A COMPUTATIONAL STUDY OF CO_2, N_2, AND CH_4 ADSORPTION IN ZEOLITES

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The adsorption properties of CO_2, N_2 and CH_4 in all-silica zeolites were studied using molecular simulations. Adsorption isotherms for single components in MFI were both measured and computed showing a very good agreement. In addition simulations in other all silica structures were performed for a wide range of pressures and temperatures and for single components, binary, and ternary mixtures with several bulk compositions. The adsorption selectivity was analyzed for mixtures with bulk composition of 50:50 CO_2/CH_4, 50:50 CO_2/N_2, 10:90 CO_2/N_2 and 5:90:5 $CO_2/N_2/CH_4$ in MFI, MOR, ISV, ITE, CHA and DDR showing high selectivity of adsorption of CO_2 over N_2 and CH_4 that varies with the type of crystal and with the mixture bulk composition.

INTRODUCTION

The development of new advanced adsorbents for gas separation in many industrial applications via adsorption processes is receiving increasing attention. These materials need to be characterized for a wide variety of gases. Zeolites as adsorbents are rapidly becoming the technology of choice for the petroleum and chemical industry for minimizing their emissions to the environment, mainly volatile organic compounds. Besides their well-known importance in many industrial catalytic processes, zeolites are currently finding broad applications in industry, especially in environmentally sensitive industrial processes. Separation of methane, nitrogen, and carbon dioxide mixtures is a challenging research topic for both environmental and economical reasons. From the environmental point of view, it is necessary to develop effective separation technologies to reduce the carbon dioxide emissions that are noticeably increasing due to the use of fossil fuels. From the economical point of view, the removal of carbon dioxide from natural gas and the recovery of methane from landfill gas (containing methane, carbon dioxide and small amounts of nitrogen) are examples of interesting separations. Among the potential routes explored for gas separations, adsorption processes involving zeolites have shown an increasing importance because these materials have a high thermal, mechanical, and chemical stability. Besides, the zeolite pores have a size comparable to the molecular dimensions of many substances (Breck, 1974) and therefore they show peculiar mechanisms of diffusion in which the framework plays the most important role (Auerbach et al., 2003; Dubbeldam et al., 2005; Dubbeldam et al., 2003; Krishna et a., 2002).

Zeolites are aluminosilicates with crystalline structures constructed from TO_4 tetrahedra (T = Si, Al). These crystals are characterized by a uniform three-dimensional pore

system, with pores that vary in shape and of precisely defined diameters within molecular dimensions. Most of the zeolitic materials investigated to date for separations of mixtures involving carbon dioxide, nitrogen, and methane belong to the MFI-type (Bernal et al., 2004; Gardner et al., 2002; Harlick and Tezel, 2002; Makrodimitris et al., 2001; Poshusta et al. 1999; van den Broeke et al., 1999; Yu et al., 2006), although other structures such as MOR (Delgado et al., 2006), LTA (Goj et al., 2002; Nam et al., 2005), FAU (Hasegawa et al., 2001; Jia and Murad, 2004; Kusakabe et al., 1999), DD3R (Himeno et al., 2006; Tomita, et al., 2004), CHA (Grey et al., 2001), and SAPO-34 (Bodoardo et al., 2005; Poshusta et al., 1998) have also been studied. The mechanism for separation in zeolites can be quite complex since variations in the size and geometry of the cavities and pores will contribute to the overall performance of the zeolites (Krishna et al., 2002; Schenk et al., 2002).

Molecular simulations are currently playing an important role in developing our understanding of the relation between microscopic and macroscopic properties of confined molecular fluids in zeolites (Auerbach et al., 2003; Dubbeldam et al., 2003; Maesen et al., 2006). A good knowledge of the adsorption properties of these materials can be helpful to explain the underlying mechanisms of adsorption and diffusion processes, as well as to identify further applications of zeolites as catalysts and adsorbents (Garcia-Perez et al., 2007)

METHODOLOGY

The adsorption isotherms were computed using Monte Carlo (MC) simulations in the grand canonical (GC) ensemble. The zeolite lattices are rigid during simulations, with static atomic charges that are assigned by choosing $q_{Si} = +2.05$ and $q_O = -1.025$, following the work of Jaramillo and Auerbach (Jaramillo and Auerbach, 1999). The

crystallographic data are available elsewhere (Baerlocher et al., 2001). The interactions between guest molecules adsorbed (CO_2, N_2, and CH_4) with other adsorbates and with the zeolite are modelled by Lennard-Jones and Coulombic potentials. The Coulombic interactions in the system are calculated by Ewald summation for periodic systems (Frenkel and Smit, 2002). The interactions dominated between adsorbed molecules and the zeolite are dispersive forces between the pseudo-atoms and the oxygen atoms of the zeolite (Bezus et al., 1978; Kiselev et al., 1985) and the interactions of silicon and aluminium are considered through an effective potential with only the oxygen atoms. The internal structure of the adsorbate and the adsorbate-adsorbate interactions are as important as the properties dominated by the strong interactions with the force field produced by the zeolite (adsorbate-adsorbent). We are using force field parameters that accurately reproduce the properties of pure gas adsorption of CO_2, N_2, and CH_4, as well as their mixtures in different types of all-silica zeolites. Most of these force field parameters were firstly fitted to reproduce the adsorption isotherms in silicalite and secondly validated in other pure silica structures. CH_4 molecules are described with an united atom model, in which each molecule is treated as a single interaction center (Ryckaert and Bellemans, 1978). CO_2 molecules are taken linear and rigid with bond length C–O of 1.16Å according to the model developed by Harris and Young (Harris and Yung, 1995). N_2 molecules are modeled as a dumbbell with a rigid interatomic bond of 1.098Å. The partial charges of N_2 and CO_2 are distributed around each molecule to reproduce experimental quadrupole moment. The interaction between adsorbed molecules is described with Coulombic and Lennard-Jones terms. The parameters for methane are taken from Dubbeldam *et al.* (Dubbeldam et al., 2004b) and Calero *et al.*(Calero et al., 2004) . In this work we are using the model proposed by Harris *et al.* (Harris and Yung, 1995) for CO_2 and the model proposed by Murthy *et al.*

(Murthy and Singer, 1987) for N_2. These models were also used by Watanabe *et al*. (Watanabe et al. 1995) and Makrodimitris *et al.* (Makrodimitris et al., 2001). The partial charges and Lennard-Jones parameters used in our simulations are listed in Table 1. The Lennard-Jones potentials are shifted and cut at 12 Å. The number of unit cells in the simulation box was chosen such that the minimum length in each of the coordinate directions was larger than 24 Å. Periodic boundary conditions were employed. Further GCMC details are available in previous publications (Calero et al., 2004; Dubbeldam et al., 2004a; Dubbeldam et al., 2004b).

Experimental adsorption isotherms were performed for nitrogen and carbon dioxide in MFI at several temperatures. The zeolite used in this investigation was kindly supplied by ITQ and corresponds to a virtually pure porous crystalline silicon dioxide; the highly siliceous form of silicalite-1 with the MFI crystal structure. The porous network of the zeolite was characterized by means of helium density (2.36 g cm^{-3}) and N_2 adsorption isotherm at 77 K (see Figure X). In good agreement with literature (Llewellyn et al., 1993), the experimental N_2 isotherm at 77 K silicalite exhibits tow adsorption sub-steps. The initial adsorption step up to p/po < 0.1 corresponds to microporous pore filling. The second sub-step occurs at relative pressures between 0.1-0.3 and the volume adsorbed of nitrogen increase by 25 cm^3 STP g^{-1}. This behaviour has been interpreted as an adsorbate transition from a lattice fluid-like phase to crystalline-like solid one (i.e., solidification type phase transition) (Llewellyn et al., 1993).

Detailed experimental methods were reported and discussed elsewhere (García-Pérez et al., 2006). Briefly, prior to the adsorption measurements the samples were outgassed in-situ under vacuum at 673 K overnight to remove any adsorbed impurities. A Micromeritics ASAP 2010 gas adsorption analyzer was used to accurately measure the N_2 uptake at 77 K in the pressure range from 10^{-4} kPa to 100 kPa. The instrument was

equipped with a molecular drag vacuum pump and three different pressure transducers (0.133 kPa, uncertainty within 0.12 % of reading; 1.33 kPa and 133 kPa, uncertainty within 0.15 % of reading) to enhance the sensitivity in the low-pressure range, which is especially useful in adsorption studies on microporous materials. The CO_2 adsorption isotherms were carried out in a TriStar 3000 from Micromeritics, using a circulating temperature-controlled bath, in the pressure range from 10^{-1} kPa up to 120 kPa. The gaseous adsorptives, N_2 and CO_2, where purchased with an ultra-high purity (i.e., 99.9992 and 99.995 %, respectively).

RESULTS AND DISCUSSION

We have performed molecular simulations to 1) reproduce our measured single component isotherms in MFI, 2) compare with available experiments of CH_4, CO_2, and N_2 single and binary mixtures in MFI, DDR, ITE and ISV zeolites (Baerlocher et al., 2001), 3) predict the location of the molecules in the crystal pores and 4) obtain ternary mixture adsorption isotherms for a given bulk composition. To study the ternary mixture adsorption behavior we have selected three structures with different type of porous: MOR (structure with one-dimensional channels), MFI (structure with intersecting channels), and CHA (structures with cages separated by narrow windows). Our computed and measured adsorption isotherms for CO_2 at 253K, 273K, and 303K are shown in Figure 1. Additional adsorption isotherms for CO_2 and N_2 in MFI were obtained for several temperatures and compared with available previous data. Figure 1 shows good agreement between our computed isotherm for N_2 at 308 K and the one of Goj *et al.* (Goj et al., 2002). Similar good agreement is observed between the data obtained in this work for CO_2 and the experimental measurements of Zhu *et al.* (Zhu et al., 2006), Hirotani *et al.* (Hirotani et al., 1997), Sun *et al.*(Sun et al., 1998), and

Choudhary et al. (Choudhary and Mayadevi, 1996). Adsorption isotherms of CO_2, CH_4, and N_2 in MOR were computed at 300 K and 210 K and compared with the isotherms of Delgado et al .(Delgado et al., 2006) and Webster et al. (Webster et al., 1999) as shown in Figure 2a. The calculated isotherms prove excellent agreement with experiments in all range of pressures. The small discrepancies between our results and the experimental values are due to the Si/Al ratio of the MOR structures used in the experimental measurements. Simulations were performed for pure silica MOR whereas experimental data for methane and CO_2 were obtained for H-MOR with Si/Al = 6 and 7 protons per unit cell, and experimental data of N_2 were obtained for Na-MOR with Si/Al = 20 and 2 sodium cations per unit cell.

Figure 2b compares the simulated isotherms of CO_2, CH_4, and N_2 in CHA with the experimental isotherms of Li et $al.(Cao$ et $al.,$ $2004)$ for SAPO-34 -an isotype of CHA- proving very good agreement up to the range of pressures used for the experimental isotherms. The computed values for N_2 are also in excellent agreement with previous data of Grey et $al.$ $(Grey$ et $al.,$ $2001)$.

Besides computing the adsorption of pure components in various zeolites, we have performed simulation on mixtures of the selected gases. Figure 3 shows the obtained adsorption isotherms for equimolar mixtures of CO_2/N_2 in MFI at 308 K (Figure 3a) and the computed adsorption selectivity for the equimolar and the 10:90 CO_2/N_2 bulk mixture in MFI at the same temperature (Figure 3b). Similar calculations were performed for ITE (50:50 bulk mixture) and ISV (50:50 and 10:90 bulk mixture) at 498 K and 308 K, respectively. The resulting simulation data are shown in Figure 4. The selectivity is defined as the ratio of adsorbed molar fraction over bulk molar fraction. Our results are consistent with the previous atomistic results of Goj et al(Goj et al.,

2002) proving for all the structures the preferential adsorption of CO_2 over N_2. The preferential adsorption of carbon dioxide is partially due to its large quadrupole moment that strengths the adsorbate-adsorbent coulombic interactions, thereby increasing the adsorption in the structure. A similar behavior can be therefore expected during the adsorption of CO_2/CH_4 mixtures and the obtained results in MFI and DDR structures are shown in Figure 5. The simulated isotherms are in concordance with previous experimental (Babarao et al., 2007; Zhu et al., 2006) results (Figure 5a). The adsorption selectivity is favorable for CO_2 in both cases and remains almost constant with the increase of pressure. The adsorption of CO_2 is almost unaffected by the presence of nitrogen, but N_2 adsorption is extremely sensitive to presence of CO_2. Figure 5b shows the isothermal-isobaric (100 kPa) gas phase adsorbed diagram for the mixture methane and carbon dioxide on DDR (298 K) and MFI (313 K). Our results indicate a fast rise in the mole fraction of CO_2 in adsorbed phases at low CO_2 fraction in gas phase. This behavior has also been observed by Himeno *et al.* (Himeno et al., 2006) and Harlick and Tezel (2003) in DDR and MFI respectively and is attributable to the dominant CO_2 adsorption in the binary system. Our results are in perfect agreement with those obtained by Himeno but show some discrepancies with the experimental data of Harlick and Tezel for MFI that can be explained by the differences in the structures. The simulations for this work have been performed in all silica MFI whereas Harlick and Tezel used ZSM-5. As we mentioned before the coulombic interactions between the CO_2 and the electric field of the zeolite will favor the preferential adsorption of carbon dioxide over methane in the structure. This selectivity will be enhanced in protonated aluminosilicates structures as ZSM-5 since these materials exhibit stronger local electric fields than the all silica zeolites.

The computed adsorption isotherms for 50:50 mixtures of CO_2 and CH_4 and 5:95 mixtures of CO_2 and N_2 in MOR are shown in Figure 6a and 6b, respectively. CO_2 adsorbs better than methane and N_2 in this structure for all range of pressures. MOR type structures consists of main parallel channels connected with small side channels called side-pockets. These pockets are the preferred adsorption sites for small molecules (such as CO_2, N_2 and CH_4) at room temperature. When these sites are filled, the main channels become occupied. In a mixture of CO_2 with CH_4 or N_2 the former adsorbs preferentially in the side pockets and the latter fill then the main channels. This can be clearly observed in Figure 6 from the snapshots taken from our simulations at 1000 kPa and room temperature. At the lower pressures CO_2 molecules adsorb in the side pockets and once these are full they adsorb in the main channels together with the CH_4 and N_2 molecules.

The adsorption isotherms for 5:5:90 bulk ternary mixture of CH_4, CO_2, and N_2 were computed at 300 K for a range of pressures that spans from 0.01 to 107 kPa. Figure 7 shows that as for the binary mixtures, CO_2 achieves the highest adsorption in all cases. The lower or higher CO_2 adsorption selectivity is decided by the shape and the size of the crystal pore. CO_2 achieves the highest adsorption when increasing the confinement due to a combination of entropic (it is bigger than CH_4 and N_2) and coulombic (higher quadrupole moment than CH_4 and N_2) effects. Hence, CHA with small cages separated by narrow windows provides higher selectivity than MOR -with wide one dimensional channels- and this one higher than MFI that is formed by three dimensional intersecting channels.

CONCLUSIONS

This work analyzes the adsorption behaviour of CO_2, N_2, and CH_4 in all silica zeolites. Isotherms for pure components were measured and computed, showing in all cases a very good agreement with previous available experiments. The adsorption selectivity for binary and ternary mixtures is always in favour of CO_2 and strongly depends on the type of structure and on the mixture bulk composition. Our simulations provide a tool to predict 1) the adsorption behaviour of multicomponent mixtures and 2) the location of the molecules for a given temperature, pressure, and bulk chemical composition.

Nomenclature

p   Pressure

po   Saturation pressure

q_{Si} Point charge of silicon

q_O Point charge of oxygen

FIGURE CAPTIONS

Figure 1: Computed (Sim) and measured (Exp) adsorption isotherms of CO_2 and N_2 in MFI-type zeolite. Previous experimental. (Choudhary and Mayadevi, 1996; Hirotani et al., 1997; Sun et al., 1998; Zhu et al., 2006) and simulation (Goj et al., 2002) data are included for comparison.
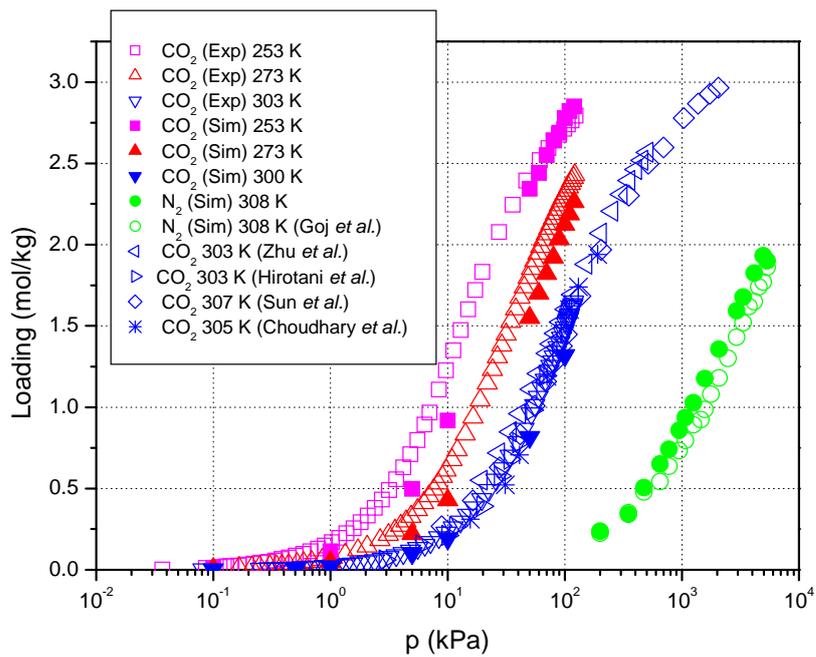
Figure 2: Computed adsorption isotherms of CO_2, CH_4, and N_2 in (a) MOR-type zeolite and (b) CHA-type zeolite at several temperatures. Available experimental data are included for comparison. (Cao et al., 2004; Delgado et al., 2006; Grey et al., 2001; Webster et al., 1999).

Figure 3: Molecular simulations of CO_2/N_2 mixtures in MFI at 308 K. a) Adsorption isotherm of the equimolar bulk mixture compared with previous simulation data(Goj et al., 2002) b) CO_2/N_2 selectivity for the equimolar (50:50) and the 10:90 bulk mixtures.

Figure 4: Molecular simulations of CO_2/N_2 mixtures in ITE (50:50 bulk mixture) and ISV (50:50 and 10:90 bulk mixture). Simulations were performed at 498 and 308 K, respectively and previous atomistic data are included for comparison (Goj et al., 2002).

Figure 5: Molecular simulations of CO_2/CH_4 mixtures in zeolites compared with previous experimental (Babarao et al., 2007; Harlick and Tezel, 2003; Zhu et al., 2006) and theoretical (Himeno et al., 2006) data. a) Equimolar bulk mixtures in MFI at 303 K b) Isothermal, isobaric (100 kPa) gas phase-adsorbed-phase diagram in DDR at 298 K and MFI at 313 K.

Figure 6: Computed adsorption isotherms of mixtures of CH_4, CO_2 and N_2 in MOR at 300 K. The snapshots show the molecular locations at 1000 kPa. a) 50:50 bulk CH_4/CO_2 mixture, b) 5:95 bulk CO_2/N_2 mixture.

Figure 7: Computed adsorption isotherms of the 5:5:90 bulk $CH_4/CO_2/N_2$ mixture in MFI, MOR, and CHA zeolites at 300 K.

Table 1. Partial charges and Lennard-Jones force field parameters for adsorbent-adsorbate and adsorbate-adsorbate interactions. Top-left corner ε / k_B (K). Bottom-right corner σ (Å)

	O_{zeo}	CH_4	C	O_{CO_2}	N
CH_4	115 　　　3.47	158.5 　　　3.72	66.77 　　　3.24	112.96 　　　3.38	75.96 　　　3.52
C	50.2 2.7815	66.77 　　　3.24	28.129 　　　2.76	47.59 　　　2.89	32.0 　　　3.04
O_{CO_2}	84.93 2.9195	112.96 　　　3.38	47.59 　　　2.89	80.507 　　　3.033	54.13 　　　3.18
N	58.25 3.062	75.96 　　　3.52	32.0 3.04	54.13 　　　3.18	36.4 　　　3.32

	O_{zeo}	C	O_{CO_2}	N	Dummy (N_2)
Charge [e⁻]	-1.025	+0.6512	-0.3256	-0.40484	+0.80968

Figure 1: Computed (Sim) and measured (Exp) adsorption isotherms of CO_2 and N_2 in MFI-type zeolite. Previous experimental. (Choudhary and Mayadevi, 1996; Hirotani et al., 1997; Sun et al., 1998; Zhu et al., 2006) and simulation (Goj et al., 2002) data are included for comparison.

Figure 2: Computed adsorption isotherms of CO_2, CH_4, and N_2 in (a) MOR-type zeolite and (b) CHA-type zeolite at several temperatures. Available experimental data are included for comparison. (Cao et al., 2004; Delgado et al., 2006; Grey et al., 2001; Webster et al, 1999).

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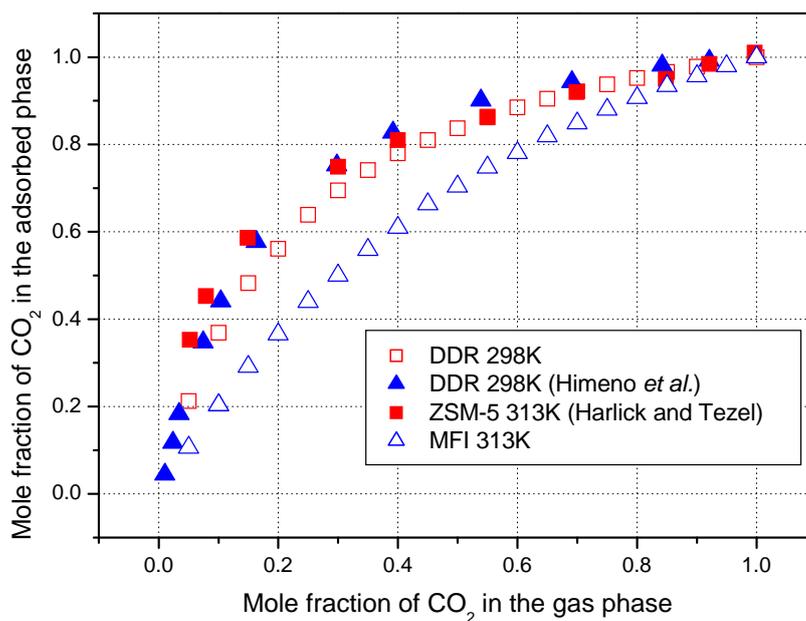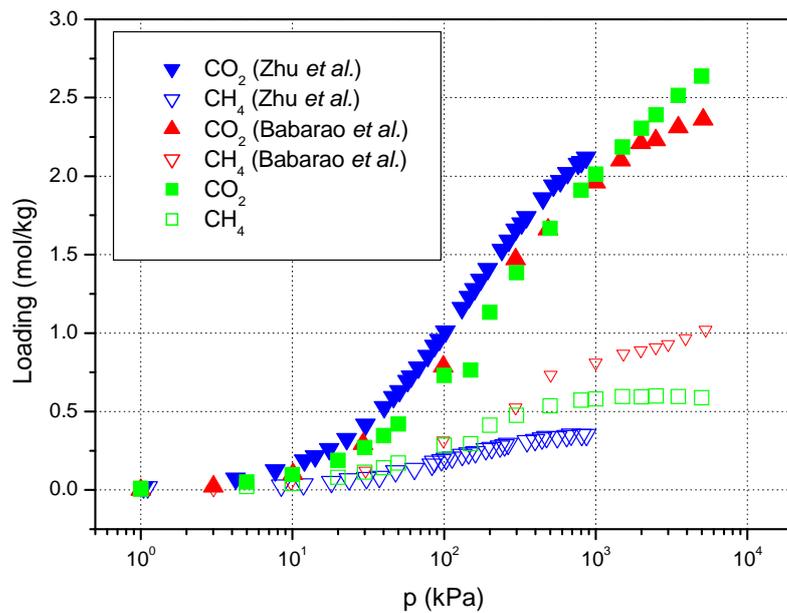
Figure 6: Computed adsorption isotherms of mixtures of CH_4, CO_2 and N_2 in MOR at 300 K. The snapshots show the molecular locations at 1000 kPa. a) 50:50 bulk CH_4/CO_2 mixture , b) 5:95 bulk CO_2/N_2 mixture.
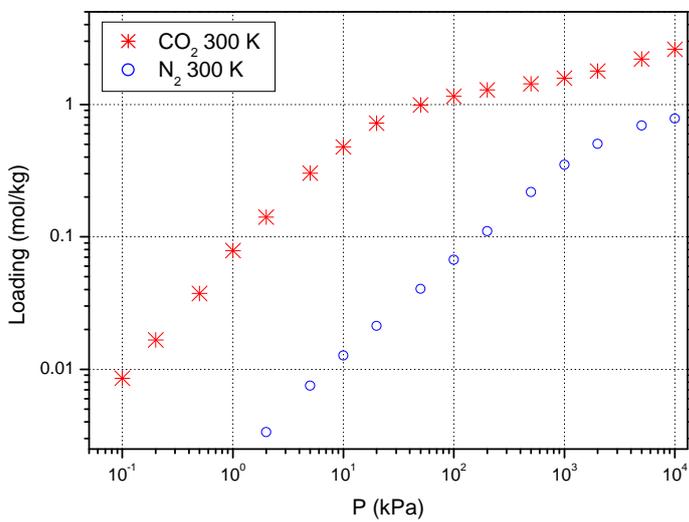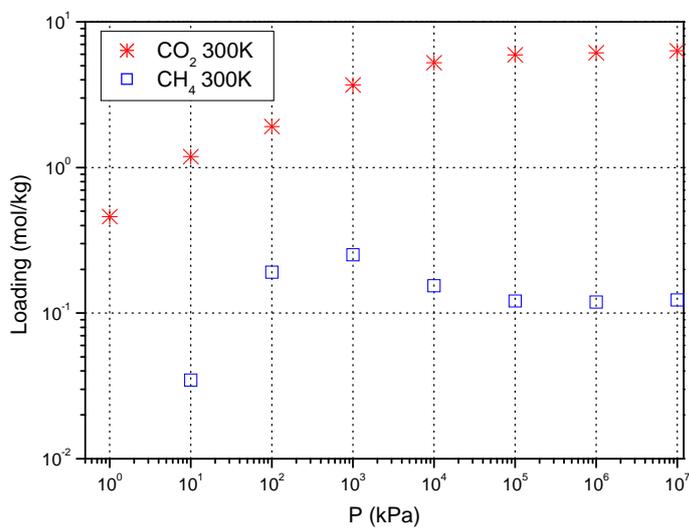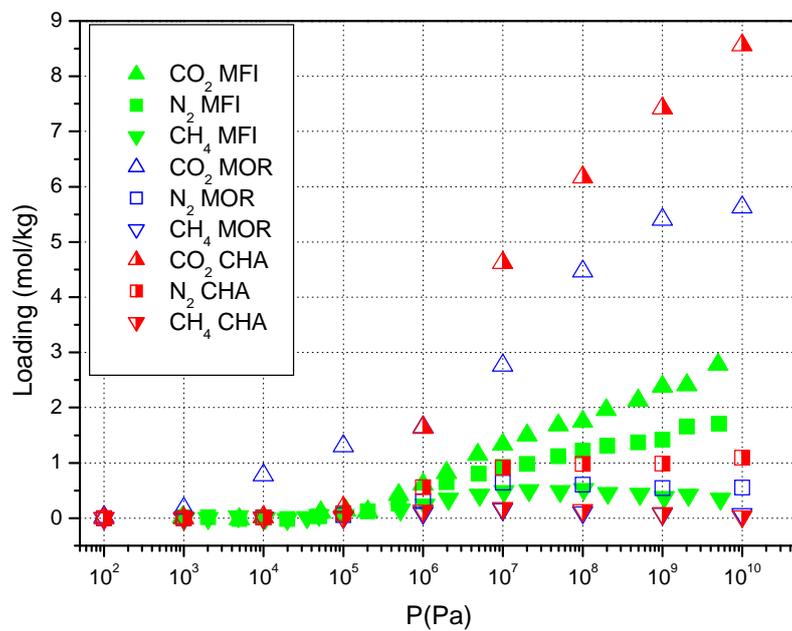
Figure 7: Computed adsorption isotherms of the 5:5:90 bulk $CH_4/CO_2/N_2$ mixture in MFI, MOR, and CHA zeolites at 300 K.

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