

A computational study of CO₂, N₂, and CH₄ adsorption in zeolites

E. García-Pérez · J.B. Parra · C.O. Ania ·
A. García-Sánchez · J.M. van Baten · R. Krishna ·
D. Dubbeldam · S. Calero

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Abstract The adsorption properties of CO₂, N₂ and CH₄ in all-silica zeolites were studied using molecular simulations. Adsorption isotherms for single components in MFI were both measured and computed showing good agreement. In addition simulations in other all silica structures were performed for a wide range of pressures and temperatures and for single components as well as binary and ternary mixtures with varying bulk compositions. The adsorption selectivity was analyzed for mixtures with bulk composition of 50:50 CO₂/CH₄, 50:50 CO₂/N₂, 10:90 CO₂/N₂ and 5:90:5 CO₂/N₂/CH₄ in MFI, MOR, ISV, ITE, CHA and DDR showing high selectivity of adsorption of CO₂ over N₂ and CH₄ that varies with the type of crystal and with the mixture bulk composition.

Keywords Adsorption isotherms · Zeolites · Separations · Carbon dioxide · Methane · Nitrogen

Abbreviations

p Pressure, Pa
p₀ Saturation pressure, Pa
q_{Si} Point charge of silicon
q_O Point charge of oxygen

1 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 emissions to the environment, of 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. The zeolite pores have a size comparable to the molecular dimensions of many

E. García-Pérez · S. Calero (✉)
Department of Physical, Chemical and Natural Systems,
University Pablo de Olavide, Ctra. Utrera km. 1, 41013 Seville,
Spain
e-mail: scalero@upo.es

J.B. Parra · C.O. Ania
Energy and Environment Department, Instituto Nacional del
Carbón, CSIC, P.O. 73, 33080 Oviedo, Spain

A. García-Sánchez · J.M. van Baten · R. Krishna
van 't Hoff Institute for Molecular Sciences, University of
Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam,
The Netherlands

D. Dubbeldam
Chemical and Biological Engineering Department, Northwestern
University, 2145 Sheridan Road, Evanston, IL 60208, USA

substances (Breck 1974) and therefore they show peculiar mechanisms of diffusion in which the framework geometry plays the most important role (Auerbach et al. 2003; Dubbeldam et al. 2003, 2005; Krishna et al. 2002).

Zeolites are aluminosilicates with crystalline structures constructed from TO_4 tetrahedra ($T = \text{Si}, \text{Al}$). These crystals are characterized by a uniform three-dimensional pore structure, with pores that vary in shape and of well-defined diameters of 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. 2007; Tomita et al. 2004), CHA (Grey et al. 2001), and SAPO34 (Bodoardo et al. 2005; Li 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 zeolite (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). We use here molecular simulations to analyze the influence of both, structure and bulk mixture composition on the adsorption of CH_4 , CO_2 , and N_2 , and on the selectivity performance of *all silica zeolites*. 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).

2 Methodology

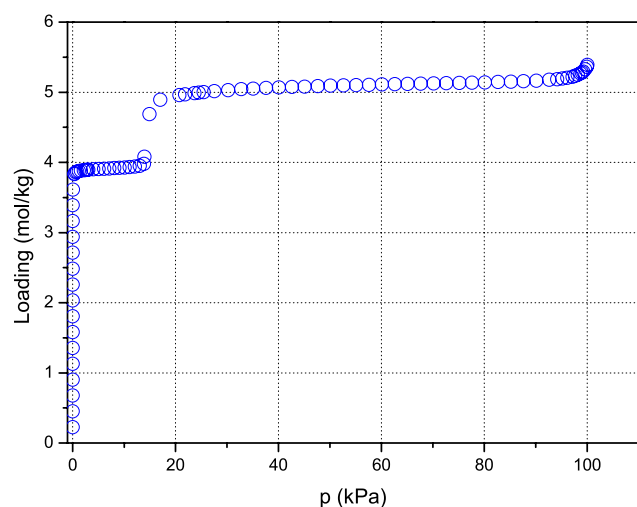
The adsorption isotherms were computed using Monte Carlo (MC) simulations in the grand canonical (GC) ensemble. The zeolite lattices are assumed rigid during simulations, with static atomic charges that are assigned by choosing $q_{\text{Si}} = +2.05$ and $q_{\text{O}} = -1.025$, following the work of 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 fitted to reproduce the adsorption isotherms in silicalite and 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 1.16 Å 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 1.098 Å. The partial charges of N_2 and CO_2 are distributed along 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. (2004b) and Calero et al. (2004). In this work we are using the model proposed by Harris et al. (1995) for CO_2 and the model proposed by Murthy et al. (1980) for N_2 . These models were also used by Watanabe et al. (1995) and 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, 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 (Lillerud 2001) 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 Fig. 1). In good agreement with literature (Llewellyn et al. 1993), the experimental N_2 isotherm at 77 K silicalite exhibits two adsorption sub-steps. The initial adsorption step up to $p/p_0 < 0.1$ 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 $25 \text{ cm}^3 \text{ STP g}^{-1}$. This behaviour has been interpreted

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 _{CO2}	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 _{CO2}	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 _{CO2}	N	Dummy (N ₂)
Charge [e ⁻]	-1.025	+0.6512	-0.3256	-0.40484	+0.80968

**Fig. 1** Measured adsorption isotherm of N₂ in MFI-type zeolite at 77 K

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 (Parra 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 N₂ 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 CO₂ adsorp-

tion 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 adsorbates, N₂ and CO₂, were purchased with an ultra-high purity (i.e., 99.9992 and 99.995%, respectively).

3 Results and discussion

We have performed molecular simulations to (1) reproduce our measured single component isotherms in MFI, (2) compare with available experiments of CH₄, CO₂, and N₂ 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 CO₂ at 253 K, 273 K, and 303 K are shown in Fig. 2. Additional adsorption isotherms for CO₂ and N₂ in MFI were obtained for several temperatures and compared with available previous data. Figure 2 shows good agreement between our computed isotherm for N₂ at 308 K and the one of Goj et al. (2002). Similar good agreement is observed between the data obtained in this work for CO₂ and the experimental measurements of Zhu et al. (2006), Hirotani et al. (1997), Sun et al. (1998), and Choudhary et al. (1996). Adsorption isotherms of CO₂, CH₄, and N₂ in MOR were computed at 300 K and 210 K and compared with the isotherms of Delgado et al. (2006) and Webster et al. (1999) as shown in Fig. 3a. The calculated isotherms show excellent agreement

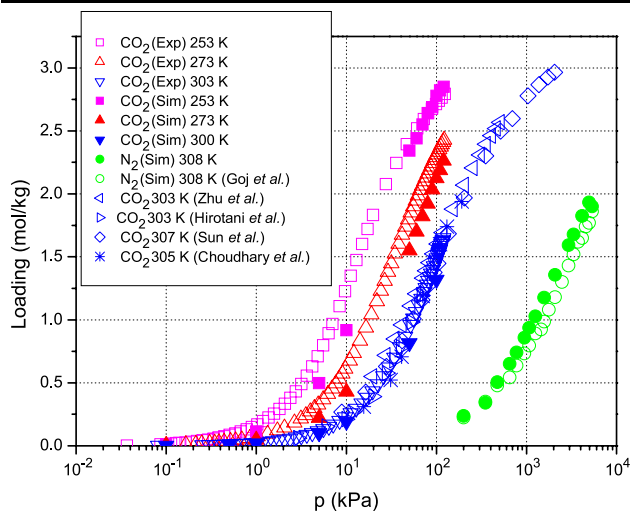


Fig. 2 Computed (*Sim*) and measured (*Exp*) adsorption isotherms of CO₂ and N₂ in MFI-type zeolite. Previous experimental (Choudhary and Mayadevi 1996; Hirotsani et al. 1997; Sun et al. 1998; Zhu et al. 2006) and simulation (Goj et al. 2002) data are included for comparison

with experiments in all range of pressures. The small discrepancies between our results and the experimental values are attributed 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 CO₂ were obtained for H-MOR with Si/Al = 6 and 7 protons per unit cell, and experimental data of N₂ were obtained for Na-MOR with Si/Al = 20 and 2 sodium cations per unit cell.

Figure 3b compares the simulated isotherms of CO₂, CH₄, and N₂ in CHA with the experimental isotherms of Li 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 N₂ are also in excellent agreement with previous data of 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 4 shows the obtained adsorption isotherms for equimolar mixtures of CO₂/N₂ in MFI at 308 K (Fig. 4a) and the computed adsorption selectivity for the equimolar and the 10:90 CO₂/N₂ bulk mixture in MFI at the same temperature (Fig. 4b). 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 Fig. 5. 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. (2002) proving for all the structures the preferential adsorption of CO₂ over N₂. The preferential adsorption of carbon dioxide is partially due to its large quadrupole moment that strengthens the adsorbate-adsorbent Coulombic interactions, thereby increasing the

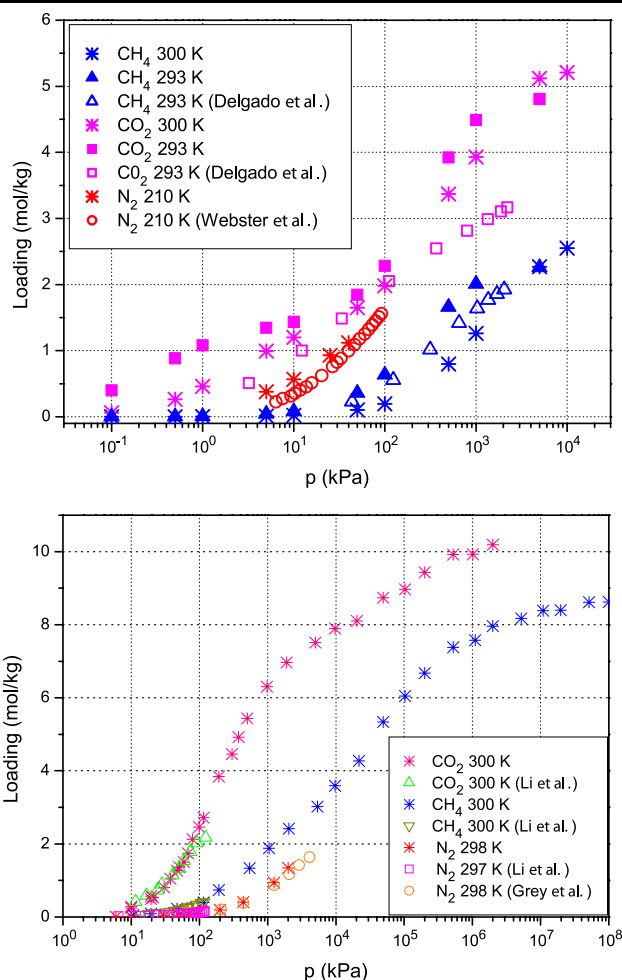


Fig. 3 Computed adsorption isotherms of CO₂, CH₄, and N₂ in (*upper panel*) MOR-type zeolite and (*lower panel*) CHA-type zeolite at several temperatures. Available experimental data are included for comparison (Delgado et al. 2006; Grey et al. 2001; Li et al. 2004; Webster et al. 1999)

adsorption in the structure. Similar behaviour can be therefore expected during the adsorption of CO₂/CH₄ mixtures and the obtained results in MFI and DDR structures are shown in Fig. 6. The simulated isotherms are in concordance with previous experimental results (Babarao et al. 2007; Zhu et al. 2006), as shown in Fig. 6a. The adsorption selectivity is favorable for CO₂ in both cases and is nearly constant with increasing pressure. The adsorption of CO₂ is almost unaffected by the presence of nitrogen, but N₂ adsorption is extremely sensitive to presence of CO₂. Figure 6b 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 CO₂ in adsorbed phases at low CO₂ fraction in gas phase. This behavior has also been observed by Himeno et al. (2007) and Harlick and Tezel (2003) in DDR and MFI respectively and is attributed to the dominant CO₂ adsorption in the binary system. Our results

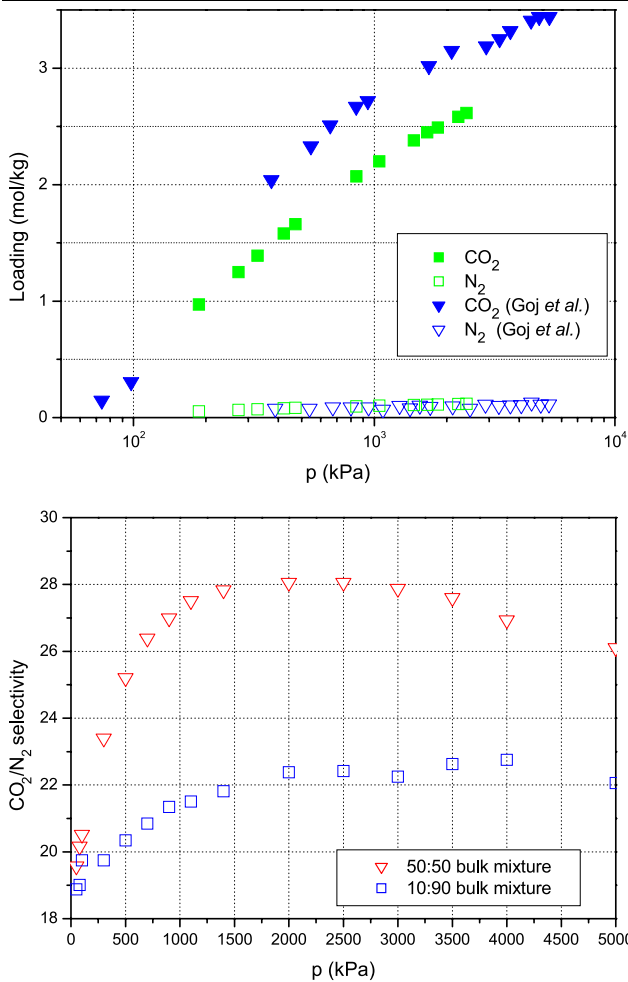


Fig. 4 Molecular simulations of CO₂/N₂ mixtures in MFI at 308 K. (Upper panel) Adsorption isotherm of the equimolar bulk mixture compared with previous simulation data (Goj et al. 2002). (Lower panel) CO₂/N₂ selectivity for the equimolar (50:50) and 10:90 bulk mixtures

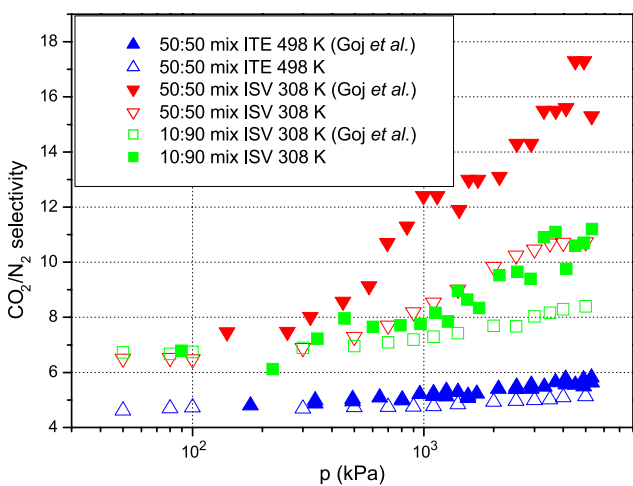


Fig. 5 Molecular simulations of CO₂/N₂ mixtures in ITE (50:50 bulk mixture) and ISV (50:50 and 10:90 bulk mixture). Simulations were performed at 498 and 308 K, respectively and previous atomistic data are included for comparison (Goj et al. 2002)

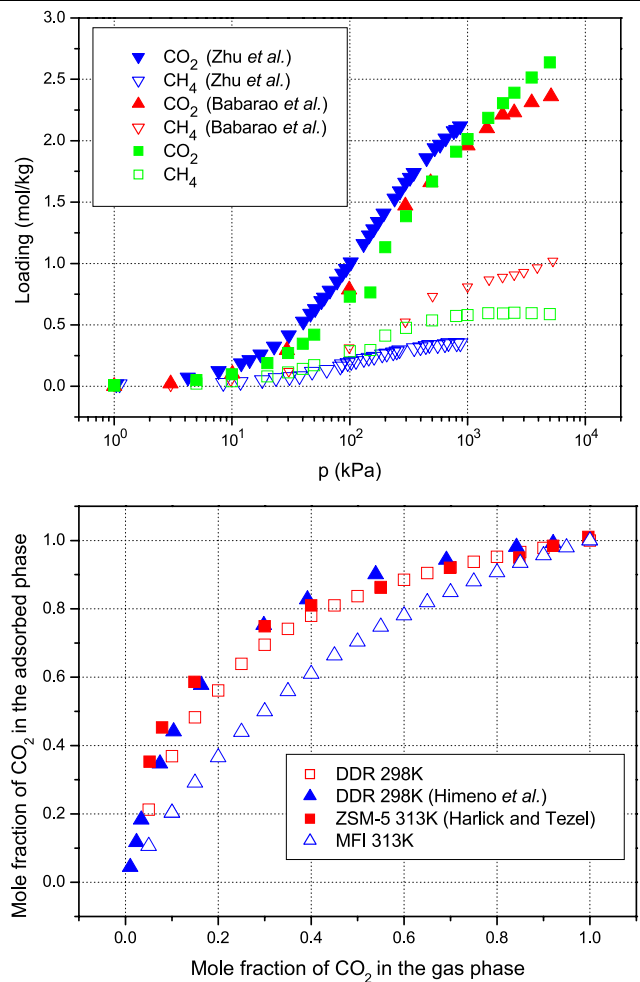


Fig. 6 Molecular simulations of CO₂/CH₄ mixtures in zeolites compared with previous experimental (Babarao et al. 2007; Harlick and Tezel 2003; Zhu et al. 2006) and theoretical (Himeno et al. 2007) data. (Upper panel) Equimolar bulk mixtures in MFI at 303 K. (Lower panel) Isothermal, isobaric (100 kPa) gas phase-adsorbed-phase diagram in DDR at 298 K and MFI at 313 K

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 CO₂ 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 CO₂ and CH₄ and 5:95 mixtures of CO₂ and N₂ in MOR are shown in Figs. 7a and 7b, respectively. CO₂ adsorbs stronger than methane and N₂ in this structure for all range of pressures. MOR structures consist of parallel chan-

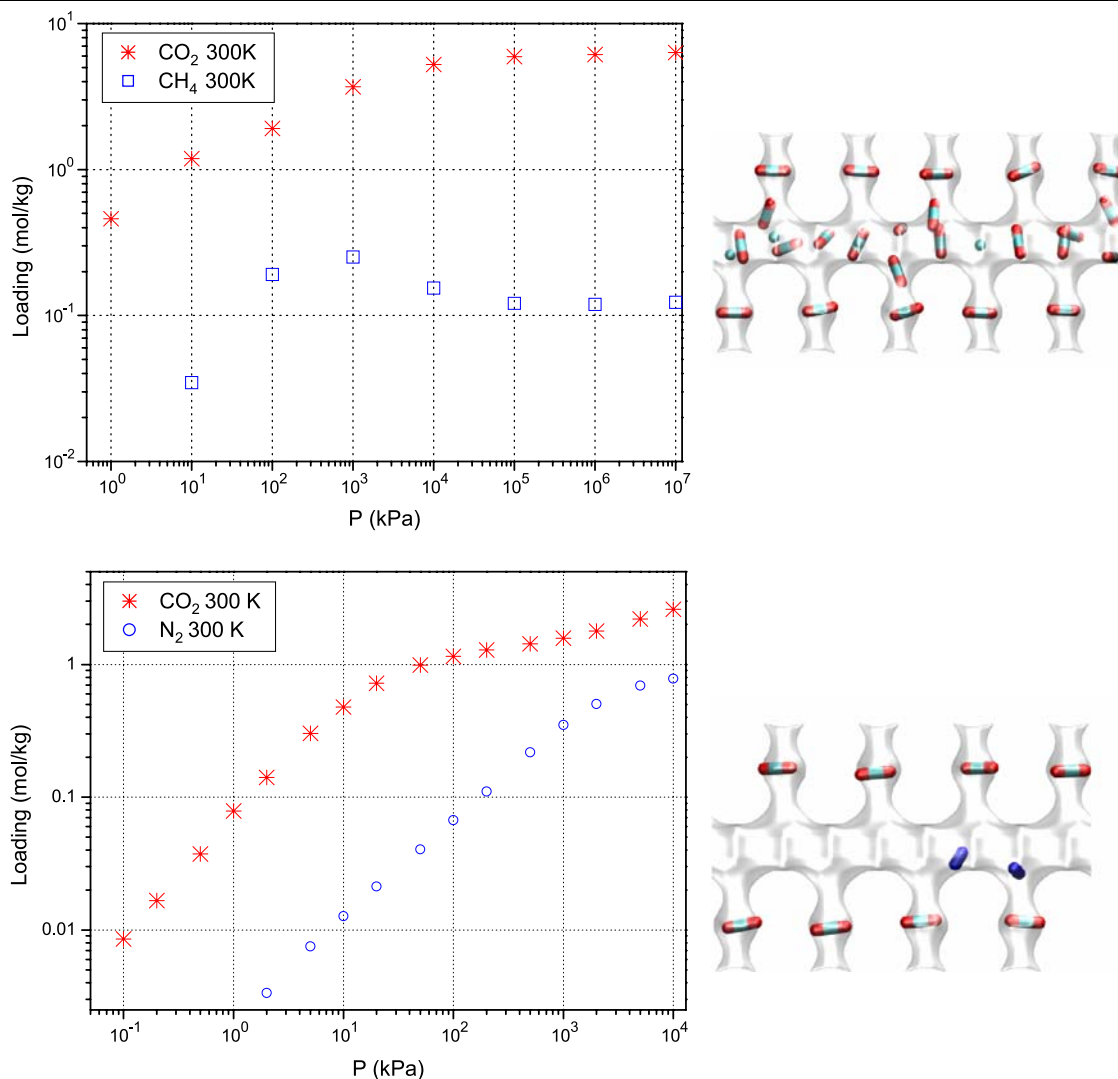


Fig. 7 Computed adsorption isotherms of mixtures of CH₄, CO₂ and N₂ in MOR at 300 K. The snapshots show the molecular locations at 1000 kPa. (*Upper panel*) 50:50 bulk CH₄/CO₂ mixture, (*lower panel*) 5:95 bulk CO₂/N₂ mixture

nels with small side-pockets. These pockets are the preferred adsorption sites for small molecules (such as CO₂, N₂ and CH₄) at room temperature. When these sites are filled, the main channels become occupied. In a mixture of CO₂ with CH₄ or N₂, the former adsorbs preferentially in the side pockets and the latter fill then the main channels. This can be clearly observed in Fig. 7 from the snapshots taken from our simulations at 1000 kPa and room temperature. At low pressure CO₂ molecules adsorb in the side pockets. Once these are full, they adsorb in the main channels together with the CH₄ and N₂ molecules.

The adsorption isotherms for 5:5:90 ternary mixture of CH₄, CO₂, and N₂ were computed at 300 K for a range of pressures that spans from 0.01 to 107 kPa. Figure 8 shows that as for the binary mixtures, CO₂ achieves the highest adsorption in all cases. The lower or higher CO₂ adsorption selectivity is decided by the shape and the size of the crystal

pore. CO₂ achieves the highest adsorption when increasing the confinement due to a combination of entropic (it is bigger than CH₄ and N₂) and Coulombic (higher quadrupole moment than CH₄ and N₂) 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.

4 Conclusions

This work analyzes the adsorption behaviour of CO₂, N₂, and CH₄ in all silica zeolites. Isotherms for pure components were measured and computed, showing in all cases good agreement with previous available experiments. The

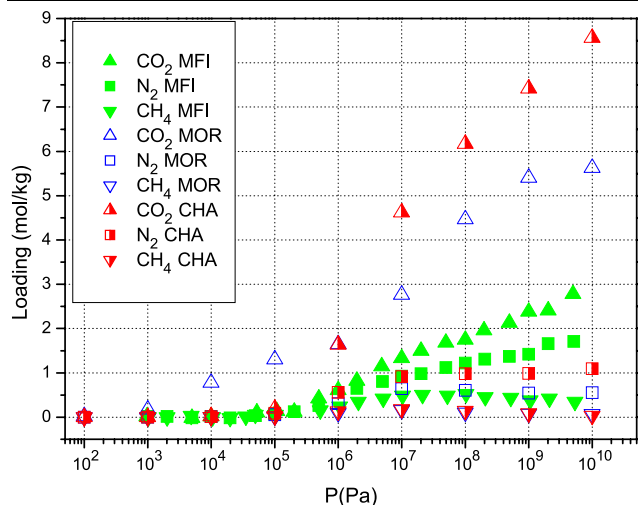


Fig. 8 Computed adsorption isotherms of the 5:5:90 bulk CH₄/CO₂/N₂ mixture in MFI, MOR, and CHA zeolites at 300 K

adsorption selectivity for binary and ternary mixtures is always in favour of CO₂ 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.

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