a shows a comparison of our simulated SO_2 adsorption isotherms in MFI at 298-373 K with the available experimental data from Deng and Lin⁶⁸. Simulations are in good agreement with experiments at all three temperatures, with a slight overestimation of the adsorption capacity at 298K. This could be attributed to the fact simulations are computed considering rigid and clean zeolite structures while zeolites can exhibit some flexibility, and experimental data is recorded on materials that may often present structural defects or impurities (i.e. adsorbed water and/or other residues from the synthesis) that would lead to a lower gas adsorption capacity. Figure 2b shows the perfect match between our experimental and computed adsorption isotherms of CO in MFI. The good agreement at several temperatures obtained for both CO and SO_2 validates the forcefields used in this study for both gases.

Figure 2. Comparison of simulated (open symbols) and experimental (closed symbols) pure component adsorption isotherms of (a) sulfur dioxide and (b) carbon monoxide in MFI at various temperatures. Experimental values of sulfur dioxide are taken from Deng and Lin⁶⁸.

3.2. Isosteric heats of adsorption and Henry coefficients

Computed isosteric heats of adsorption for sulfur dioxide, carbon dioxide, and carbon monoxide as a function of the pore volume of the zeolites at 298 K are shown in Figure 3. The results show higher absolute values of sulfur dioxide, following the trend $\text{SO}_2 > \text{CO}_2 > \text{CO}$ regardless the zeolite. Similar trends were reported by Ding and Yazaydin² for several MOFs. This behaviour can be related to the shape and size of the molecules in combination with the Coulombic interactions between the adsorbate and the adsorbent. Among the three gases, SO_2 is not only the biggest molecule (molecular diameter, 4.11-4.29 Å)^{43, 69} but also has the highest dipole moment. More specifically, molecular size seems to be more important than polarity since the interaction with all zeolites is stronger for carbon dioxide (i.e., 3.90 Å)^{69, 70} than for carbon monoxide (i.e., 3.69 Å)^{69, 70}. We also observed bigger differences among the values obtained for SO_2 since the fitting of the bulkier molecules is more dependent on the pore system. In a similar way, differences between the heats of adsorption of structures with similar topology and pore volume are larger for sulfur dioxide than for

the other two molecules. As a general rule, zeolitic frameworks with high pore volumes exhibit low heats of adsorption for all three studied gases. Some structures such as MOR, AFY, and TER escape from this trend. To understand this anomalous behaviour we computed the average occupation profiles of the gases inside the structures.

Figure 3. Computed isosteric heats of adsorption of carbon monoxide (red), carbon dioxide (blue), and sulfur dioxide (green) as a function of the pore volume of the structures at 298 K. Open symbols show the results obtained for channels-type zeolites and closed symbol for the interconnected cages-type zeolites. The directionality of the pore space is represented by circles (1D), squares (2D) or diamonds (3D).

For instance, the isosteric heats of adsorption of SO_2 and CO in MOR (1D channels-type zeolite) are higher than expected; the corresponding average occupation profiles depicted in Figure 4 show that this is linked to the confinement effect of these gases at low coverage in the side pockets of MOR, being the preferential sites of adsorption¹⁷. SO_2 and CO commensurate better than CO_2 in the pockets for a combined effect of geometry and polarity, thus the occupation density of the side pockets is larger for SO_2 followed by CO , and CO_2 . The average occupation profiles obtained for AFY (Figure 4) also revealed the existence of specific adsorption sites for sulfur dioxide and carbon monoxide, while carbon dioxide is only

adsorbed in the big-straight channels of the host where the interaction with the structure is weaker.

Figure 4. Average occupation profiles obtained in AFY (top), and MOR (bottom) for one molecule of carbon monoxide (top right), carbon dioxide (bottom left), and sulfur dioxide (bottom right). The figure shows the projection of the center of mass of the molecules over x-y (AFY) and y-z (MOR) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structures. The atomic structures are represented by the oxygen and silica atoms in red and yellow respectively. Grid surfaces where the accessible part appears in blue and the non-accessible part is colored in gray are also depicted.

The different behaviour of the heat of adsorption is due to the preferential sites of adsorption in which bulkier molecules fit better due to a mere size entropy effect (i.e., confinement)²⁷. In TER, a 2D channel-type structure, sulfur dioxide shows the highest occupation density of the sites, followed by carbon dioxide and carbon monoxide (Figure S5 in ESI). In zeolite TER, the intersections between the channels are the preferential adsorption sites, as opposed to other zeolites of the same group (SFG and NES) where molecules are preferentially adsorbed in the wide channels (Figures S6 and S7 in ESI). The aforementioned effect can also explain the differences on the heats of adsorption obtained for the three gases in LTL and DON (1D channel-type) or those found in MEL, MFI, ITR, and SZR (3D channel-type). As shown in the average occupation profiles obtained for MEL (Figure 5) sulfur dioxide is preferentially adsorbed in the main straight interconnecting channels, whereas the molecules of carbon dioxide and carbon monoxide can also be found in the intersections of the channels. For MFI the three gases follow the same trend as in MEL (Figure S8 in ESI), while the preferential adsorption sites in ITR and SZR are the intersecting channels and the big straight channels respectively (Figures S9 and S10 in ESI).

Figure 5. Average occupation profiles obtained for one molecule of carbon monoxide (top right), carbon dioxide (bottom left), and sulfur dioxide (bottom right) in (a) MEL, (b) KFI and (c) SBE zeolites. The figures show the projections of the center of mass of the molecules over the x-y plane. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (top left). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part is colored in blue and the non-accessible part is colored in gray).

A number of investigated structures have SO_2 and CO_2 preferential adsorption sites that are neither side pockets, straight channels nor intersecting channels. For example, the preferential sites of adsorption in the 2D cage-type structures MWW and KFI are the windows that communicate cages (Figure S11 in ESI). As a result, the heats of adsorption of SO_2 and CO_2 in KFI are higher than expected from general trends, since the gases are not adsorbed in the big cages but in a small cavity created by the windows between cages (Figure 5). Similarly, the preferential adsorption sites for SBE (Figure 5) and FAU (Figure S12 in the ESI) are the windows connecting big cages. Despite these two structures displayed among the highest pore volumes analyzed in this work, they also exhibit the highest values of heat of adsorption. This is contrary to the general trend: the larger the pore volume the lower the heat of adsorption. On the other hand, we did not observe a direct correlation between the topology of the zeolites and the isosteric heats of adsorption. An observation that a local structure feature can dominate adsorption properties such as heat of adsorption and Henry coefficient was recently used to develop an efficient screening approach for carbon capture materials⁷¹⁻⁷⁴.

Figure 6. (a) Computed Henry coefficients of sulfur dioxide over carbon dioxide at room temperature and (b) adsorption selectivity of sulfur dioxide over carbon dioxide, from the ternary mixture (SO_2 , CO_2 , and CO with ratio 20:40:40) at room pressure and temperature. Both as a function of the pore volume of the structures. Open symbols show the results obtained for channels-type zeolites and closed symbols to the interconnected cages-type zeolites. The directionality of the pore space is represented by circles (1D), squares (2D), or diamonds (3D).

The selectivity of the zeolites at low pressure for gas component i over j at a given temperature can be estimated using the ratio between the Henry coefficient of each gas (K_{H_i}/K_{H_j}). The dependence of the selectivity at low coverage with the pore volume of the structure for SO_2 over CO_2 and CO_2 over CO at 298 K is shown in Figures 6a and 7a, respectively. The trends are similar to those obtained for the heats of adsorption, with higher selectivities obtained for the structures showing the lowest pore volumes. Again, MOR and AFY follow an anomalous trend of selectivity, with values for SO_2/CO_2 and CO_2/CO larger and lower, respectively, than those of other structures with similar pore volumes. Also, those structures where bulky molecules fit better (MEL, MWW, SBE and FAU) exhibit higher selectivity of sulfur dioxide over carbon dioxide. In case of CO_2/CO selectivity, it follows the trend: $3\text{D} > 2\text{D} > 1\text{D}$ for structures with similar pore volumes due to the appearance of preferential sites of adsorption at the intersections of the channels. In addition, the fact that the occupation density of the preferential adsorption sites is higher in FAU than in SBE is the reason that leads to higher values of selectivity for the former than for the latter.

Figure 7. (a) Computed Henry coefficients of carbon dioxide over carbon monoxide at room temperature and (b) adsorption selectivity of carbon dioxide over carbon monoxide, from the binary equimolar mixture at room pressure and temperature. Both as a function of the pore volume of the structures. Open symbols show the results obtained for channels-type zeolites and closed symbols to the interconnected cages-type zeolites. The directionality of the pore space is represented by circles (1D), squares (2D), or diamonds (3D).

In summary: The highest values of heat of adsorption for carbon monoxide were found for JRY, FER, and FAU. These three structures also exhibit the strongest interaction with carbon dioxide. FER and MTF are the structures with higher selectivity of carbon dioxide over carbon monoxide. MOR and FAU are the structures with higher heats of adsorption for sulfur dioxide, and therefore with higher selectivity of sulfur dioxide over carbon dioxide.

3.3. Adsorption selectivity from ternary mixture.

In a multicomponent system the adsorption selectivity of a component i over a component j (S_{ij}) is defined as $(x_i/y_i)/(x_j/y_j)$ where $x_{i,j}$ are the molar fractions in the adsorbed phase and $y_{i,j}$ the molar fractions in the bulk phase. Figure 6b shows the adsorption selectivities of sulfur dioxide over carbon dioxide computed from the mixture 20% SO_2 , 40% CO_2 , and 40% CO at room temperature and atmospheric pressure. Table S8 in the Electronic Supporting Information collects the computed loading for each component in terms of mol of adsorbate per

kilogram of structure, and the obtained values for the selectivity for each structure.

For the ternary mixture the highest adsorption was obtained for sulfur dioxide, the gas in the lowest proportion in the bulk, regardless the zeolite structure. The adsorption of carbon dioxide is drastically reduced by the presence of sulfur dioxide, in agreement with the studies of Ding and Yazaydin², whereas the adsorption of carbon monoxide is almost negligible.

The SO_2/CO_2 selectivity is higher for the structures with lower pore volume, in a similar way already described for the heats of adsorption and the selectivity estimated at low coverage. Due to their low pore volumes, few structures such as JRY, PON and ITW (1D channel-type), FER (2D channel-type), or STW (3D channels-type), show extremely high SO_2/CO_2 selectivities. In these structures the loading of carbon dioxide is extremely low, and the confinement effect of SO_2 (main component in the adsorbed phase) also enhances the SO_2/CO_2 selectivity. The packing effect of the gases gradually disappears in structures with higher pore volumes, leading to lower values of selectivity, with the exception of AFY (structure with high pore volume showing high selectivity). The heat of adsorption of sulfur dioxide in this zeolite was higher than in other structures with similar pore volume. This stronger interaction of SO_2 with the structure also implies higher loading of sulfur dioxide. The high heat of adsorption in combination with the size entropy effect previously described²⁷ explains the high selectivity for AFY. Due to the large pore volume of this structure this selectivity could be enhance with a slightly increase of the pressure.

At this stage it is important to highlight that some of the aforementioned different heats of adsorption at low coverage are not observed at higher coverages. As the preferential sites of adsorption at low coverage are filled and the gas loading rises (increasing pressure), molecules are adsorbed in other sites where the gas-host interaction is weaker. A good example of this behaviour is found in FAU, which exhibits an extremely high heat of adsorption for sulfur dioxide at zero loading. The preferential adsorption sites at low coverage for FAU are the windows that interconnect the big cages. The strength of the interaction is very high at the windows but not at the big cages. At higher loadings most molecules tend to be adsorbed in the latters and it is for this reason that the loading of sulfur dioxide and carbon dioxide at room pressure in the ternary mixtures is low and therefore the selectivity is also very low.

The CO_2/CO selectivity for the ternary mixture under the studied conditions (ca. 20% SO_2 , 40% CO_2 , and 40% CO at room temperature and atmospheric pressure) cannot be obtained since the adsorption of carbon dioxide is drastically reduced by the presence of sulfur dioxide and the adsorption of carbon monoxide is almost negligible. For a good understanding of the competition of carbon dioxide and carbon monoxide, we performed adsorption isotherms for the

equimolar binary mixture at room temperature and atmospheric pressure using the most representative structures of each group.

3.4. Adsorption selectivity from CO₂/CO binary mixtures.

Figure 7b shows the CO₂/CO adsorption selectivity for equimolar binary mixtures in several zeolites at atmospheric pressure and room temperature. Table S9 in ESI summarizes the loading of each gas in each structure as well as the adsorption selectivity. As predicted from the low coverage regime (Fig. 7b), CO₂ is selectively adsorbed over CO in all the structures, which is attributed to the bigger size of CO₂ that allows a better fit in the structures. Comparatively, carbon dioxide loading in the studied structures is lower than that of sulfur dioxide under the same conditions of pressure and temperature in the ternary mixture. Differences in the adsorbed amount between carbon monoxide from the binary mixture and sulfur dioxide from the ternary were about 1-3 mol/kg lower in channels-type zeolites and 0.5-2 mol/kg in interconnected cages-type. As in the case of the ternary mixtures, the selectivity is higher for the zeolites displaying low pore volumes. In addition, for a given pore volume it follows the trend: 3D>2D>1D due to the effect of the channels intersection previously explained.

In the binary CO₂/CO mixture, the adsorption selectivity of all the structures shows the same trend described for the Henry coefficient selectivities. Unlike sulfur dioxide, the weaker interaction of CO₂ and CO with the structures reduces the loading, thus just low-medium coverage is reached at the given conditions of pressure and temperature. Therefore the behaviour is similar to that shown with the Henry coefficients. Only FAU showed lower adsorption selectivity than the expected from the Henry coefficients. This is due to the high pore volume of the zeolite and the low gas loading, avoiding the competition between both gases for the preferential sites of adsorption of the structure.

3.5. Self-diffusion and permselectivity from ternary mixture

Table 2 shows the averaged self-diffusion coefficients, calculated for sulfur dioxide and carbon dioxide from the slope of the Mean Square Displacement of the adsorbed molecules from the ternary mixture as described above. This parameter was used to discard the zeolites in which the diffusion of sulfur dioxide and carbon dioxide is very low. Thus only zeolites with self-diffusivity values between 10⁻¹⁰ and 10⁻⁸ m²/s were selected to analyze permselectivity. Permselectivity for SO₂ over CO₂ in these structures is depicted in Figure 8, defined as the product of the adsorption selectivity and the diffusion selectivity.

Table 2. Average self-diffusion coefficients for sulfur dioxide and carbon dioxide from the ternary mixture at room pressure and temperature.

Zeolite	SO ₂ Self-diff (10 ⁻⁸ m ² s ⁻¹)	CO ₂ Self-diff (10 ⁻⁸ m ² s ⁻¹)	Zeolite	SO ₂ Self-diff (10 ⁻⁸ m ² s ⁻¹)	CO ₂ Self-diff (10 ⁻⁸ m ² s ⁻¹)
ASV	0.047	0.061	MFI	0.042	0.035
DON	0.672	0.916	ITR	0.126	0.117
ITW	0.007	0.007	SBT	0.545	0.654
JRY	0.011	0.01	STW	0.004	0.002
LAU	0.005	0.004	SZR	0.013	0.029
LTL	0.049	0.081	ITQ-3	0.004	0.002
MOR	0.037	0.111	MTF	0.003	0.005
NAT	0.028	0.024	SAS	0.031	0.025
PON	0.002	0	DDR	0.01	0.004
AFR	0.069	0.117	LEV	0.005	0.002
FER	0.029	0.057	MWW	0.149	0.157
IWV	0.122	0.179	CHA	0.016	0.011
NES	0.146	0.192	ERI	0.007	0.003
SFO	0.066	0.129	FAU	1.08	1.43
SFG	0.067	0.074	ITQ-29	0.035	0.021
TER	0.073	0.074	KFI	0.001	0.002
AFY	0.028	0.055	PAU	0.003	0.004
BEC	0.417	0.484	RHO	0.005	0.002
BOG	0.175	0.237	SBE	0.241	1.03
MEL	0.038	0.034			

In agreement with the results previously described, permselectivity is higher in structures with lower pore volume, showing JRY and NAT as the best structures for the separation of SO₂ from gas mixtures containing CO₂ and CO. It is interesting to highlight that there are some structures with low pore volume in which the packing effect made them to have extremely high adsorption selectivity. The synergy between the adsorption and diffusion of a mixture in zeolites for separation processes has been recently proven using both simulations and experiments⁷⁵. Therefore, zeolites such as ITW, PON, and STW, that were initially considered good candidates based on their adsorption selectivity, are further discarded due to the poor diffusion. On the other hand AFY, zeolite with high pore volume and high storage capacity, also has reasonable diffusion and shows high permselectivity. Therefore, this structure raises as a good candidate for the selective adsorption of sulfur dioxide over carbon dioxide, perhaps working at slightly higher pressures in order to improve its adsorption selectivity.

Figure 8. Permselectivity of sulfur dioxide over carbon dioxide from the ternary mixture (SO_2 , CO_2 , and CO with ratio 20:40:40) at room pressure and temperature, as a function of the pore volume of the structures. Open symbols show the results obtained for channels-type zeolites and closed symbols to the interconnected cages-type zeolites. The directionality of the pore space is represented by circles (1D), squares (2D), or diamonds (3D). Zeolites with self-diffusion coefficients in orders between 10^{-9} and 10^{-9} m^2/s are colored in green, those around 10^{-10} m^2/s in red, and the rest in grey.

IV. Conclusions

We employed a combination of experiments and molecular simulations to study adsorption and diffusion processes of sulfur dioxide, carbon dioxide, and carbon monoxide in zeolites. Our work shows that out of the three molecules, sulfur dioxide has the strongest interaction with the frameworks due to its largest size and polarity. We screened zeolite structures taking into account not only low coverage adsorption properties but also the adsorption capacity, selectivity, and so forth at the temperature and/or pressure relevant of the separation process. This study outperforms previous works and demonstrates that the prediction of materials for separation uses should be based on both adsorption and diffusion performance.

For the selective adsorption of SO_2 over CO_2 and CO at atmospheric pressure and room temperature, zeolitic structures with channels-type pore topology and low pore volumes, such as JRY or NAT, are the most adequate. However, to separate carbon dioxide from carbon monoxide as a second step of this removal process, higher pressures (or lower temperatures) would be necessary to improve the selectivity and adsorption capacity. On the other hand, structures with high pore volumes, such as AFY, FAU or SBE, could exhibit better storage capacity also working at higher pressure.

We reemphasize that each of the studied structures performs better under different conditions, and pose different opportunities for applications in adsorption, diffusion, and separation. Our study provides an interesting perspective to obtain useful information on their optimum working conditions in terms of pressure and temperature to achieve high gas adsorption capacities and SO_2 selectivity. This knowledge could be used for further enhancement of a variety of adsorption/separation processes.

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Notes and references

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Zeolite Screening for the Separation of Mixtures Containing SO₂, CO₂ and CO gases

Electronic Supporting Information

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Table S1. Topological and geometrical parameters describing pore systems in IZA zeolites. Each structure is characterized in terms of number of pore systems (#PS). For structures with #PS>0, each pore system (PS ID) is characterized in terms of dimensionality (dim), the diameter of the largest spheres: included (Di), free (Df) and included along free sphere path (Dif) as well as the character of the pore system (C- channel, IC – interconnected cage).

Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC	Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC
ABW	2	0	3.61	3.1	3.61	1	C	APD	4	0	4.19	3.23	4.19	1	C
		1	3.61	3.1	3.61	1	C			1	4.2	3.23	4.2	1	C
ACO	1	0	3.9	3.16	3.9	3	C			2	4.2	3.23	4.2	1	C
AEI	1	0	6.9	3.44	6.9	3	IC			3	4.19	3.23	4.19	1	C
AEL	2	0	5.22	4.07	5.22	1	C	AST	0						
		1	5.22	4.07	5.22	1	C			ASV	1	0	4.95	4.03	4.95
AEN	2	0	3.9	3.18	3.9	2	C	ATN	2	0	5.51	3.71	5.51	1	C
		1	3.9	3.18	3.9	2	C			1	5.51	3.71	5.51	1	C
AET	2	0	7.77	7.16	7.77	1	C	ATO	3	0	5.34	5.09	5.34	1	C
		1	7.77	7.16	7.77	1	C			1	5.34	5.09	5.34	1	C
AFG	0									2	5.34	5.09	5.34	1	C
AFI	1	0	7.56	7.02	7.56	1	C	ATS	2	0	6.57	6.36	6.57	1	C
AFN	2	0	4.75	3.09	4.75	1	IC			1	6.57	6.36	6.57	1	C
		1	4.75	3.09	4.75	1	IC	ATT	1	0	4.88	3.39	4.88	2	C
AFO	2	0	5.03	4.33	5.03	1	C	ATV	2	0	3.9	3.04	3.9	1	C
		1	5.03	4.33	5.03	1	C			1	3.9	3.04	3.9	1	C
AFR	2	0	7.82	6.57	7.82	2	C	AWO	4	0	4.49	3.26	4.49	1	C
		1	7.82	6.57	7.82	2	C			1	4.49	3.26	4.49	1	C
AFS	1	0	9.11	5.61	9.11	3	IC			2	4.48	3.26	4.48	1	C
AFT	1	0	7.14	3.28	7.14	3	IC			3	4.48	3.26	4.48	1	C
AFX	1	0	7.11	3.33	7.11	3	IC	AWW	2	0	6.9	3.77	6.9	1	IC
AFY	1	0	7.42	5.5	7.42	3	C			1	6.88	3.77	6.88	1	IC
AHT	0							BCT	0						
ANA	0							BEA	1	0	6.1	5.63	6.1	3	C
APC	0							BEC	1	0	6.23	5.91	6.23	3	C

Table S2. Topological and geometrical parameters describing pore systems in IZA zeolites. Each structure is characterized in terms of number of pore systems (#PS). For structures with #PS>0, each pore system (PS ID) is characterized in terms of dimensionality (dim), the diameter of the largest spheres: included (Di), free (Df) and included along free sphere path (Dif) as well as character the of the pore system (C- channel, IC – interconnected cage).

Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC	Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC
BIK	2	0	3.76	3.14	3.76	1	C	CON	1	0	6.77	5.2	6.77	3	C
		1	3.76	3.14	3.76	1	C	CZP	1	0	3.75	3.24	3.75	1	C
BOF	2	0	5.15	4.18	5.15	1	C	DAC	2	0	4.79	3.4	4.79	2	C
		1	5.15	4.17	5.15	1	C			1	4.79	3.4	4.79	2	C
BOG	1	0	7.49	6.48	7.49	3	C	DDR	3	0	7.06	3.25	7.06	2	IC
BPH	1	0	9.11	5.61	9.11	3	IC			1	7.06	3.25	7.06	2	IC
BRE	0									2	7.06	3.25	7.06	2	IC
BSV	2	0	4.76	3.44	4.76	3	C	DFO	1	0	10.89	6.79	10.89	3	IC
		1	4.76	3.44	4.76	3	C	DFT	1	0	4.18	3.25	4.18	1	C
CAN	1	0	5.76	5.42	5.76	1	C	DOH	0						
CAS	0							DON	2	0	8.17	7.67	8.17	1	C
CDO	2	0	4.97	3.04	4.97	2	IC			1	8.17	7.67	8.17	1	C
		1	4.97	3.04	4.97	2	IC	EAB	2	0	6.62	3.14	6.62	2	IC
CFI	2	0	7.07	6.86	7.07	1	C			1	6.61	3.14	6.61	2	IC
		1	7.07	6.86	7.07	1	C	EDI	1	0	4.86	3.04	4.86	1	IC
CGF	0							EMT	1	0	10.99	6.97	10.99	3	IC
CGS	2	0	5.3	3.61	5.3	1	C	EON	3	0	5.6	2.84	5.6	2	IC
		1	5.31	3.61	5.31	1	C			1	7.27	6.39	7.27	1	C
CHA	1	0	6.74	3.32	6.74	3	IC			2	7.27	6.39	7.27	1	C
CHI	4	0	3.51	3.23	3.51	1	C	EPI	2	0	4.92	3.22	4.92	2	IC
		1	3.51	3.23	3.51	1	C			1	4.92	3.22	4.92	2	IC
		2	3.51	3.23	3.51	1	C	ERI	1	0	6.3	3.02	6.3	3	IC
		3	3.51	3.23	3.51	1	C	ESV	2	0	5.67	3.25	5.67	1	IC
CLO	2	0	15.32	5.91	15.32	3	IC			1	5.67	3.26	5.67	1	IC
		1	10.18	3.79	10.18	3	IC	ETR	1	0	9.61	8.92	9.61	1	C

Table S3. Topological and geometrical parameters describing pore systems in IZA zeolites. Each structure is characterized in terms of number of pore systems (#PS). For structures with #PS>0, each pore system (PS ID) is characterized in terms of dimensionality (dim), the diameter of the largest spheres: included (Di), free (Df) and included along free sphere path (Dif) as well as the character of the pore system (C- channel, IC – interconnected cage).

Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC	Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC
EUO	2	0	6.26	4.54	6.26	1	C	ISV	1	0	6.36	5.78	6.36	3	C
		1	6.26	4.54	6.26	1	C	ITE	4	0	7.77	3.81	7.77	1	IC
EZT	2	0	5.9	5.61	5.9	1	C			1	7.77	3.81	7.77	1	IC
		1	5.91	5.61	5.91	1	C			2	7.77	3.81	7.77	1	IC
FAR	0									3	7.77	3.81	7.77	1	IC
FAU	1	0	10.7	6.95	10.7	3	IC	ITH	1	0	6.28	4.67	6.28	3	C
FER	2	0	5.41	4.29	5.16	2	C	ITR	1	0	5.96	4.71	5.96	3	C
		1	5.41	4.29	5.16	2	C	ITW	2	0	4.16	3.47	4.16	1	C
FRA	0									1	4.16	3.47	4.16	1	C
GIS	1	0	4.57	2.87	4.57	3	IC	IWR	1	0	6.9	5.51	6.9	3	C
GIU	0						C	IWS	1	0	7.62	6.26	7.62	3	C
GME	1	0	7.11	6.68	7.11	3	C	IWV	2	0	8.12	6.63	8.12	2	C
GON	2	0	5.66	4.87	5.66	1	C			1	8.12	6.63	8.12	2	C
		1	5.66	4.87	5.66	1	C	IWW	1	0	6.55	5.84	6.55	3	C
GOO	0							JBW	1	0	3.85	3.32	3.85	1	C
HEU	4	0	5.21	3.27	5.21	1	IC	JRY	2	0	4.1	3.72	4.1	1	C
		1	4.68	3.1	4.68	1	IC			1	4.1	3.72	4.1	1	C
		2	4.68	3.1	4.68	1	IC	KFI	1	0	10.17	3.64	10.17	3	IC
		3	5.21	3.27	5.21	1	IC	LAU	2	0	5.47	3.67	5.47	1	C
IFR	2	0	6.56	5.98	6.56	1	C			1	5.47	3.67	5.47	1	C
		1	6.56	5.98	6.56	1	C	LEV	3	0	6.39	3.13	6.39	2	IC
IHW	2	0	6.07	3.27	6.07	2	IC			1	6.39	3.13	6.39	2	IC
		1	6.07	3.27	6.07	2	IC			2	6.39	3.13	6.39	2	IC
IMF	2	0	6.68	4.87	6.68	2	C	LIO	0						
		1	6.68	4.87	6.68	2	C	LIT	0						

Table S4. Topological and geometrical parameters describing pore systems in IZA zeolites. Each structure is characterized in terms of number of pore systems (#PS). For structures with #PS>0, each pore system (PS ID) is characterized in terms of dimensionality (dim), the diameter of the largest spheres: included (Di), free (Df) and included along free sphere path (Dif) as well as the character of the pore system (C- channel, IC – interconnected cage).

Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC	Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC
LOS	0							MRE	2	0	5.73	5.19	5.73	1	C
LOV	1	0	4.25	3.38	3.73	3	C			1	5.73	5.18	5.73	1	C
LTA	1	0	10.24	3.81	10.24	3	IC	MSE	1	0	6.49	5.98	6.49	3	C
LTF	2	0	7.76	7.1	7.76	1	C	MSO	0						
		1	6.51	6	6.51	3	C	MTF	2	0	5.58	3.63	5.58	1	IC
LTL	1	0	9.61	7.1	9.61	1	C			1	5.58	3.63	5.58	1	IC
LTN	0							MTN	0						
MAR	0							MTT	2	0	5.52	4.55	5.52	1	C
MAZ	2	0	7.69	7.1	7.69	1	C			1	5.52	4.54	5.52	1	C
		1	5.63	2.85	5.63	3	IC	MTW	2	0	5.31	5.08	5.31	1	C
MEI	1	0	7.66	6.45	7.66	1	C			1	5.31	5.08	5.31	1	C
MEL	1	0	6.87	4.77	6.87	3	C	MVY	0						
MEP	0							MWW	2	0	9.29	3.98	9.29	2	IC
MER	4	0	6.25	3.8	6.25	1	IC			1	5.73	4.17	5.73	2	C
		1	3.59	2.8	3.59	1	C	NAB	1	0	3.76	3.09	3.76	3	C
		2	6.25	3.8	6.25	1	IC	NAT	4	0	3.95	3.84	3.95	1	C
		3	3.59	2.8	3.59	1	C			1	3.95	3.84	3.95	1	C
MFI	1	0	5.94	4.28	5.94	3	C			2	3.95	3.84	3.95	1	C
MFS	2	0	6.21	4.94	6.21	1	C			3	3.95	3.84	3.95	1	C
		1	6.21	4.94	6.21	1	C	NES	2	0	6.17	4.66	6.17	2	C
MON	1	0	3.74	3.13	3.74	3	C			1	6.17	4.66	6.17	2	C
MOR	2	0	6.2	6.03	6.2	1	C	NON	0						
		1	6.2	6.03	6.2	1	C	NPO	1	0	3.34	3.1	3.34	1	C
MOZ	2	0	9.63	7.14	9.63	1	C	NSI	2	0	3.45	2.87	3.45	1	C
		1	6.5	6.05	6.48	3	C			1	3.45	2.87	3.45	1	C

Table S5. Topological and geometrical parameters describing pore systems in IZA zeolites. Each structure is characterized in terms of number of pore systems (#PS). For structures with #PS>0, each pore system (PS ID) is characterized in terms of dimensionality (dim), the diameter of the largest spheres: included (Di), free (Df) and included along free sphere path (Dif) as well as the character of the pore system (C- channel, IC – interconnected cage).

Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC	Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC
OBW	1	0	8.86	4.78	8.86	3	IC	RWR	4	0	3.92	2.83	3.92	1	C
OFF	1	0	6.49	6.04	6.49	3	C			1	3.92	2.83	3.92	1	C
OSI	2	0	6.26	5.88	6.26	1	C			2	3.92	2.83	3.92	1	C
		1	6.26	5.88	6.26	1	C			3	3.92	2.83	3.92	1	C
OSO	1	0	5.67	5.47	5.67	3	C	RWY	1	0	14	5.89	14	3	IC
OWE	1	0	5.2	3.38	5.2	2	IC	SAF	2	0	6.23	5.73	6.23	1	C
PAR	2	0	3.68	3.19	3.68	1	C			1	6.23	5.73	6.23	1	C
		1	3.68	3.19	3.68	1	C	SAO	1	0	8.22	6.28	8.22	3	C
PAU	3	0	10.08	3.66	10.08	3	IC	SAS	2	0	8.53	3.82	8.53	1	IC
		1	6.22	3.3	6.22	3	IC			1	8.54	3.82	8.54	1	IC
		2	10.08	3.66	10.08	3	IC	SAT	1	0	6.17	2.85	6.17	3	IC
PHI	2	0	5	3.23	5	2	IC	SAV	1	0	8.28	3.7	8.28	3	IC
		1	5	3.23	5	2	IC	SBE	2	0	12.09	6.81	12.09	3	IC
PON	2	0	4.5	3.9	4.5	1	C			1	12.09	6.81	12.09	3	IC
		1	4.5	3.9	4.5	1	C	SBN	2	0	4.39	3.4	4.39	2	C
PUN	1	0	4.98	3.95	4.97	3	C			1	4.4	3.4	4.4	2	C
RHO	2	0	10.03	3.66	10.03	3	IC	SBS	1	0	10.97	6.87	10.97	3	IC
		1	10.03	3.66	10.03	3	IC	SBT	1	0	10.39	6.94	10.38	3	C
RRO	2	0	3.87	3.51	3.87	1	C	SFE	1	0	6.23	5.81	6.23	1	C
		1	3.87	3.51	3.87	1	C	SFF	2	0	7.07	4.94	7.07	1	C
RSN	2	0	4.24	3.37	3.73	2	C			1	7.08	4.94	7.08	1	C
		1	4.24	3.37	3.73	2	C	SFG	1	0	6.35	4.98	6.35	2	C
RTE	2	0	6.4	3.58	6.4	1	IC	SFH	4	0	7.66	6.36	7.66	1	C
		1	6.4	3.58	6.4	1	IC			1	7.66	6.36	7.66	1	C
RTH	2	0	7.63	3.74	7.63	1	IC			2	7.66	6.35	7.66	1	C
		1	7.63	3.74	7.63	1	IC			3	7.66	6.35	7.66	1	C
RUT	0							SFN	2	0	7.46	6.3	7.46	1	C
										1	7.46	6.3	7.46	1	C

Table S6. Topological and geometrical parameters describing pore systems in IZA zeolites. Each structure is characterized in terms of number of pore systems (#PS). For structures with #PS>0, each pore system (PS ID) is characterized in terms of dimensionality (dim), the diameter of the largest spheres: included (Di), free (Df) and included along free sphere path (Dif) as well as the character of the pore system (C- channel, IC – interconnected cage).

Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC	Zeolite	#PS	PS ID	Di	Df	Dif	dim	PC
SFO	2	0	7.48	6.55	7.48	2	C	TOL	0						
		1	7.48	6.55	7.48	2	C	TON	2	0	5.04	4.65	5.04	1	C
SFS	1	0	7.03	5.47	7.03	2	C			1	5.04	4.65	5.04	1	C
SGT	0							TSC	1	0	15.86	3.68	15.85	3	IC
SIV	1	0	4.98	3.28	4.98	3	IC	TUN	1	0	8.04	4.99	8.04	3	IC
SOD	0							UEI	4	0	5.11	3.36	5.11	1	IC
SOF	1	0	4.74	3.82	4.74	3	C			1	5.11	3.36	5.11	1	IC
SOS	2	0	4.38	3.81	4.38	1	C			2	5.11	3.36	5.11	1	IC
		1	4.38	3.82	4.38	1	C			3	5.11	3.36	5.11	1	IC
SSF	1	0	7.26	5.76	7.26	2	C	UFI	2	0	9.69	3.49	9.69	2	IC
SSY	2	0	6.92	5.54	6.92	1	C			1	9.69	3.49	9.69	2	IC
		1	6.93	5.53	6.93	1	C	UOS	2	0	5.3	3.73	5.3	1	C
STF	2	0	7.22	5.04	7.22	1	C			1	5.3	3.74	5.3	1	C
		1	7.22	5.04	7.22	1	C	UOZ	0						
STI	4	0	5.81	4.53	5.81	1	C	USI	2	0	6.32	5.84	6.32	2	C
		1	5.81	4.54	5.81	1	C			1	6.32	5.84	6.32	2	C
		2	5.81	4.54	5.81	1	C	UTL	2	0	8.7	7.12	8.7	2	C
		3	5.81	4.54	5.81	1	C			1	8.7	7.12	8.7	2	C
STO	4	0	6.4	5.35	6.4	1	C	VET	1	0	5.99	5.58	5.99	1	C
		1	5.75	4.96	5.75	1	C	VFI	1	0	11.4	10.99	11.4	1	C
		2	6.31	5.61	6.31	1	C	VNI	0						
		3	6.35	5.39	6.35	1	C	VSV	4	0	3.73	3.37	3.73	2	C
STT	2	0	6.56	3.66	6.56	1	IC			1	3.73	3.37	3.73	2	C
		1	6.56	3.66	6.56	1	IC			2	3.73	3.37	3.73	2	C
STW	1	0	4.9	4.48	4.9	3	C			3	3.73	3.37	3.72	2	C
SVR	1	0	5.34	4.55	5.34	3	C	WEI	1	0	3.79	3.03	3.79	3	C
SZR	1	0	5.58	4.29	5.58	3	C	WEN	1	0	4.96	3.62	4.96	2	C
TER	2	0	6.17	4.68	6.17	2	C	YUG	0						
		1	6.17	4.68	6.16	2	C	ZON	2	0	5.2	3.12	5.2	1	IC
THO	2	0	4.47	3.29	4.47	1	C			1	5.2	3.12	5.2	1	IC
		1	4.48	3.29	4.48	1	C								

Table S7. Unit cell length and angle, pore volume, surface area, and references of the crystallographic positions of some representative zeolites used in this study. The selection is based on pore character and pore space dimensionality.

Zeolite	Crystallographic positions	Unit cell			Angles unit cell			Pore Volume (cm ³ /g)	SSA (Helium) (m ² /g)
		a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)		
ASV	Baerlocher et al.	8.67	8.67	13.92	90	90	90	0.10	305.30
DON	Wessels et al.	14.97	8.48	30.03	90	102.65	90	0.17	508.77
ITW	Baerlocher et al.	10.45	15.03	8.95	90	90	90	0.10	382.27
JRY	Baerlocher et al.	8.17	9.20	17.29	90	90	90	0.09	333.56
LAU	Artioli and Stahl	14.85	13.17	7.54	90	110.32	90	0.13	471.29
LTL	Newsam	18.47	18.47	7.48	90	90	120	0.17	553.03
MOR	Gramlich	18.11	20.53	7.53	90	90	90	0.15	477.93
NAT	Baerlocher et al.	13.85	13.85	6.42	90	90	90	0.12	436.30
PON	Baerlocher et al.	8.91	9.21	16.09	90	90	90	0.09	329.22
AFR	Baerlocher et al.	22.31	13.57	6.97	90	90	90	0.25	817.97
FER	Morris et al.	18.72	14.07	7.42	90	90	90	0.13	407.45
IWV	Baerlocher et al.	27.83	26.08	13.94	90	90	90	0.27	883.36
NES	Baerlocher et al.	26.06	13.88	22.86	90	90	90	0.19	701.99
SFO	Baerlocher et al.	22.59	12.57	6.97	90	99.02	90	0.25	815.75
SFG	Baerlocher et al.	25.53	12.58	13.07	90	90	90	0.14	494.75
TER	Baerlocher et al.	9.81	23.65	20.24	90	90	90	0.18	647.26
AFY	Baerlocher et al.	12.33	12.33	8.60	90	90	120	0.29	1208.05
BEC	Baerlocher et al.	12.77	12.77	12.98	90	90	90	0.28	979.93
BOG	Pluth and Smith ENREF 43	20.24	23.80	12.80	90	90	90	0.24	817.50
MEL	Fyfe et al.	20.07	20.07	13.41	90	90	90	0.15	544.96
MFI	van Koningsveld et al.	20.02	19.90	13.38	90	90	90	0.16	547.66
ITR	Baerlocher et al.	11.67	21.97	25.17	90	90	90	0.16	572.09
SBT	Baerlocher et al.	17.19	17.19	41.03	90	90	120	0.34	1057.79
STW	Baerlocher et al.	11.89	11.89	29.92	90	90	120	0.20	804.89
SZR	Baerlocher et al.	18.87	14.40	7.51	90	90	90	0.12	398.51
ITQ-3	Cambor et al.	20.62	9.72	19.62	90	90	90	0.23	693.71
MTF	Baerlocher et al.	9.63	30.39	7.25	90	90.45	90	0.09	263.69
SAS	Baerlocher et al.	14.35	14.35	10.40	90	90	90	0.26	794.61
DDR	Gies	13.86	13.86	40.89	90	90	120	0.14	400.48
LEV	Merlino and Alberti	13.34	13.34	23.01	90	90	120	0.15	706.26
MWW	Baerlocher et al.	14.39	14.39	25.20	90	90	120	0.23	801.23
CHA	Calligaris et al.	9.46	9.46	9.46	94.1	94.1	94.1	0.25	893.81
ERI	Gard et al.	13.27	13.27	15.05	90	90	120	0.22	716.96
FAU	Hriljac et al.	24.26	24.26	24.26	90	90	90	0.33	1020.96
ITQ-29	Corma et al.	11.87	11.87	11.87	90	90	90	0.29	849.36
KFI	Parise et al.	18.67	18.67	18.67	90	90	90	0.23	786.75
PAU	Gordon et al.	35.09	35.09	35.09	90	90	90	0.16	538.21
RHO	McCusker and Baerlocher	15.03	15.03	15.03	90	90	90	0.25	783.40
SBE	Baerlocher et al.	18.53	18.53	27.13	90	90	90	0.32	938.11

Table S8. Computed amount of adsorbed molecules and adsorption selectivity from the ternary mixture (SO₂/CO₂/CO with ratio 20:40:40). These values were taken from the adsorption isotherms obtained from Monte Carlo simulations at room conditions for temperature and pressure.

Zeolite	SO ₂ loading (mol/kg)	CO ₂ loading (mol/kg)	CO loading (mol/kg)	S SO ₂ /CO ₂	S CO ₂ /CO
ASV	1.750	0.040	0.005	86.761	8.730
DON	1.062	0.235	0.016	9.029	14.816
ITW	2.810	0.024	0.008	238.558	3.018
JRY	2.682	0.021	0.002	256.479	9.693
LAU	2.226	0.107	0.003	41.689	31.387
LTL	1.412	0.245	0.014	11.547	17.406
MOR	2.472	0.164	0.004	30.059	40.659
NAT	3.829	0.052	0.007	147.817	7.755
PON	2.620	0.021	0.002	247.229	8.635
AFR	3.055	0.341	0.016	17.928	21.103
FER	2.295	0.021	0.001	220.820	20.079
IWV	3.033	0.362	0.016	16.744	22.008
NES	1.791	0.331	0.010	10.822	33.355
SFO	2.830	0.359	0.017	15.754	20.809
SFG	1.925	0.119	0.005	32.325	26.184
TER	2.924	0.160	0.003	36.443	53.852
AFY	6.780	0.084	0.006	161.626	14.905
BEC	2.097	0.481	0.020	8.723	23.992
BOG	2.528	0.393	0.012	12.855	31.683
MEL	2.594	0.054	0.002	95.872	35.978
MFI	2.748	0.055	0.001	100.558	47.259
ITR	2.321	0.149	0.006	31.163	24.254
SBT	0.968	0.324	0.039	5.980	8.388
STW	4.519	0.037	0.003	247.469	13.430
SZR	2.407	0.036	0.003	133.290	12.950
ITQ-3	3.116	0.259	0.004	24.059	71.405
MTF	1.249	0.047	0.002	52.800	21.257
SAS	2.335	0.415	0.016	11.244	25.918
DDR	1.610	0.133	0.003	24.137	52.881
LEV	1.928	0.367	0.009	10.501	40.805
MWW	2.933	0.264	0.010	22.198	26.446
CHA	2.409	0.369	0.013	13.057	27.801
ERI	2.191	0.252	0.008	17.371	32.525
FAU	0.803	0.278	0.035	5.778	7.925
ITQ-29	2.673	0.384	0.017	13.916	22.950
KFI	2.091	0.397	0.011	10.528	35.640
PAU	2.179	0.191	0.006	22.830	31.904
RHO	1.090	0.310	0.024	7.029	13.069
SBE	1.173	0.228	0.036	10.271	6.430

Table S9. Computed amount of adsorbed molecules and adsorption selectivity from the binary equimolar mixture (CO_2/CO). These values were taken from the adsorption isotherms obtained from Monte Carlo simulations at room conditions for temperature and pressure.

Zeolite	CO_2 loading (mol/kg)	CO loading (mol/kg)	S CO_2/CO	Zeolite	CO_2 loading (mol/kg)	CO loading (mol/kg)	S CO_2/CO
ITW	0.611	0.048	12.787	MTF	0.71	0.013	55.363
JRY	1.127	0.042	27.092	SAS	0.873	0.065	13.469
MOR	0.513	0.094	5.477	DDR	0.946	0.026	36.461
FER	1.451	0.035	41.73	LEV	1.116	0.051	21.68
SFG	0.823	0.034	23.958	MWW	1.148	0.053	21.579
TER	1.241	0.062	20.024	CHA	0.915	0.061	14.923
MEL	1.619	0.034	47.466	FAU	0.255	0.046	5.567
MFI	1.551	0.042	36.63	PAU	0.832	0.047	17.742
STW	1.84	0.06	30.782	RHO	0.384	0.054	7.16
ITQ-3	1.252	0.061	20.45	SBE	0.406	0.059	6.918

Figure S1. Vapor-liquid equilibrium curve of sulfur dioxide: Comparison of experimental¹ (blue squares) and simulation data (red circles). Note that the force field performs well even near the critical point, where it is well established that Gibbs Ensemble Monte Carlo provides values with large error bars².

Figure S2. Pore landscapes of the selected 1D and 2D channels-type zeolites. The inner surface of the pores is highlighted in yellow. The color codes for atoms are red and beige for oxygen and silicon, respectively.

3D Channels: 1st row: AFY, BEC, BOG, MEL; 2nd row: MFI, ITR, SBT; 3rd row: STW, SZR

Figure S3. Pore landscapes of the selected 3D channels-type zeolites. The inner surface of the pores is highlighted in yellow. The color codes for atoms are red and beige for oxygen and silicon, respectively.

1D interconnected cages: ITE, MTF, SAS

2D interconnected cages: DDR, LEV, MWW

3D interconnected cages: 1st row: CHA, ERI, FAU, LTA; 2nd row: KFI, PAU; 3rd row: RHO, SBE

Figure S4. Pore landscapes of the selected zeolites of three considered classes of interconnected cages. The inner surface of the pores is highlighted in yellow. The color codes for atoms are red and beige for oxygen and silicon, respectively.

Figure S5. Average occupation profiles of carbon monoxide (second row), carbon dioxide (third row), and sulfur dioxide (fourth row) obtained for one molecule in TER zeolite. The figure shows the projection of the center of mass of the molecules over the x-y (left), and y-z (right) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (first row). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part is colored in blue and the non-accessible part is colored in gray).

Figure S6. Average occupation profiles of carbon monoxide (second row), carbon dioxide (third row), and sulfur dioxide (fourth row) obtained for one molecule in SFG zeolite. The figure shows the projection of the center of mass of the molecules over the x-y (left), y-z (middle), and x-z (right) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (first row). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part appears in blue and the non-accessible part is colored in gray).

Figure S7. Average occupation profiles of carbon monoxide (second row), carbon dioxide (third row), and sulfur dioxide (fourth row) obtained for one molecule in NES zeolite. The figure shows the projection of the center of mass of the molecules over the x-y (left), z-y (middle), and z-x (right) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (first row). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part appears in blue and the non-accessible part is colored in gray).

Figure S8. Average occupation profiles of carbon monoxide (second row), carbon dioxide (third row), and sulfur dioxide (fourth row) obtained for one molecule in MFI zeolite. The figure shows the projection of the center of mass of the molecules over the x-y (left), y-z (middle), and x-z (right) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (first row). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part is colored in blue and the non-accessible part is colored in gray).

Figure S9. Average occupation profiles of carbon monoxide (second row), carbon dioxide (third row), and sulfur dioxide (fourth row) obtained for one molecule in ITR zeolite. The figure shows the projection of the center of mass of the molecules over the x-y (left), y-z (middle), and x-z (right) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (first row). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part appears in blue and the non-accessible part is colored in gray).

Figure S10. Average occupation profiles of carbon monoxide (second row), carbon dioxide (third row), and sulfur dioxide (fourth row) obtained for one molecule in SZR zeolite. The figure shows the projection of the center of mass of the molecules over the x-y (left), y-z (middle), and x-z (right) planes. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (first row). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part appears in and while the non-accessible part is colored in gray).

Figure S11. Average occupation profiles of carbon monoxide (top right), carbon dioxide (bottom left), and sulfur dioxide (bottom right) computed for one molecule in MWW zeolite. The figure shows the projection of the center of mass of the molecules over the x-y plane. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (top left). The atomic structure is represented by oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted, where the accessible part appears in blue and the non-accessible part is colored in gray.

Figure S12. Average occupation profiles of carbon monoxide (top right), carbon dioxide (bottom left), and sulfur dioxide (bottom right) computed for one molecule in FAU zeolite. The figure shows the projections of the center of mass of the molecules over the x-y plane. The color graduation indicates the occupational density (from black to yellow). To guide the view we add a representation of the structure (top left). The atomic structure is represented by the oxygen and silica atoms in red and yellow respectively. A grid surface is also depicted (where the accessible part is colored in blue and the non-accessible part is colored in gray).

Notes and references

1. National Institute of Standards and Technology, <http://www.nist.gov/index.html>, Accessed January, 2013.
2. A. Z. Panagiotopoulos, Gibbs ensemble techniques, 1995.