# Molecular Simulation of Adsorption of Short Linear Alkanes and Their Mixtures in Silicalite

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*Configurational-bias Monte Carlo simulations in the grand-canonical ensemble are employed to compute adsorption isotherms of methane, ethane, propane, butane and binary mixtures of methane – ethane, methane – propane, ethane – propane, and methane – butane in the zeolite silicalite. Comparison of the simulation results with the limited experimental data available shows good agreement. For ethane at room temperature, a small inflection point in the isotherm was observed due to a surprising ordering of the ethane molecules in the zeolite. For the simulation of a methane – ethane mixture, at low pressure ethane is preferentially adsorbed, while at high pressures methane replaces ethane due to entropic effects.*

## Introduction

The discovery of large natural-gas reservoirs has led to research in the area of methane coupling to ethylene/ethane (Lunsford, 1995; Fox, 1993; Tsang et al., 1995) as a possible economic method for the direct conversion of methane. Despite the huge number of catalysts tested so far, the yield to $C_2$ hydrocarbons still remains too low to be commercially viable. Catalyst development alone does not seem very promising for a breakthrough. Recently a laboratory recycle reactor–separator system has been introduced, which significantly increased the overall yield to $C_2$ components (Makri et al., 1996). In this system, the reactor is coupling to a zeolite absorber where the $C_2$ fraction of the reaction stream is adsorbed by the zeolite and separated from the methane, that is, recycled to the reactor feed.

A better understanding of the adsorption of these mixtures on zeolites is very important for the optimization of adsorptive separation processes. Experimental measurements of the adsorption isotherms of mixtures is very time-consuming, and as a consequence experimental data are scarce. Molecular simulation techniques, like Monte Carlo (MC), seem to offer an attractive alternative method for the computation of multicomponent adsorption isotherms.

MC simulations have been widely used for studying adsorption in many types of geometrical pores, such as slitlike,

cylindrical, spherical, and zeolitic structures (Nicholson and Parsonage, 1982; Catlow, 1992; Okayama et al., 1995). In this article, we report the results of MC simulations of single components and binary mixtures of short linear alkanes in silicalite. The simulations were performed at several temperatures and over a wide range of pressures.

## Model and Simulation Details

### Model

For the alkane–alkane interactions, the united atoms representation was used, in which the $CH_4$, $CH_3$, and $CH_2$ groups are considered as a single interaction center (Ryckaert and Bellemans, 1978). The intermolecular interaction between two united atoms is described with a Lennard-Jones potential

$$u(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \quad r_{ij} < R_c$$

$$u(r_{ij}) = 0 \quad r_{ij} \geq R_c, \quad (1)$$

in which $r_{ij}$ is the distance between pseudoatoms $i$ and $j$; $\epsilon$ is the energy parameter; $\sigma$ is the size parameter; and $R_c$ is the cutoff radius of the potential.
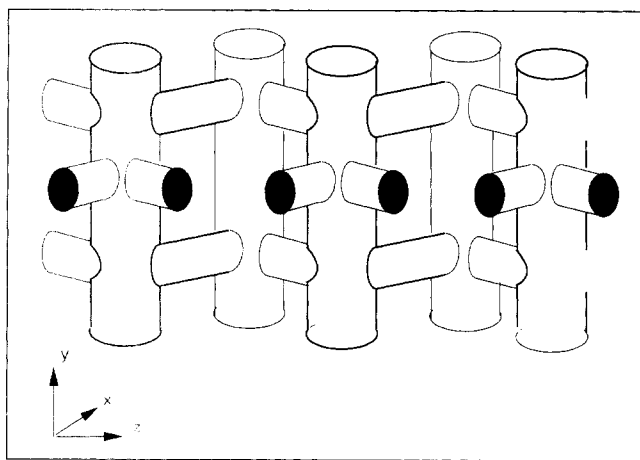
**Figure 1. Silicalite.**

Straight channels (y-direction) are connected by zigzag channels (x-z plane) that cross at intersections.

Following the work of Kiselev and coworkers (Bezus et al., 1978), we assumed the zeolite to be rigid. The potential at a series of grid points is initially calculated and stored. During the simulations, the potential at a given position in the zeolite can be calculated by interpolation using this grid (June et al., 1990a).

All simulations have been performed in the zeolite silicalite. Silicalite is a pure siliceous zeolite having the ZSM-5 structure. It has both straight elliptical channels and zigzag channels that cross at the intersections. In Figure 1, the pore structure of silicalite is shown. Alkane–zeolite interactions are assumed to be dominated by dispersive interactions, which are described with a Lennard-Jones potential as well. Since the size as well as polarizability of the Si atoms are much smaller than those of the O atoms, the contribution of the Si atom to the total potential is small and is taken into account in the oxygen–alkane interaction parameters. The Lennard-Jones parameters for the alkane–zeolite interactions were fitted to experimental data of the Henry coefficient and the heat of adsorption of linear $C_1$–$C_4$ at 300 K. In this fit, we used equal Lennard-Jones size parameters for all alkane–zeolite interactions, because in that case all alkane–zeolite interactions can be calculated using only one grid, which saves computer memory during the simulation in particular for multicomponent systems. This results in four adjustable parameters ($\epsilon_{CH_4}$, $\epsilon_{CH_3}$, $\epsilon_{CH_2}$, and $\sigma_{CH_i}$) that describe the alkane–zeolite interactions. Table 1 shows that it is possible to obtain very good agreement between experimental data and simulations using this constraint. See Appendix A for further details of the model.

## Simulations

Adsorption isotherms are conveniently computed by Monte-Carlo simulations in the grand-canonical ($\mu VT$) ensemble. This ensemble mimics a zeolite in (open) contact with a reservoir that fixes the temperature and the chemical potential of each component. In addition to particle displacements, in grand-canonical MC simulations one also attempts to add or remove molecules from the zeolite. To ensure that such a simulation is reliable one should have a sufficient number of successful particle additions/removals. For atomic adsorbents one can have a sufficient number of accepted moves in the pressure range of interest using conventional algorithms. For longer chain alkanes these particle additions/removals require the use of special techniques to make the insertion of these molecules possible. Smit (1995a) has shown that the configurational-bias Monte Carlo (CBMC) technique (Siepmann and Frenkel, 1992; Frenkel et al., 1992; de Pablo et al., 1992; Siepmann, 1993) can be combined with the grand-canonical ensemble to make the insertion of long chains possible. In this study we used an improvement of the CBMC technique from Vlugt et al. (1998) for the simulation of ethane and longer chains.

All simulations for single components were carried out at 275 K, 300 K, 325 K, and 350 K. The number of MC cycles was $1 \times 10^5$, which is sufficient to calculate the adsorbed amount accurately. The number of trial moves in a cycle is equal to the number of adsorbed molecules. For binary mixtures, the simulations were performed at 300 K and various compositions. The number of MC cycles was increased to 1.5 $\times 10^5$. In addition, the isotherm of a binary mixture of methane and ethane with a fixed gas-phase composition (50% methane and 50% ethane) was calculated at 250 K. Further details of the simulations can be found in Appendix B.

## Results and Discussion

### Single components

Adsorption isotherms of short alkanes in silicalite have been determined by several groups (Papp et al., 1984; Richard and Rees, 1987; Ding et al., 1988; Yamazaki et al., 1988; Golden and Sircar, 1989; Abdul-Reham et al., 1990; Rees et al., 1991; Otto et al., 1991; Hufton and Danner, 1993; Hampson and Rees, 1993; Sun et al., 1998). In this study, the simulation results were compared with the work of Sun et al. (1998) and Abdul-Rehman et al. (1990). In the work of Abdul-Rehman et al. experimental data are available not only for single components, but also for binary mixtures. In Smit (1995b), it is shown that the results of Abdul-Rehman et al. are in good agreement with the other experimental studies. Abdul-Rehman et al. used Linde-S115 silicalite, which is

**Table 1. Simulated Henry Coefficients and Heats of Adsorption vs. Experimental Data***

| Molecule | $\ln(K/[\text{mmol/g/atm}])_{exp}$ | $\ln(K/[\text{mmol/g/atm}])_{sim}$ | $-\Delta H_{exp}/[\text{kJ/mol}]$ | $-\Delta H_{sim}/[\text{kJ/mol}]$ |
|---|---|---|---|---|
| Methane | $-0.30$ | $-0.27$ | $-20.0$ | $-20.0$ |
| Ethane | 2.73 | 2.64 | $-31.0$ | $-30.6$ |
| Propane | 4.94 | 4.84 | $-40.0$ | $-39.0$ |
| Butane | 7.45 | 7.33 | $-50.0$ | $-50.0$ |

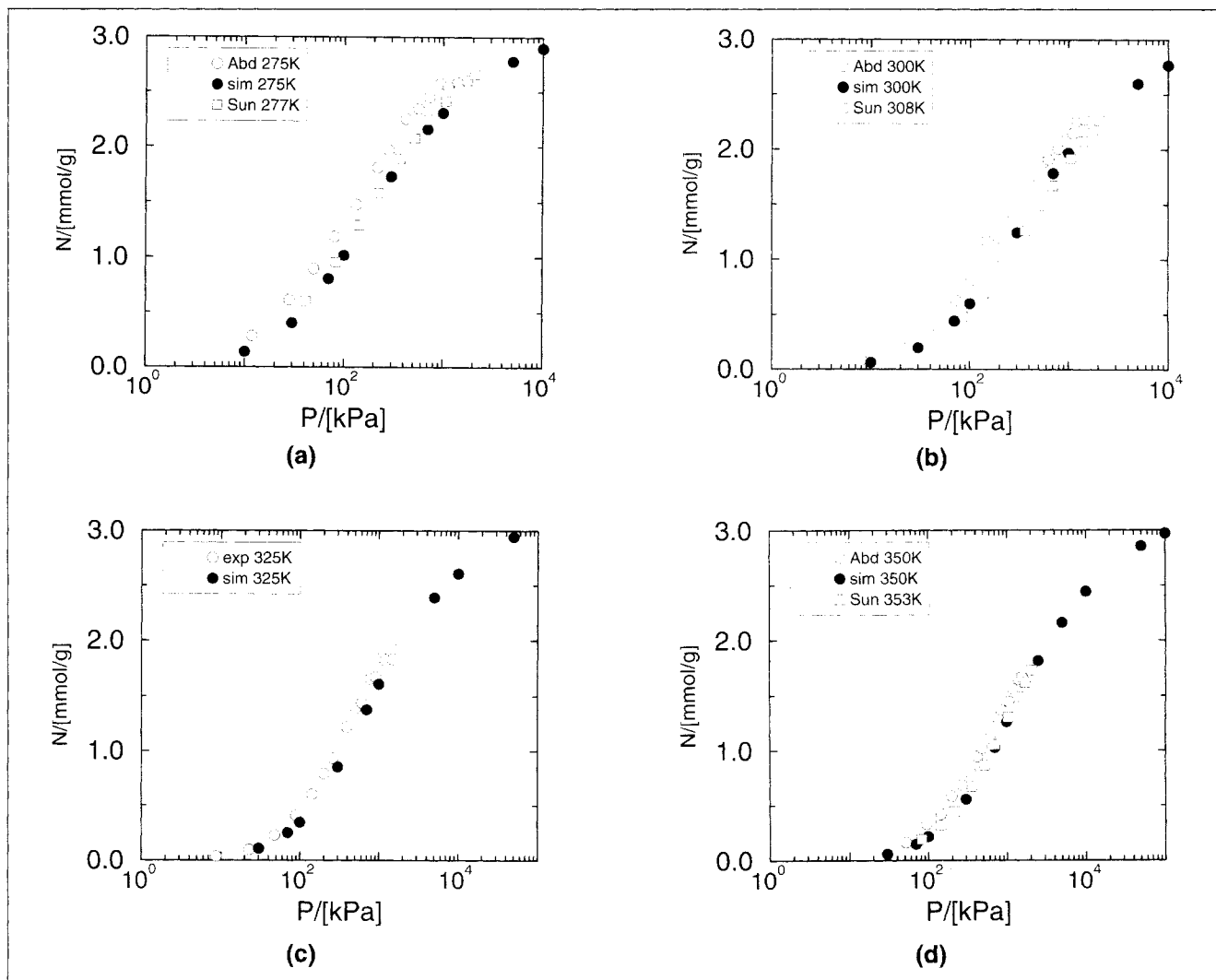*Taken from Smit (1995b) and Shen and Rees (1991).
$T = 300$ K.

**Figure 2. Adsorption isotherms of methane in silicalite at various temperatures.**

Experimental data of Abdul-Rehman et al. (1990) and Sun et al. (1998).

bonded with 20% clay binder (silica). To compare the simulation results with their experimental data, we have assumed that this 20% clay binder does not contribute to the adsorption.

Previous simulations of the single components focused on a comparison with experimental results at room temperature (see Smit, 1995b, for a comprehensive list of references). Here we are interested in whether these models also correctly describe the adsorption isotherms at other temperatures.

*Methane.* The simulated adsorption isotherms of methane are compared in Figure 2 with the experimental data. The simulations slightly underestimate the amount adsorbed for all temperatures. Considering the accuracy of the experimental data, the agreement is satisfactory.

*Ethane.* The results for ethane are presented in Figure 3. Also for ethane the agreement with the experimental data is very good, although there is some deviation of the experiments of Sun et al. (1998) from both the data of Abdul-Rehman and the simulations. It is interesting to note that at low temperatures (275 K and 300 K), the simulations show a small

inflection point in the adsorption isotherm at almost maximum loading. This inflection point disappears at higher temperatures. Such an inflection point suggests special ordering effects of the ethane molecules in the zeolite. To investigate these ordering effects, we have determined the density probability distribution of finding the center of mass of the ethane molecules at a particular position in the zeolite. This distribution is determined at a pressure just below (Figure 4, left) and above (Figure 4, right) the pressure corresponding to the inflection point.

At low pressures (Figure 4, left) we find a nearly uniform distribution over the various channels of the zeolite. At high pressures (Figure 4, right) this probability distribution shows a surprising ordering. Figure 4 (left) clearly shows a repeating pattern of ethane molecules that are "locked" in the zigzag channels between two intersections. Apparently the size of the ethane molecules is such that they can form a structure that is commensurate with the zeolite structure, which means that the sum of the size of two ethane molecules and their repulsion distances is exactly equal to the length of a zigzag
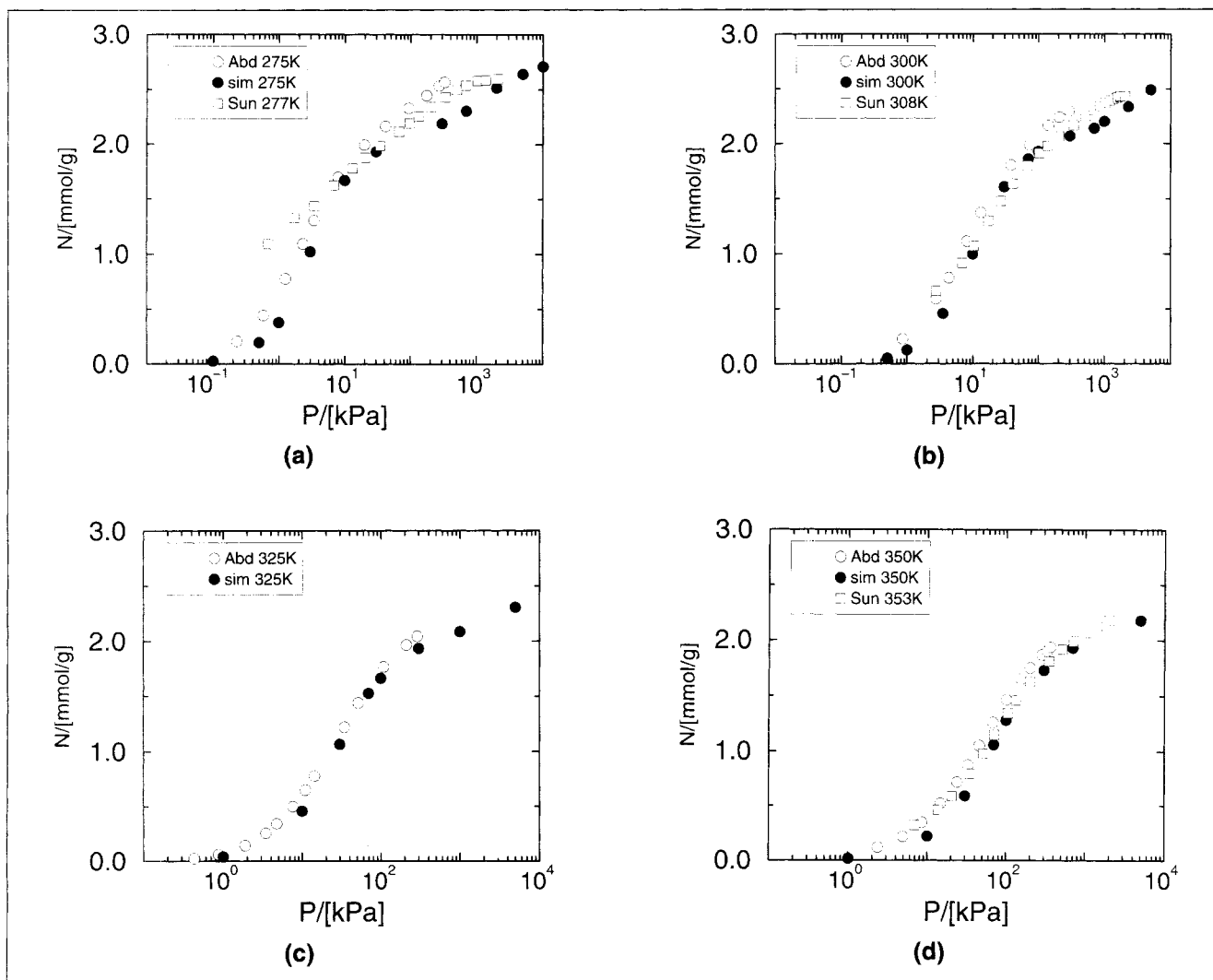
**Figure 3. Adsorption isotherms of ethane in silicalite at various temperatures.**

At 275 K and 300 K there is a small kink in the isotherms. Experimental data of Abdul-Rehman et al. (1990) and Sun et al. (1998).
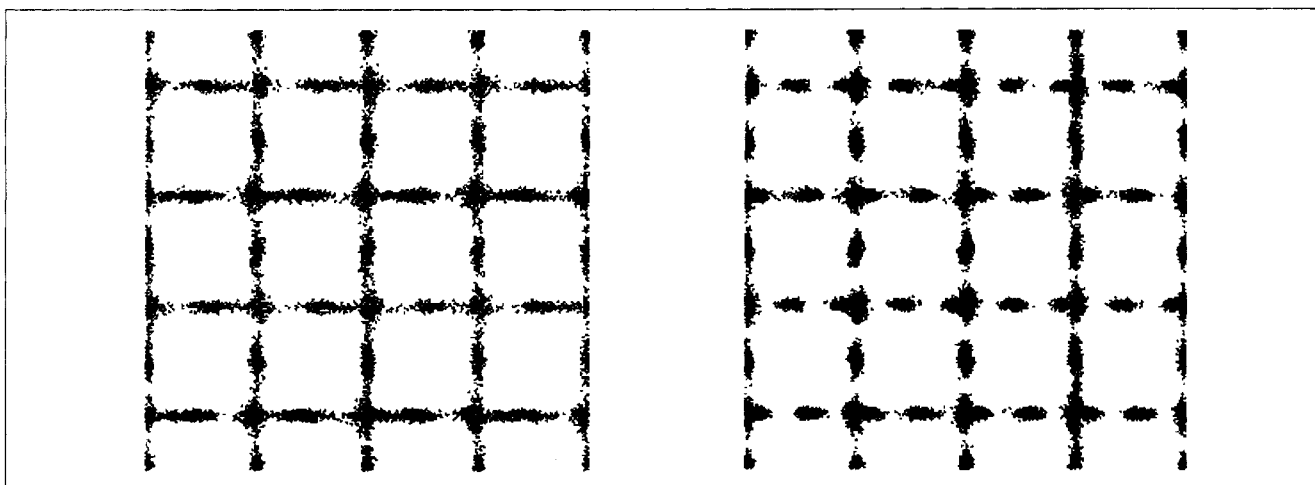


**Figure 4. Density distribution of ethane in silicalite at 300 K at low pressure (10 kPa, left) and at high pressure (10⁵ kPa, right).**

The zigzag channels are from left to right, the straight channels are from upper to lower. These figures were obtained by plotting the center of mass of the ethane molecules at various steps.

channel. This effect takes place when the channel interiors are occupied. A similar effect has been observed for hexane and heptane (Smit and Maesen, 1995) and xenon (June et al., 1990b), but it is surprising that for ethane similar effects may also exist. Detailed inspection of the experimental curve of Abdul-Rehman et al. (1990) for $T = 275$ K also suggests a small inflection. It is amusing to note that we did not observe an inflection point in the isotherms for methane, propane, or butane (see next subsection).

*Propane and Butane.* A comparison of the simulated and experimental adsorption isotherms is shown in Figure 5 for propane and in Figure 6 for butane. The simulations describe the experimental data for all temperatures very well. At low temperatures (275 K), the experimental data of Abdul-Rehman et al. (1990) for both propane and butane show a sharp increase at the maximum loading that is not reproduced by the simulations. This increase is probably due to capillary condensation. Since the experiments have been performed on pellets, the adsorbed amount would include capillary condensation at the exterior of the zeolite crystals, while for the simulation we mimicked an infinitely large zeolite crystal.

## Binary mixtures

The results in the previous subsection show that our simulation model can describe the single-component isotherms very well. We have used the same model to calculate adsorption isotherms of the following binary mixtures: methane–ethane, methane–propane, ethane–propane, and methane–butane. For these systems we can compare our results with the data of Abdul-Rehman et al. (1990) and Dunne et al. (1997) (only for methane–ethane).

For separations, one is usually interested in the partitioning of the two components of the gas and adsorbed phases. The results of these experiments are presented in *x-y* diagrams. In Figure 7 the experimental results for methane–ethane are compared with the simulations, showing a good agreement.

It is interesting to look at the simulated adsorption isotherms of the mixture. In Figure 8 the isotherm for a 50%–50% mixture at $T = 250$ K is presented. At low pressures ethane is preferentially adsorbed. This can be understood from the fact that ethane has a heat of adsorption that
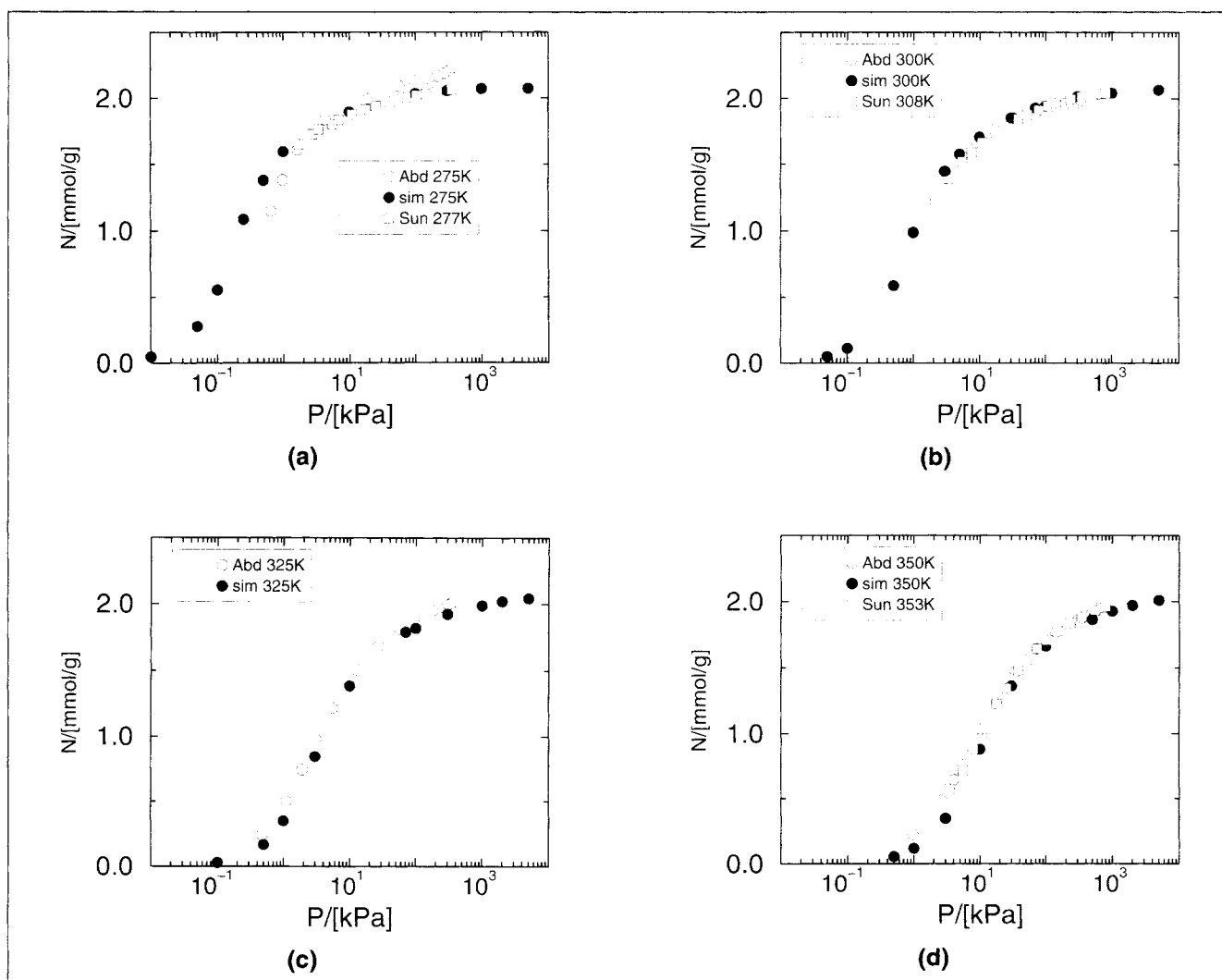


**Figure 5. Adsorption isotherms of propane in silicalite at various temperatures.**

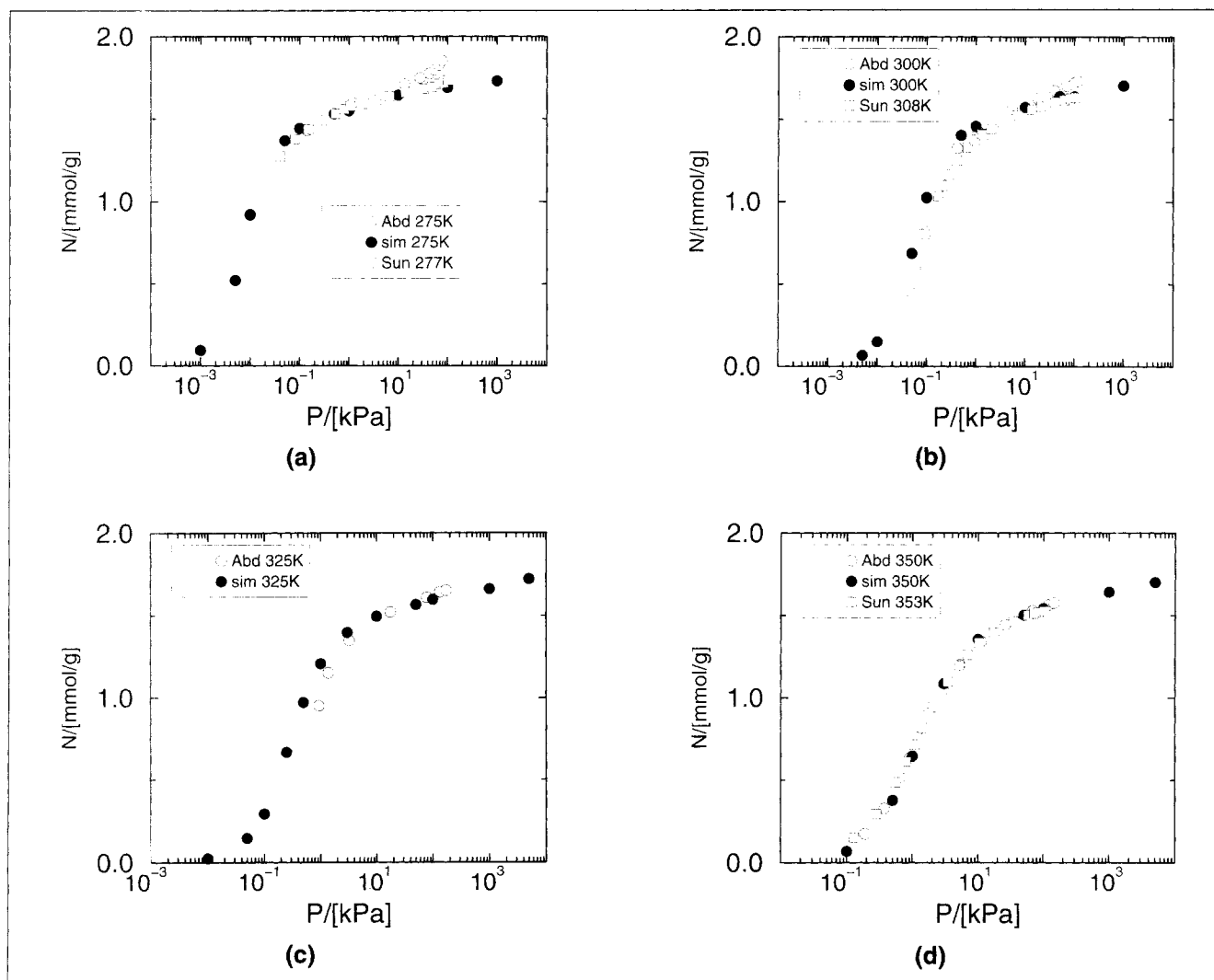Experimental data of Abdul-Rehman et al. (1990) and Sun et al. (1998).

**Figure 6. Adsorption isotherms of butane in silicalite at various temperatures.**

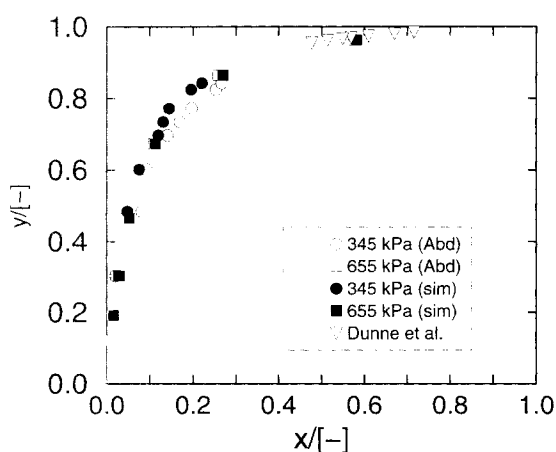Experimental data of Abdul-Rehman et al. (1990) and Sun et al. (1998).



**Figure 7. x-y Diagram of a mixture of methane–ethane, at a total pressure of 345 and 655 kPa.**

Experimental data of Abdul-Rehman et al. (1990) and Dunne et al. (1997). $T = 300$ K. $y$ and $x$ are the mole fractions of methane in, respectively, gas and zeolite. Note that the data of Dunne et al. were measured at a total pressure between 36 and 76 kPa depending on $y$.

is approximately twice the heat of adsorption of methane. At high pressure, however, methane replaces ethane. Also at high pressures, where the zeolite is almost completely filled, entropic effects become more important. A zeolite completely filled with ethane has approximately the same energy as a zeolite filled with methane. However, the entropy of the methane-filled zeolite is much higher. This is the reason why at high pressure the small molecules always win. These entropy effects have been predicted theoretically by Talbot (1997) and Bakaev and Steele (1997) for hard rods on a line. Our simulations support these predictions of Talbot for a realistic model of zeolite adsorption.

The $x$-$y$ diagrams of mixtures of ethane–propane, methane–propane, and methane–butane are presented in Figure 9. The agreement of the simulations with the experimental data is reasonable. The figures show that for adjacent components (methane–ethane and ethane–propane), the agreement between simulation and experiment is satisfied. However, for nonadjacent components (such as methane–propane and methane–butane), there is some deviation between simulation and experimental results. This suggests that some
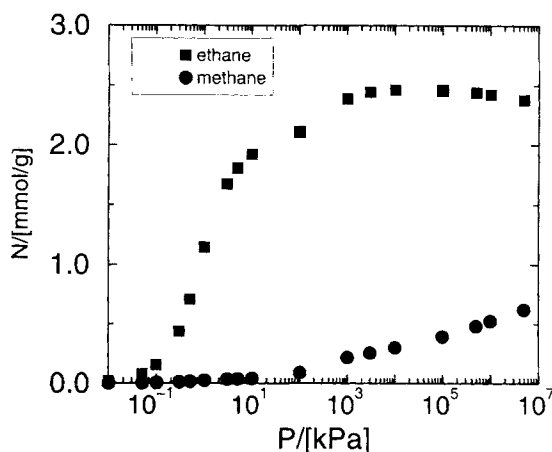
**Figure 8. Adsorption isotherm of a mixture of methane and ethane (50%–50%) at 250 K.**

On the $x$-axis, the partial pressure of methane and ethane is listed.

modification of interaction parameters may be needed for nonadjacent components, such as different values for the alkane–zeolite Lennard-Jones size parameters for different united atoms.

## Concluding Remarks

In this study, adsorption isotherms of single components and binary mixtures of short linear alkanes in silicalite have been calculated with MC simulations at various temperatures. The simulated adsorption isotherms are in satisfactory agreement with the available experimental data. These simulations indicate that it is possible to use simulations to make a reasonable estimate of the specific adsorption in mixtures on the basis of interaction parameters that have been optimized for single components (see Appendix A).

For the adsorption isotherm of ethane we observed at low temperature an inflection point that is attributed to special



**Figure 9. x-y Diagrams of ethane–propane, methane–propane, and methane–butane at a total pressure of 345 kPa.**

$T = 300$ K. $y$ and $x$ are the mole fractions of the smallest alkane in gas and zeolite, respectively.

ordering of the ethane molecules. Such a special order was not observed for methane, propane, and butane. It would be interesting to see if these ordering effects could be confirmed experimentally.

For the simulations of methane–ethane mixtures we observed that at low pressure ethane is preferentially adsorbed, while at high pressures methane replaces ethane due to entropic effects.

## Acknowledgments

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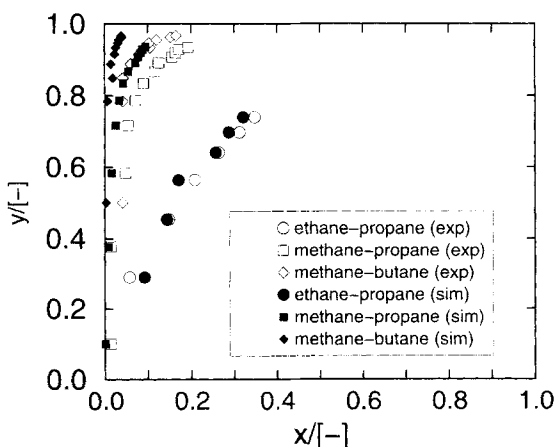Lunsford, J. H., "The Catalytic Oxidative Coupling of Methane," *Angew. Chem.*, **34**, 970 (1995).

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## Appendix A: Details of the Model

The Lennard-Jones parameters for the alkane–alkane interactions were taken from the work of Siepmann et al. (1997)

**Table A1. Lennard-Jones Parameters Used in this Study**

|  | $\epsilon/k_B/[K]$ | $\sigma/[\text{Å}]$ |
|---|---|---|
| $CH_4 - CH_4$ | 148.0 | 3.73 |
| $CH_3 - CH_3$ | 98.1 | 3.77 |
| $CH_2 - CH_2$ | 47.0 | 3.93 |
| $O - CH_4$ | 96.5 | 3.60 |
| $O - CH_3$ | 80.0 | 3.60 |
| $O - CH_2$ | 58.0 | 3.60 |

and from Verlet and Weis (1972) for methane. These parameters were fitted to reproduce vapor–liquid equilibria of various linear alkanes. All Lennard-Jones parameters are listed in Table A1. Interaction parameters between different united atoms $i$ and $j$ were calculated using the Jorgensen mixing rules (Jorgensen et al., 1984)

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \qquad (A1)$$

$$\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}. \qquad (A2)$$

The Lennard-Jones potential for all interactions was truncated at 13.8 Å, and the usual tail corrections have been applied (Allen and Tildesley, 1987). All bond lengths were fixed at 1.53 Å. For $C_3$ and $C_4$, intramolecular interactions between three successive atoms are described with a harmonic bond-bending potential (van den Ploeg and Berendsen, 1982):

$$u^{\text{bend}}(\theta) = \frac{1}{2}k_\theta[\theta - \theta_0]^2, \qquad (A3)$$

with $\theta_0 = 113.0°$ and $k_\theta/k_B = 62{,}500$ K rad$^{-2}$. For $C_4$, intramolecular interactions between four successive atoms are described with a torsion potential (Wang et al., 1993)

$$u^{\text{tors}}(\phi) = C_0 + C_1\cos(\phi) + C_2\cos^2(\phi) + C_3\cos^3(\phi), \qquad (A4)$$

with $C_0/k_B = 1{,}009.728$ K, $C_1/k_B = 2{,}018.446$ K, $C_2/k_B = 136.341$ K, and $C_3/k_B = -3{,}164.52$ K.

## Appendix B: Details of the Simulations

For calculation of the Henry coefficients and the heats of adsorption, ordinary NVT simulations were used (Smit and Siepmann, 1994). To calculate adsorption isotherms, the MC technique is used in the grand-canonical ensemble ($\mu$VT). In this simulation scheme, there are three types of trial moves:

1. Displacement of a particle. A randomly selected particle is given a randomly chosen displacement. The maximum displacement is adjusted to an overall acceptance of 50%.

2. Insertion/removal of a particle. It is selected at random, whether an attempt is made to insert a particle at a random position or to remove a randomly selected particle.

3. Complete regrow. A randomly selected particle is regrown at a random position in the simulation cell.

To simulate chain molecules, the configurational-bias Monte Carlo (CBMC) technique was used. In CBMC, a chain is grown segment by segment in a favorable direction instead of a completely random insertion. This introduces a bias that can be removed by a modification of the acceptance rule.

**Table B1. Probabilities of Selecting a Trial Move for Various Molecules**

|          | Displacement | Rotation | Particle Swap | Total Regrowth | Partial Regrowth |
|----------|--------------|----------|---------------|----------------|------------------|
| Methane  | 0.3          | —        | 0.5           | 0.2            | —                |
| Ethane   | 0.2          | 0.2      | 0.4           | 0.1            | 0.1              |
| Propane  | 0.2          | 0.2      | 0.4           | 0.1            | 0.1              |
| Butane   | 0.2          | 0.2      | 0.4           | 0.1            | 0.1              |

CBMC has already been proven to be several orders of magnitude more efficient than conventional MC for chain molecules. (Siepmann and Frenkel, 1992; Frenkel et al., 1992; de Pablo et al., 1992; Siepmann, 1993). In this scheme, three additional MC trial moves were included in the simulations of $C_2$ and larger alkanes:

1. Rotation of a molecule. A chain molecule is selected at random and is given a random rotation around its center of mass. The maximum rotation angle is adjusted to an overall acceptance of 50%.

2. Partial regrow. A randomly selected molecule is partially regrown using the CBMC algorithm in a randomly chosen direction starting at a randomly chosen segment.

3. Insertion/removal of a chain molecule using the CBMC scheme (Smit, 1995a).

The acceptance rules of these trial moves can be found in Frenkel and Smit (1996). The probabilities of selecting a trial move are listed in Table B1. To speed up the simulations, the recently developed dual cutoff configuration-bias Monte Carlo (DC-CBMC) technique is used (Vlugt, 1998). This method uses a second interaction cutoff radius to bias the selection of a trial segment, leading to a significant speedup of the CBMC trial moves.