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Molecular simulation study of wet flue gas adsorption on zeolite 13X

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ABSTRACT

Understanding the effect of moisture in an adsorbent that is selective to CO_2 over N_2 is central to the design and development of adsorption technology for CO_2 capture and concentration from power plant flue gas. Molecular simulations of wet flue gas adsorption on Zeolite 13X were here performed in the grand canonical (μVT) ensemble using the Monte Carlo technique in atomistic detail. The generated multicomponent isotherm data spanned the complete gas mixture composition range for adsorbing species CO_2, N_2 and H_2O from 25 °C to 75 °C at 1atm. The adsorption simulations consisted of faujasite zeolite crystal structures with a fixed Si/Al ratio of 1.31, Na^+ cation mobility and beta sodalite cage blocking of CO_2 and N_2 using 4 Å radius virtual blocking spheres. Simulated equilibrium isotherm data demonstrated that the presence of even small amounts of water vapor in the gas mixture has a significant impact on the adsorbate loadings for the remaining gas components in Zeolite 13X. Structural analysis with radial distribution functions revealed a shift in CO_2 adsorption away from the framework structure towards α-cavity pore centres and exclusion from sites adjacent to Na^+(II) when H_2O is present in the gas mixture. A degree of competitive adsorption of CO_2 at Na^+(III) sites persists at up to 15% relative humidity (RH) at 298 K (0.5 mol% H_2O) with significant lateral adorbate-H_2O interactions but exclusion beyond that threshold. Lower CO_2 loadings were associated with the growth of hydrogen bonded clusters with major changes complete by RH = 20% at 298 K.

1. Introduction

Following the publication of the International Energy Agency (IEA) 2 °C scenario (2DS) [1], a target for the carbon capture industry of 4 Gigatonne CO_2 per year by 2040 was announced at the 22nd Session of the Conference of the Parties (COP 22) to the United Nations Framework Convention on Climate Change (UNFCCC) [2,3]. Rapid deployment of a first generation carbon capture technology to point sources of CO_2 emissions is required to quickly taper the rate of global warming and meet this target. Adsorption technology is one of the leading options currently being explored for post-combustion carbon dioxide capture and concentration (CCC) from flue gas. Among the adsorption based processes, Vacuum Swing Adsorption (VSA) on Zeolite 13X (Z13X or NaX) has been widely studied for CCC from (synthetic) dry flue gas containing 10–15% CO_2 in balance nitrogen. However, real flue gas will always contain moisture. Competition between H_2O and CO_2 for adsorption in Z13X has a large impact on the VSA process performance, leading to considerations for the use of a guard bed adsorbent such as silica gel [4] or alternative processes to dehydrate the feed gas to a suitable extent. However, in any real dehydration process, trace levels of moisture are expected in the exit gas stream. Despite the sensitivity of CO_2 capture performance of Z13X to moisture, wet flue gas on Z13X has been addressed in only a few adsorption process studies using extrapolation of limited available equilibrium data for CO_2/H_2O mixtures [4,5].

In general, adsorbate molecules can move across the adsorbent surface under the influence of a multi-faceted surface potential energy due to crystalline or amorphous pore structures, ionic and/or functionalized group distributions, crystallographic defects and impurities. During surface migration, adsorbates are therefore presented with a diverse and non-uniform energetic landscape with concomitant opportunities to interact with other adsorbates, depending on the local chemical and geometric environment. The combination of adsorbent heterogeneity and strong adsorbate interactions is an aspect that is particularly important to consider when polar H_2O molecules persist in the adsorbate layer. Lateral adsorbate intermolecular interactions can reduce the number of molecules of a species capable of interacting vertically with adsorption sites. The relative importance of vertical and lateral interactions evolve during an adsorption process as adsorbate composition changes and thus influences adsorbent selectivity for a

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species by potentially preventing the formation of a complete monolayer of that species. Additional complexity may arise during chemisorption when bound sites interact laterally with adsorbate or vacant sites. For physical adsorption on an ionic adsorbent, the overall potential energy ϕ is given by the sum of six terms [6]:

$$\phi = \phi_D + \phi_R + \phi_P + \phi_{F\mu} + \phi_{\dot{F}Q} + \phi_S \tag{1}$$

Equation (1) describes component interaction energies that include dispersion and repulsion, polarization/induction (electric field-induced dipole), electric field-permanent dipole, electric field gradient (EFG)-quadrupole and lateral adsorbate-adsorbate interaction energies, respectively. The first two terms are non-specific to an adsorbate and occur in all adsorbents. They represent attractive interactions caused by fluctuations in electron shells creating instantaneous dipoles that correlate with surrounding molecules and close-range repulsive interactions due to the finite size of molecules. These van der Waals (vdW) interactions vary as distances between interacting pairs change and may be represented using the Lennard-Jones(LJ) potential, with the distance between an interacting pair r, governed by the Boltzmann factor at a particular temperature. The next three terms are electrostatic in nature. For an ionic adsorbent with large enough ion separations to avoid field cancellations, a strong electric field can polarize an adsorbate with available outer shell electrons. The polarization potential energy, $\phi_P \propto 1/r^4$, depends on the sorbate static isotropic polarizability α, which typically increases with molecular weight or volume as the nuclear charge's control over electrons weakens and leaves more available for polarization. Despite the relatively low molecular weight of H_2O in flue gas, one may note from Table 1 that the asymmetric H_2O molecule with its lone pair electrons has a polarizability approaching that of linear N_2. A plot of the observed initial heat of adsorption against polarizability for inert sorbates with interaction energies $\phi_D + \phi_R + \phi_P$ on an adsorbent shows a monotone increasing characteristic curve for that adsorbent. Superimposing the initial heats of adsorption for adsorbates with electric moments, H_2O, N_2 and CO_2, against the characteristic curve for Z13X reveals by difference the importance of electrostatic potentials among the components of wet flue gas adsorption on Z13X [7]. Calculations at the Density Functional Theory/Coupled Cluster (DFT/CC) level have confirmed that dispersion interactions account for approximately 50% of the overall adsorption enthalpy of pure CO_2 in faujasite zeolites [8].

The next two electrostatic and adsorbate-specific terms in equation (1) may be considered relative to each other: $\phi_{F\mu} \propto 1/r^2$ and $\phi_{\dot{F}Q} \propto 1/r^3$ [9], leading one to expect that adsorption of mixtures of polar and quadrupolar species may be dominated by electric field-dipole interactions in ionic based molecular sieve adsorbents rather than the interaction of EFGs with quadrupoles. A smaller ionic radius, 0.97 Å for Na^+ in the zeolite structure, has a larger impact in determining the pairwise distance r and the ionic charge magnitude further influences the contribution of the electrostatic potentials to the total interaction energy of adsorption, ϕ, or heat of adsorption. The last term in equation (1) is typically considered secondary in a representation of the correct landscape for the adsorption energy distribution (AED) primarily by the former terms in the same equation. For non-ideal mixtures in particular, this assumption needs to be considered with caution when both polar and ionic species are present. Table 1 further details important physical properties of the three major constituents of flue gas, including kinetic diameter [10], dipole moment [11], quadrupole moment [12,13], polarizability [9] and possible Infra-Red (IR) activity. Kinetic diameters of molecules in their ground states are here based on published empirical fitting of virial coefficient data to LJ potentials and later reviewed for dry gases using *ab initio* quantum mechanical(QM) calculations to have a basis with an iso-electronic density level of 0.0015 a.u. or e/a_0^3, where e is the elementary charge and a_0 is the Bohr radius [14]. Only the first non-zero multipole moments of molecules are shown in Table 1 (scalar properties independent of the reference system).

Table 1
Physical parameters of the major constituents of conventional fossil fuel combustion power plant flue gas mixtures.

Molecular Property	CO_2	N_2	H_2O
			
d (Å) [10]	3.30	3.64	2.65
μ (D) [11]	0.00	0.00	1.8546
Q x 10^{40} (Cm^2) [12,13]	-14.31 ± 0.74	-4.65 ± 0.08	~ 0.0
α x 10^{24} (cm^3) [9]	2.91	1.74	1.45
IR activity, ν (cm^{-1})	670, 2350	–	1590, 3660, 3760

d = Kinetic Diameter; μ = Dipole Moment; Q = Quadrupole Moment; α = Polarizability
1 $Debye(D) \approx 3.33564x10^{-30}Cm$; $e = 1.6022 \times 10^{-19}$ C; $a_0 = 5.29 \times 10^{-11}$ m.

Considering the dry flue gas components in Table 1, the close size of CO_2 and N_2 molecules (~0.34 Å difference in empirical kinetic diameters) but differing quadrupole moments and polarizabilities, suggests the nature of physisorbents that could be effective to separate these species based on equilibrium selectivity. These include adsorbents with strong EFGs along the adsorbate molecular axis of symmetry caused by asymmetrical or strongly localized point charge distributions on the adsorbent surface. In this case, both the position *and* orientation of the quadrupolar adsorbate molecule contribute to the electrostatic interaction. The orientation dependent quadrupolar interaction energy may cause a loss in rotational freedom of the sorbate compared to the bulk gas phase that can be investigated experimentally and indeed found to occur for CO_2 and N_2 in the supercages of Z13X [6].

A comparison of pure component ppm level adsorption of CO_2 and H_2O in balance N_2 on natural chabazite, Z13X and alumina has been made for air pre-purification systems [15]. It should be noted that NaA is more commonly considered a drying agent alternative to Silica Gel (SG) in engineering applications. It is suited to obtain bone dry air due to a strong hydrophilic character and small pores but has a lower working capacity than alumina for PSA air drying applications [16]. A comparison of the adsorption isotherms for H_2O on 4A Zeolite and alumina in this study illustrated the importance of equilibrium isotherm shape at low partial pressures for adsorbent selection. A review of the factors that influence CO_2 adsorption in zeolites highlighted that the presence of moisture can favour the formation of bicarbonates, which increases the energy required for regeneration of more strongly bound CO_2 [17]. Chemisorption of CO_2 with oxygen bridging sites in zeolite frameworks to form carbonates can also decrease the accessibility of CO_2 to cations and thus inhibit CO_2 adsorption. This study also raised pore size as a factor for comparing CO_2/N_2 selectivity and CO_2 adsorption capacity by comparing NaA and NaX zeolites. Small pores in NaA can afford greater selectivity but lower capacity for CO_2 while furthermore a three-dimensional pore structure in NaX facilitates transport of CO_2 and thus separation performance.

For pure gas adsorption in ionic adsorbents, an increase in surface coverage and lateral interactions can shield electrostatic interactions with solvated cations and decrease the isosteric heat of adsorption with loading to different extents in the order $H_2O > CO_2 > N_2$. Pure species isosteric heats of adsorption may be briefly described [18]. A decreasing trend with loading as strongly bound sites occupy before weakly bound sites fill indicates energetic heterogeneity. An increasing trend with loading, typically at intermediate to high loadings, is indicative of lateral interactions. The absence of a trend with loading indicates energetic homogeneity. The shielding of the electrostatic field by water adsorption in zeolite ZSM5 has been discussed in terms of a loss of orientational freedom of H_2O molecules to facilitate clathrate formation at high loadings [19]. With Na^+ cations at the clathrate cores, hydrogen bonding within a clathrate can raise the heat of adsorption at higher loadings. It should be noted that Z13X has a significantly higher micropore volume and cation density than ZSM5, thus facilitating a greater extent of hydrogen bonding and clathrate